AGRONOMIC IMPLICATION OF THE COMPETITIVE ADSORPTION BETWEEN NH_4^+ AND K^+ IN A SELECTED COCOA GROWING SOIL IN NIGERIA

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ABSTRACT

Nutrient deficiency is a major factor contributing to the downward trend in cocoa production in Nigeria. The most available and commonly used fertilizer in Nigeria comes as compound fertilizer (N:P:K; 15:15:15). When NH_4 is used as N source in compound fertilizer, there is the possibility of chemical interactions between K^+ and NH_4^+ in soil solution due to similarities in their chemical properties. In order to appraise the impact of chemical interactions between K^+ and NH_4^+ on potassium bioavailability, subsamples were equilibrated in solution containing only potassium ions and other subsamples equilibrated in solution containing ammonium and potassium ions. Potassium adsorption was significantly higher in soil treated with K solution than soil treated with K-NH_4 solution. The study showed that, application of N: P: K fertilizer that has NH_4 as its N source could result in the reduction of potassium storage capacity of the soil for plant use

Key words: *Potassium, Ammonium, fertilizer, adsorption, cocoa*

1.INTRODUCTION

Cocoa (*Theobroma cacao*) is the major cash crop that contributes to foreign earning in Nigeria. It is one of the most important tropical crops in West Africa. West Africa contributes 70% of the world's cocoa production (Wessel and Quist-Wessel, 2015). Nigeria used to be one of the largest producers of cocoa in the world but her interest in the crop suffered a grave setback when the discovery of crude oil was made. Apart from the interference of crude oil commercialization on the nation's interest in cocoa, there are other factors that have contributed to the downward trend in cocoa production in Nigeria. These include: ageing of cocoa trees, ageing of farmers, pests and diseases and nutrients deficiency in soil.

In spite of the low soil fertility occasioned by continuous cocoa cultivation without nutrient replenishment, most cocoa farmers in Nigeria do not use fertilizer on cocoa (Ogunlade et al 2009). Most of them have the mindset that their plantations are usually enriched from the decay of annual leaf litter fall. On the contrary, Ogunlade and Iloyanomon (2009) showed that the quantity of leaf litter and their nutrient contents especially P, K and Ca were not sufficient to make up for the annual nutrient mining for cocoa beans production. According to Omotoso, (1975), production of 1000kg of cocoa beans removes about 20kg N, 41kg P and 10kg K from the soil.

Potassium is one of the major nutrients required by cocoa. A significant role is played by potassium in enhancing crop quality. High level of available K improves the physical quality, disease resistance and shelf life of fruits and vegetables used for human consumption. The effect of K deficiency can cause reduced yield potential and quality long before visible symptoms appear. Plants depend upon potassium to regulate the opening and closing stomates. Every major step for the synthesis of protein in plant requires potassium. The "reading" of the genetic code in plant cells for protein production would be impossible without adequate potassium. When plants are deficient in potassium, proteins are not synthesized despite an abundance of available nitrogen. Instead, protein precursors such as amino acids, amides and nitrate accumulate.

In fertilizer formulation, there are two major forms of Nitrogen: NO_3 nitrogen and NH_4 nitrogen. Either of the two compounds of nitrogen can be used by fertilizer manufacturers as nitrogen source. In a situation where NH_4 is used as N source, the presence of NH_4 and K in the same fertilizer brings the question of possible interactions between these two soil nutrients. When fertilizer containing NH_4 and K dissolves in soil solution, NH_4^+ and K^+ are produced. The two are monovalent cations and have similar chemical properties. Hence, the possibility of chemical interaction cannot be ruled out which could ultimately impair the bioavailability of either or both of the nutrient. The study was therefore carried out to evaluate the impact of adsorption competition between NH_4^+ and K^+ on potassium adsorption in soil.

2. MATERIALS AND METHODS

2.1 Soil physicochemical properties

Soil samples were collected with soil auger under existing cocoa plantation at Ikom (5°52` N, 8°48`E) in Cross River State, Nigeria. The sampling was done at several points within the plantation at a depth of 0-15cm using soil auger. All the obtained samples were bulked and thoroughly mixed. The composite sample was air-dried, sieved and processed according to standard procedure (A.O.A.C, 1995). Soil pH was measured in 1:1 soil: water ratio, nitrogen was determined using Kjeldahl digestion method (AOAC, 1995) while particle size was determined by hydrometer method (Bouyoucos, 1951). Available phosphorus was determined by Bray 1 method (Bray & Kurtz, 1945), organic carbon was determined by the wet digestion dichromate acid-oxidation method (Olsen and Sommers, 1982). Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were extracted with 1N ammonium acetate buffered at pH 7.0 (Thomas, 1982). Exchangeable Ca, Mg, Zn and Mn in the extract were quantified using Bulk Scientific Atomic Absorption Spectrophotometer while K and Na were determined with Jenway PFP 7 flame photometer. Exchangeable acidity was determined by extracting the soil samples with 1N KCl and titrating the extract with 0.05 NaOH using phenolphthalein indicator (Mcclean, 1965). Effective CEC was determined by summation method.

2.2 Batch adsorption

Since the experiment was a comparative study, the sorption procedures for soil sample in solution with solely K^+ and that containing both K^+ and NH_4^+ were carried out simultaneously. One gram (1g) of the soil sample was measured into five 50ml centrifuge tubes. The samples were equilibrated in 20ml solutions containing 20, 40, 60, 80 and 100mg KL^{-1} and 20, 40, 60, 80 and 100mg K-NH_4 L^{-1}. 2 drops of toluene was added to each sample in order to minimize microbial activities. The batch equilibration was done in a mechanical shaker for 24 hours at room temperature (25°C). The amount of K and NH_4 adsorbed was calculated from concentration difference before and after equilibration.

3. RESULTS AND DISCUSSION

Result of particle size analysis showed that the investigated soil was clay in nature with 14% sand, 10.50 % silt and 75.40 % clay. The calcium content of the soil was 2.10cmolkg^{-1}. The obtained extractable calcium was below the critical level of calcium (5.0cmolkg^{-1}) in cocoa soil. Magnesium content of the soil (0.31cmolkg^{-1}) was also below the critical level (0.8cmolkg^{-1}) required in cocoa soil. Similarly, the obtained value for extractable K (0.26cmolkg^{-1}) was lower than the critical level (0.3cmolkg^{-1}) of potassium in soil meant for cocoa production (Egbe et al. 1989). Phosphorus with a concentration level of 11.40mgkg^{-1} was adequate in the soil while the value obtained for organic carbon (2.25%) was lower than 3% which is the critical level for organic carbon in soil meant for cocoa cultivation. Soil pH was 5.15 which implies that the soil is acidic in nature. Nitrogen content of the soil was 2.16%. The calculated exchangeable acidity in the soil was 2.10. On the other hand, the exchangeable Fe, Mn and Cu was 15.00, 8.52 and 0.78 mgkg^{-1} respectively. Sodium concentration was 0.52 cmol kg^{-1}. The low concentration of N, K, P, Ca and Mg in the investigated soil is an indicator pointing to the fact that the soil is deficient of plant nutrients. Several cocoa soils in Nigeria are depleted of plant nutrients due to annual harvest of cocoa pods without replenishing the soil through fertilizer application.

Table 1: Physicochemical properties of soil.

Soil Parameter	Concentration/Amount
Particle size	
Sand	14.10%
Clay	75.40
Silt	10.50
Exchangeable bases	
K^+	0.26 (cmol kg^{-1})
Na^+	0.52 (cmol kg^{-1})
Ca^{2+}	2.10 (cmol kg^{-1})
Mg^{2+}	0.31 (cmol kg^{-1})
Exchangeable acidity	2.1
Organic carbon	2.25 %
pH (H_2O)1:1	5.15

Available P	11.40 $mgkg^{-1}$
Nitrogen	2.16 %
Exchangeable micronutrients	
Mn	8.52 ($mgkg^{-1}$)
Fe	15.00 ($mgkg^{-1}$)
Cu	0.78 ($mgkg^{-1}$)
Zn	10.24 ($mgkg^{-1}$)

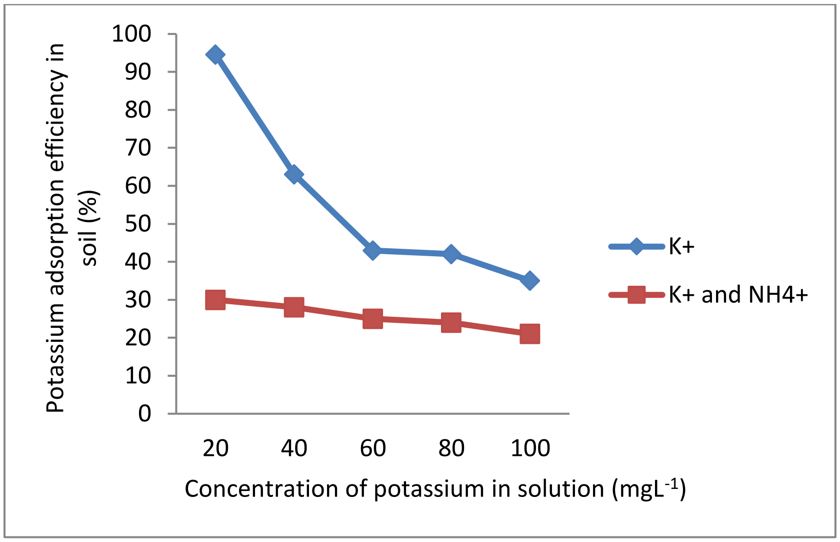

Figure 1: Potassium adsorption efficiency

Results (figure 1) shows that 94.6% of potassium ion in solution was adsorbed in soil treated with solution containing 20 $mgKL^{-1}$ while 30% of solution K was adsorbed in soil treated with solution containing 20 $mgNH_4$-K. Observation shows a 64.6% decrease in potassium adsorption as a result of competitive adsorption between potassium and ammonium ions on the soil particles. Treatment of the soil sample with solution containing 40 $mgKL^{-1}$ resulted in the adsorption of 63% of K in solution while only 28% of K in solution was adsorbed in soil sample equilibrated in solution containing both ammonium and potassium ions (40 mg $K\text{-}NH_4L^{-1}$). Result implies that, 35% reduction in potassium adsorption occurred as a result of competitive adsorption between the two ions. In soil sample treated with 60$mgKL^{-1}$, 43% of the solution K was adsorbed while 25% of solution K was adsorbed in soil sample equilibrated in solution containing 60$mgK\text{-}NH_4L^{-1}$. Adsorption efficiency was reduced by 18% as a consequence of both NH_4^+ and K^+ competing for same adsorption sites on the soil particles. Similar trend in K adsorption was observed when the soil sample was equilibrated in solution containing 80 and 100$mgKL^{-1}$. General observation shows a decrease in percent adsorption as the concentration of K increased in solution. The decrease was an indication of saturation of adsorption sites with the monovalent K^+ ions. Adsorption rate decreased gradually approaching a plateau due to continuous decrease in the concentration of driving force (Tsai *et al*, 2005). At higher solution concentration, adsorbate on adsorbent decreases due to saturation of adsorption sites as a result of increase in the number of ions competing for available binding sites (Puranik and Paknikar, 1999). Similar reduction in adsorption efficiency with increase in solution K was reported on soil obtained from North Kashmir, India (Bangroo *et al*, 2012). The observed reduction in K adsorption efficiency with increase in solution K suggests possible wastage of resources and nutrient run-off in situation where arbitrary application of K fertilizer is made without initial soil analysis. This is critical considering the fact that soil particles have limited number of sites that could hold ions for plants' use. The significant reduction of K in soil samples equilibrated in solutions containing both K^+ and NH_4^+ was due to competitive adsorption of both ions on same adsorption sites in soil particles. In solution containing only K^+ ions, competition for the available sites was limited to one type of competition (inter-ionic which involved only K^+ ions). However, when solution containing both K^+ and NH_4^+ ions come in contact with soil surfaces, the competition for available adsorption sites was no longer limited to k inter-ionic competition. Rather, the competition for available sites became a multiple type (Inter-ionic competition among K^+ ions, inter-ionic competition among NH4+ ions and inter-ionic competition between K^+ and NH_4^+ ions). The competition between K^+ and NH_4^+ ions for same adsorption sites on the soil surface was mainly due to similarities in the chemical nature of K^+ and NH_4^+ ions. NH_4^+ and K^+ have similar valence and size properties. Consequently, they compete for the same exchangeable sites of soil particles (Bar Tal, 2011). NH_4^+ and K^+ are both monovalent cations and have similar ionic radius of 1.43 and 1.38 A° respectively. The similarity in their chemical properties led to strong interaction between them in soil system. Owing to the fact that both ions are held by the same non-exchangeable sites in the interlayer and edges of interlayer of clay minerals, a simple competition between the two will result in the displacement of one of the two ion types and increase its fraction in soil solution (Bar Tal, 2011). According to Stehouwer and Johnson, (1991) simultaneous injection of anhydrous ammonia and a KCl solution in a silty clay loam soil decreased K^+ ion fixation whereas the concentration of the exchangeable and soluble K^+ increased. The decrease in K^+ fixation was attributed to preferential NH_4^+ fixation blocking K^+ fixation and the increased exchangeable K^+ was explained by the decrease in K^+ fixation. Certain results from field experiments indicate that, the sequence of NH_4^+ and K^+ application may influence K fixation. Chen *et al*, (2008) reported that NH_4^+ at high rates of application before K fertilization to rice plant resulted in poor growth and reduced K uptake compared with NH_4^+ application after K fertilization. However, when NO_3^- was used as the N source, plant growth was not affected by the order in which N and K were applied. The negative impact on K availability and uptake was due to the fact NH_4^+ blocked the non-exchangeable sites, thus reducing the capacity of the soil to store K to meet the need of plants. The rate of K fertilization may also influence NH_4^+ adsorption. The report of Liu *et al*, (1997) showed that in field experiments, the soil fixation capacities of both $NH_4{}^+$ and K^+ were significantly reduced by sustained high rates of K fertilization, but not by N fertilization. The influence of K application on NH_4^+ availability in soil was also reported by Kenan *et al*, (1999) where fixation of NH_4^+ was reduced by K addition before NH_4^+ was added, and that the reduction was proportional to the amount of K previously fixed. The common forms of nitrogen fertilizer is NH_4^+ and NO_3^-. Urea is the cheapest N source (per N unit) and is the most concentrated N fertilizer (46% N); it is highly soluble. The hydrolysis process of urea yields the derivative NH_4^+ ions and thus, urea is a source of the NH_4^+ form for plant nutrition. In the field, the transformation of NH_4^+ to NO_3^- by nitrifying bacteria is usually a rapid process between days to weeks, depending on temperature, soil moisture and pH. Ideally, the form of N in a compound fertilizer should not have any antagonistic effect on K adsorption. But any anthropogenic activity that hampers the activities or population of nitrifying bacteria is capable of preventing the oxidation of NH_4^+ to NO_3^- giving room for abundant NH_4^+ in soil solution which will eventually compete with K^+ for adsorption sites on soil components.

4. CONCLUSION

The study shows the significance of chemical interaction between potassium and ammonium ions in soil as it affects the bioavailability of potassium for plants' use. The storage capacity of the soil for potassium as plant nutrient was reduced due to competition for adsorption site by cations with similar chemical properties. For optimal utilization of fertilizer by cacao plant, possible chemical interactions and chemical properties of nutrient elements or compounds intended for use in formulating compound fertilizer has to be considered before they are combined. Hence, unfavorable chemical interactions among fertilizer components could adversely affect the bioavailability of the nutrients in fertilizer.

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