

AFFECT OF CATION EXCHANGE CAPACITY ON THE AVAILABILITY OF POTASSIUM TO PLANTS IN HEAVY CLAY SOILS

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ABSTRACT

The aim of this study is to understand potassium availability for maize uptake as a function of soil supply of potassium in heavy clay Vertosol soils. Three rates of K (0, 100, 200 mg K kg⁻¹) were applied as KCl to twelve Vertosol soils and allowed to equilibrate for three days. Exchangeable cation concentrations were obtained before and after leaching with 0.0025 M CaCl₂ solution. The K activity ratio (ArK) increased following addition of K fertilizer. These increases varied between soils types according to differences in soil CEC values and initial exchangeable K status. A positive correlation between CEC and initial ($r^2= 0.76$) and final ($r^2= 0.76$) potential buffer capacity of K (PBCK) was observed. Soils with high values of PBCK had a very high capacity to protect the soil solution K concentration from depletion, whereas low PBCK would suggest the need for frequent K fertilizer application. The highest value for PBCK was associated with soil which had the greatest values of CEC, and the lowest PBCK value was related to soil with the lowest CEC values. This has implications for fertilizer application practices in maize farming. Two of the Vertosols were used to grow maize plants, with 0, 50, 100, 200 and 400 mg kg⁻¹ of K as KCl for two harvest periods. Shoot K⁺ uptake of maize plants increased significantly ($P<0.001$) with increasing K application rates. Shoot dry matter production in the soil with high initial level of exchangeable K did not respond to fertilizer K addition, while plants grown in the soil with low K, data indicate an increased dry matter production in the second harvest. A higher K⁺ concentration in plants grown in high K soils indicated that K⁺ availability was not a limiting factor for shoot growth.

INTRODUCTION

Soil potassium exists in four primary forms: soil solution, exchangeable, non-exchangeable and mineral. The amount of solution and exchangeable K is usually a fraction of total K in the soil, 1–2% and 1–10%, respectively. The bulk of soil K is usually in the non-exchangeable and mineral forms that are non-available for plant uptake (15). Research conducted on the availability of potassium, has found that a negative K balance in broad acre grain cropping systems has a significant outcome on farm output. There has

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been a decline in the plant-available reserves of K in northern Australian clay soils, and it is important to be able to detect and respond to developing K deficiencies Bell (6).

The soil cation exchange capacity (CEC) refers to the ability of the soil to hold positively charged cations and the balance of these ions can affect the uptake and to the CEC. Therefore, the objective of this research was to evaluate the availability of

K in relation to the CEC in Vertosols soils with low, moderate and high CEC, and low to high K status. It is believed that the soils with high CEC will show reduced concentrations of K in soil solution. In order to achieve this aim, two methods have been used to measure K availability: a biological method, with maize plants grown in two soil types; and a chemical or laboratory method with exchangeable and soil solution K measured in twelve heavy clay soils with different ranges of CEC.

MATERIALS AND METHODS

Soil collection

Twelve Australian soil types were collected from the northern cropping region of Australia, 10 from Queensland and two from northern NSW (Armidale and Inverell). Soils were selected to cover a range of both CEC and exchangeable K (Table 1). Soil samples were collected from the surface 10 cm, air-dried, crushed to pass a 2mm sieve and stored until analysis.

Potassium desorption method

The desorption of K was done using all 12 test soils, 2 sets of 2 g of each soil were placed in 50 mL centrifuge tubes with three rates of added K (0, 100, 200 mg K kg⁻¹) applied as a 2 mL aliquot of KCl. After three days, 18 mL of 0.0025M CaCl₂ was applied to each sample in the first set of the soils. The supernatant was analysed for soil solution cations using Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES). Soil remaining was then extracted for exchangeable cations using 18 mL of 1M NH₄OAc (pH 7) for one hour. All tubes were weighed before and after each extraction to account for entrained solution.

The second set of soils was extracted five times with 18 mL of 0.0025M CaCl₂ to mimic plant removal of K, as indicated in the preliminary experiment. The solution of CaCl₂ was applied to each soil sample, shaken for 10 minutes and then centrifuged for 5 minutes. A 5 mL aliquot of extracted solution was stored for cumulative cation extraction analysis prior to discarding all desorbed solution. Four extractions were placed together in the same container whilst the final extraction was analysed separately to establish the new equilibrium between solution and exchangeable K. All cations were measured using ICPOES.

Glasshouse studies

A potassium uptake experiment was conducted using the glasshouse facility by using two heavy clay soils from northern NSW with similar CEC but different exchangeable K (Figure 1; Table 1). Both soils were treated with

a range of K as KCl (0, 50, 100, 200 and 400 mg kg⁻¹) replicated 3 times. Three germinated maize (*Zea mays L.*) seedlings were planted in pots containing 1 kg of treated soil. Basal N (50 mg kg⁻¹ as DAP and urea) and P (20 mg kg⁻¹ as DAP) were added to all pots. Plants were watered to field capacity regularly in glasshouse bays regulated to 28°C during the day and 18°C at night for the entire growth period. After 21 days a further 18 mg kg⁻¹ of N and 20 mg kg⁻¹ of P was applied as DAP to the Inverell and Clark soils to prevent the initial of N and P deficiency.

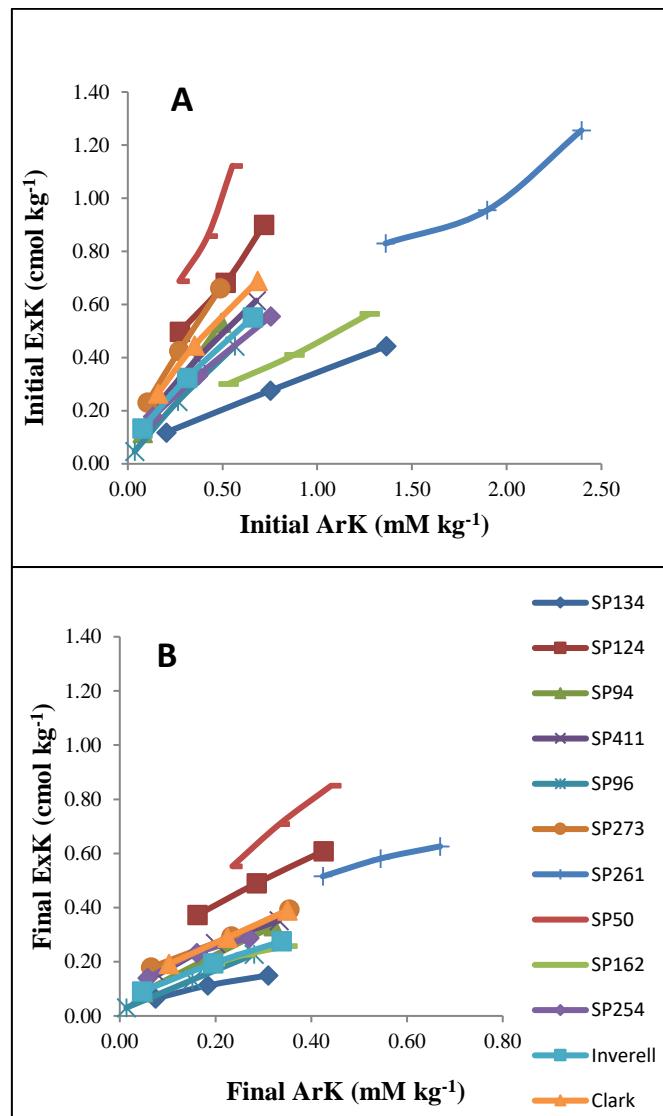


Fig 1: Relationships between exchangeable K (ExK) status and K activity ratio in solution for twelve Vertosols of varying cation exchange capacity before (A) and after (B) leaching 5 times with 0.0025M CaCl₂ solution.

After four weeks growth, maize plants were harvested 5 cm above the base of the stem, and allowed to regrow for four other weeks. A further 50 mg

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kg⁻¹ of N as urea was applied following the first harvest to all pots. Harvested plants were dried at 80°C for 72 hours in a fan forced oven, weighed, and ground to <2mm to determine K concentration in plant tissue using the sealed chamber digestion (SCD) method (3).

Table 1: Change in cation exchange capacity (CEC) (cmol kg⁻¹) in 12 Vertosol soils with different rates of K addition (mg kg⁻¹) and in exchangeable K (cmol kg⁻¹) following 5 leaching treatments.

Soil	K treatments (mg kg ⁻¹)	CEC (cmol kg ⁻¹)	Change in exchangeable K after leaching (cmol kg ⁻¹)	Leached K (cmol kg ⁻¹)
SP134	0	31.34	0.06	0.08
	100	31.80	0.17	0.25
	200	32.60	0.29	0.46
SP124	0	53.64	0.13	0.14
	100	52.68	0.19	0.24
	200	55.20	0.29	0.36
SP94	0	65.48	0.03	0.04
	100	67.87	0.09	0.14
	200	73.81	0.2	0.26
SP411	0	44.59	0.06	0.06
	100	45.83	0.13	0.18
	200	48.12	0.26	0.31
SP96	0	44.17	0.02	0.01
	100	45.02	0.1	0.13
	200	47.08	0.21	0.27
SP273	0	43.23	0.05	0.06
	100	43.98	0.13	0.16
	200	46.36	0.27	0.28
SP261	0	26.08	0.31	0.49
	100	25.45	0.37	0.67
	200	28.24	0.63	0.86
SP50	0	68.25	0.14	0.16
	100	68.16	0.15	0.22
	200	72.12	0.27	0.31
SP162	0	21.41	0.11	0.21
	100	21.61	0.18	0.32
	200	23.76	0.3	0.45
SP254	0	29.80	0.04	0.06
	100	29.86	0.1	0.17
	200	32.80	0.27	0.31
Inverell	0	44.72	0.04	0.04
	100	44.75	0.13	0.17
	200	47.69	0.27	0.32
Clark	0	44.67	0.07	0.09
	100	44.63	0.16	0.20
	200	48.66	0.30	0.32

Plant analysis

For plant tissue analysis 0.2 g of maize plants material was placed into 50mL borosilicate Schott reagent bottle, 7:3 (v/v) mixture of perchloric acid (HClO₄- 70%) and hydrogen peroxide (H₂O₂- 30%) were added to each bottle then left for two hours at room temperature. 1mL of H₂O₂ was then added and bottles placed into a warming oven at 80°C for 30 minutes, another 1mL of H₂O₂ was added after cooling the bottles for one hour, to complete the digestion of plants material another 1mL of H₂O₂ was added for 30 minutes. Volume of samples was adjusted to 25mL by adding ~20mL of deionised water after cooling the bottles. The resulting solution was filtered through Whatman filter papers (No 17) and nutrients concentration for plant digest was determined by using ICPOES.

Statistical analysis

Responses of maize to K addition were examined using analysis of variance (ANOVA) after testing all assumptions using Sigma Stat 11. Significant F tests were followed by simple least significant difference analysis to determine treatment effects. A significance level of 5% was used for all analyses.

RESULTS AND DISCUSSION

Potassium sorption and desorption

Initial solution K activity (ArK) for the 12 Vertosols used in this study ranged from 0.04 to 2.4 mM kg⁻¹ and initial exchangeable K ranged from 0.05 to 1.26 cmol kg⁻¹ (Figure 1). The CEC values ranged from 21.4 to 73.8 cmol kg⁻¹ (Table 1). There was a trend towards increasing CEC with increasing K application to each soil (Table 1).

The ArK increased following addition of K fertiliser, as expected (Figure 1). These increases varied between soil types according to differences in soil CEC values and initial exchangeable K status. High CEC soils had smaller increases in ArK whilst low CEC soils had larger increases in ArK. Leaching of the soils 5 times with CaCl₂ reduced both ArK and exchangeable K values. Low CEC soils had a larger reduction in both ArK and exchangeable K than higher CEC soils.

Q/I relationship with CEC

A positive correlation between CEC and initial ($r^2= 0.76$) and final ($r^2= 0.76$) PBCK was observed (Figure 2). The rate of change in solution K activity is slower as CEC increases, hence considerably higher K application rates are needed to maintain a steady and adequate K activity in solution as CEC increases. The differences in slope between initial and final PBCK after five desorption events and considerable K removal decreased by about 20% (Figure 2) reflecting the slower potential release of K to solution when exchangeable K is depleted.

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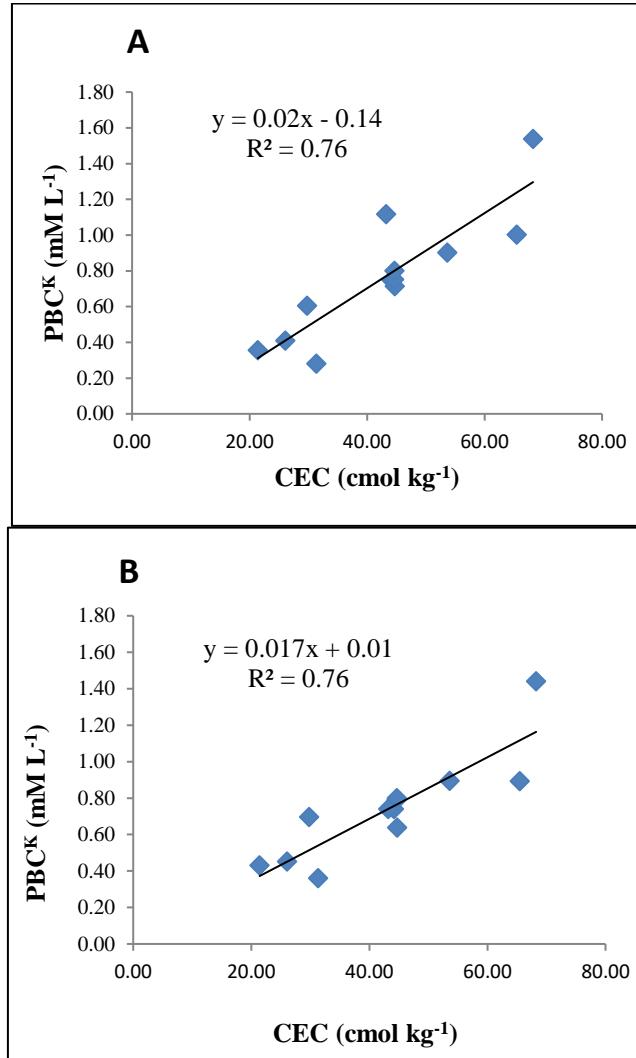


Figure 2. Relationship between the CEC of the twelve Vertosols soils, and their initial (A) and final (B) PBC_K derived by the slope of K activity ratio and exchangeable K curves in (Figure1).

Glasshouse trial

Biomass production

The Inverell and Clark soils showed significant differences ($p<0.001$) in maize shoot dry weight at both harvest periods, averaging 3.5 g pot^{-1} in the Inverell soil and 4 g pot^{-1} in Clark soil at the first harvest, and 3.2 g/pot and 3.7 g pot^{-1} respectively in the second harvest. There was also a significant interaction ($p=0.002$) between soil and K rates at both harvest periods for shoot dry weight (Table 2). In the Inverell soil at the first harvest, the application of any level of K increased dry matter above the control, but there was no difference between K additions. However, by the second harvest, dry matter production increased ($P<0.001$) linearly with K addition up to 400 mg K kg^{-1} . Initially the only response was to the addition of any K though, and the larger biomass responses occurred after plants were allowed to regrow. In contrast, K application did not increase biomass produced in the Clark soil at either harvest, and decreased it at

the highest rate in the first harvest by 10 % ($P<0.05$) (Table 2). These accords with a critical K concentration of 0.2 cmol kg^{-1} for Vertosols in this region.

Table 2. Maize plant shoots dry weights and K uptake (mg/pot/day) at different rate of K addition in two Black Vertosols with low (Inverell) and high (Clark) K status over two harvests periods at (28) and (23) days after sowing. Values are the means of three replicates

Soil	K rate	Dry weight (g/pot)			Rate of K uptake (mg/pot/day)	
		First H	Second H.	Total DW	First H	Second H.
Inverell	0	3.1	2.6	5.7	0.7	0.6
	50	3.6	3.2	6.8	1.9	1.2
	100	3.5	3.3	6.8	2.8	1.6
	200	3.6	3.4	7.0	4.3	2.9
	400	3.7	3.7	7.4	4.9	6.1
Clark	0	4.3	3.5	7.8	2.7	1.7
	50	4.0	3.5	7.4	3.4	2.0
	100	4.3	4.1	8.4	4.2	2.5
	200	4.1	3.9	8.0	4.9	4.1
	400	3.5	3.5	7.0	4.3	5.9
LSD		0.3	0.2		2.3	1.2

K uptake by Maize

Differences in dry matter produced reflected the ability of the two soils to supply K. The total uptake of K in plants grown in the Clark soil was greater than the entire K available to plants grown in the lower K status Inverell soil at all application rates $< 400 \text{ mg K kg}^{-1}$ (Figure 3). Specifically, the rate of K uptake was nearly two times higher in the Clark soil for additions $< 100 \text{ mg K kg}^{-1}$ following the first harvest (Table 2). In the control treatment, the rate of K uptake was three times higher in the Clark soil than the Inverell soil at both harvests (Table 2). The uptake of K also increased significantly ($P<0.001$) with increasing K application rates (Figure 3), with there also being a significant interaction ($P<0.001$) between K rate and soil.

The uptake of K increased linearly in response to increased initial K status by application of K fertiliser in both Inverell and Clark soils ($r^2=0.96$) (Figure 4). The Inverell soil, assuming that uptake was equivalent from the control treatment, in the K fertilized treatments that ~80% of the 100 and 200 mg K/kg additions were removed by the plant, whilst only 60% of the added K was removed in the Clark's soil.

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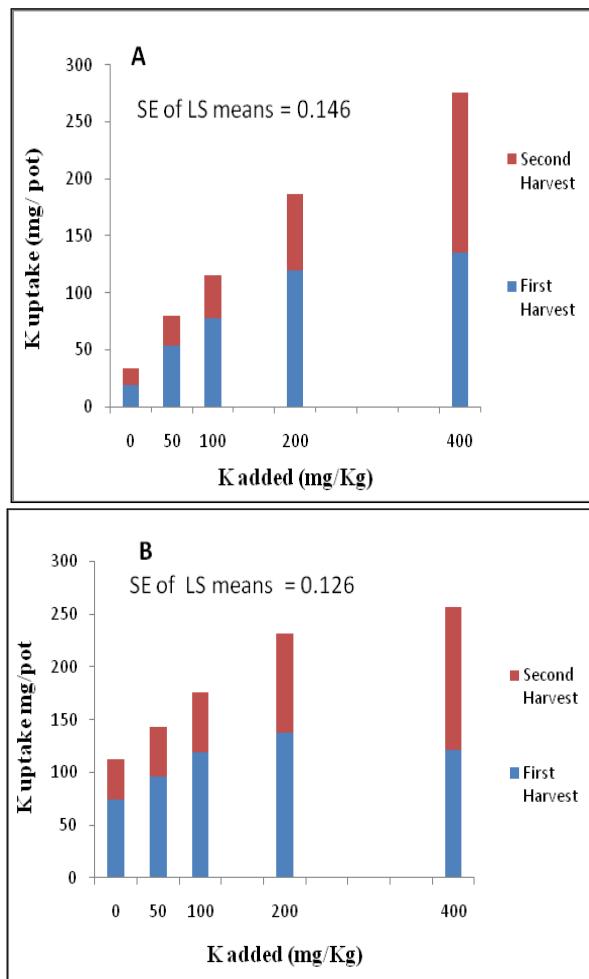


Figure 3. Potassium (K) uptake by maize (*Zea mays*) in response to increasing K addition in two Black Vertosols with low (Inverell (A)) and high (Clark (B)) K status following two harvests at (28) and (23) days after sowing. Values are the means of three replicates and significant differences ($P<0.001$) are indicated with least significant difference bars.

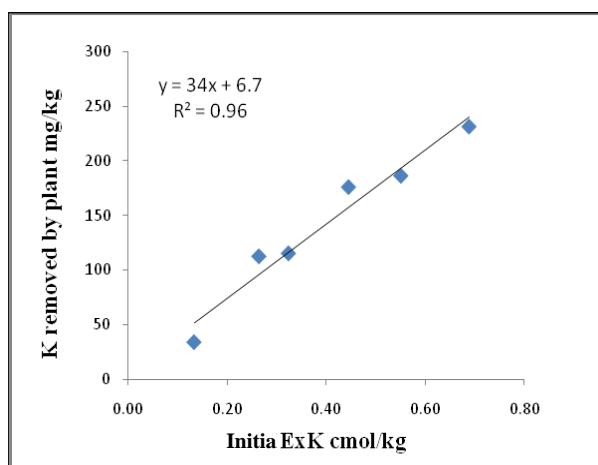


Figure 4. Potassium (K) removed by maize (*Zea mays*) growing in Inverell and Clark Vertosols following two harvests at 51 days in relation to initial K status.

Soil K chemistry

The CEC of the soil reflects the soil's ability to hold K and other cations and store them in the soil for crop uptake (4) and it has traditionally been used to index soil buffering characteristics (11). Potential buffering capacity of K (PBCK) is the slope of linear part of the Q/I plots being a measure of soil ability to maintain K activity in soil solution (1 and5). In this study, we measured PBCK by the slope of the adsorption and desorption curve rather than use a traditional Q/I curve because this method is cheaper and easier to use than Q/I curve method; we found a positive correlation between CEC and initial and final PBCK, and increase in PBCK values with increased CEC. Jimenez and Parra (10) also found close linear correlations between PBCK derived from Q/I curves data and cation-exchange capacity (CEC) ($r^2 = 0.95$) in Vertisols soils of southwestern Spain. Abaslou and Abtahi (1) also found PBCK significantly and positively correlated with the CEC ($r^2 = 0.79$) in Iranian soils. Hossein and Kalbasi (9) found highly significant relationship between PBCK and CEC ($r^2 = 0.66$, $P = 0.01$) in 15 soils from central and northern Iran.

The high PBCK values are a measure of constant availability of K in the soil solution over a long period. Therefore, soils with high values of PBCK had a very high capacity to protect the soil solution K concentration from depletion, whereas low PBCK would suggest the need for frequent K supply throughout fertilization practices (1). The highest value for PBCK was associated with soil which had the greatest values of CEC, and the lowest PBCK value was related to soil which had the least CEC values.

The variations in slope between initial and final PBCK after leaching five times was about 20%. Removal of adsorbed K from specific sites of soils by leaching or cropping increased the buffer capacities of low CEC soils ($<31 \text{ cmol kg}^{-1}$), while in high CEC ($>45 \text{ cmol kg}^{-1}$) the PBCK decreased. Schneider (14) found PBCK increased when CEC increased and when K concentration in soil solution decreased. The reduction in PBCK values of high CEC soils indicated that these soils are less able to supply K to plants than low CEC soils in the short term. Sparks and Huang (17) found that high CEC soil retains K more strongly than soils with lower CEC but soil with higher CEC has greater storage capacity and supplying power for K (4). Bell et al. (6) found that the soil solution K and ArK were much less responsive to increasing exchangeable K in black Vertosol soil that have a high K buffer capacity (PBCK) and high CEC.

The activity ratio values of K (ArK) are a measure of the availability or intensity of labile K in the soil (Sparks and Liebhardt 16). For the 12 Vertosols used in this study, the ArK increased following the addition of K fertilizer (Figure 1). The increase in ArK by K application has been reported in many previous studies. Both Beckett (5) and Sparks and Liebhardt (16) observed that high values of ArK are generally associated with K fertilization or naturally high exchangeable K levels. The greater the ArK values, the greater amount of soil solution K or plant available K. Moody and Bell (12) found that soil solution K was highly correlated with soil solution ArK. The differences in ArK values between soils were linked with the differences of soils CEC and K saturation.

Abaslou and Abtahi (1) found that ArK is negatively correlated with CEC ($r^2 = -0.74$) and clay ($r^2 = -0.80$) but in our study there was a poor relationship between ArK and CEC ($r^2 = 0.20$) data not shown. We found ArK

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increased linearly with increase exchangeable K by adding K fertiliser for each soil used in this experiment (Figure 1). The increases in ArK varied between soils according to the percentage of K saturation (exchangeable K CEC⁻¹). Beckett (5) found that ArK was proportional to exchangeable K CEC⁻¹ or percent of K saturation. So, soils with relatively constant extractable K levels but higher CEC would contribute less available K for plants.

Removal of K from soils by leaching led to a large reduction in ArK values of low CEC soils about 60 to 77% while in high CEC soils the reduction was about 20 to 40 % (Figure 1). The variations in ArK between high and low CEC soil indicated that the high CEC soils have high resistance to change in K level during the cropping season and vice versa (2).

The results showed small change in CEC of each soil used in this experiment with increasing K application. This increase may be associated with an increase in soil negative charge due to higher salinity of the equilibrating solutions.

Plant K responses

Both Inverell and Clark Vertosols used in glasshouse trial had similar CEC (44.7 cmol kg⁻¹), slightly different PBCK (0.71 and 0.80 mM L⁻¹) and different initial exchangeable K status (0.13 and 0.26 cmol/kg) respectively. Vertosols are commonly dominated by high clay mineral content, which gives these soils a high PBCK (16). The differences in PBCK for the same CEC soils may be attributed to its higher K saturation (5). The percentage of K saturation for Inverell was 0.3% whilst Clark was 0.6% of CEC. According to soil chemistry data, these soils will maintain relatively constant K availability for plants over a long period.

The results showed that the shoot K uptake of maize plants increased with increased K application in both Inverell and Clark soil at both harvests. This was also reported by DeMent et al. (8) using various species. Sparks et al. (18) found that applications of K increased the K concentrations of the corn plant leaves during the early silk growth stage. There were big differences in shoot K uptake of maize between two soils at both harvest periods, these differences related to initial K saturation. The different values of PBCK of these soils did not give a good indicator for plant K uptake as expected from the soil chemistry trial. Ram and Prasad (13) similarly observed no effect of PBCK on K uptake by sorghum plants.

Sparks and Liebhardt (16) suggested that a high PBCK value for a soil indicates a good supply of K for a long period of time and that a low PBCK indicates a need for frequent fertilization. This corresponds with Clark soil, which supplied more K at second harvest, but also high PBCK soils leads to higher K fixation and limits K availability to plants at high rate of applied K. Both Inverell and Clark Vertosols showed significant differences in maize shoot dry weight, these differences may be associated with soil physical conditions and the amount of plant available water, ultimately affecting nutrient availability. Wakeel et al. (19) found significant effect of soil types (soil texture and clay content) on shoot dry weight production of maize.

There was no significant difference in shoot dry matter of maize at the first harvest period with increase K uptake as a result of increase K application

rates. Wakeel et al. (19) also observed no significant differences in shoot dry weight of maize plants growing in three different soil types with four K levels (0, 50, 100 and 150 mg K kg⁻¹). They explained that the soils having high clay contents generally are rich in available K and have more K fixing capacity hence, crops grown on these do not respond to applied K as in our study for Clark farm soil. Following a high rate of applied K (400 mg kg⁻¹) the uptake of K in Inverell soil was higher than Clark soil at both harvests, this may be related to differences in PBCK, because high PBCK soil has ability to fix more K than low PBCK soils. There are a number of other explanations for higher K uptake in the Inverell soil at the highest K application rate. First, Clark soil may have high K fixation capacity, removing exchangeable K from the pool in equilibrium with the soil solution. Some evidence for that can be drawn through extrapolation of the exchangeable K from the soil K adsorption curves assuming that the same proportion of original soil K is removed by the plants. Second, growth may have been limited at high K availability due to limitations in N or P nutrition at the higher growth rate observed in the Clark soil. Third, differences in soil physical conditions in the pot may have limited root exploration of available K reserves as the Clark soil was heavier in nature, forming larger soil aggregates (observation only).

However, increased K uptake did not affect shoot dry weight in soil having high CEC level and high K status and higher K concentration in plants grown in heavy clay soils indicated that K availability was not the limiting factor for shoot growth. Carter and Singh (7) found the application of K fertilizer to the Vertosols soils did not have a significant effect on the shoot dry matter yield of maize, under conditions where more than adequate K was available in both soil solution and exchangeable K pools in the soil.

Conclusions

This study sought to understand K availability for maize uptake as a function of soil supply of K in heavy clay Vertosol soils. Uptake of K from each of the three rates of K, (0, 100, 200 mg K/kg) was dependant on the CEC of the soil. This would indicate that a fertiliser regime for K must first involve an understanding of the CEC of the soil in order to achieve optimal rates of application of K.

The ArK increased following addition of K fertiliser to all the soils tested. This should lead to higher K availability to plants, which was the case for the maize grown in the two soils studied. However the availability (ArK) was dependant on both the CEC and the initial exchangeable K status. There is a clear correlation between increasing CEC and increases in PBCK, indicating that an understanding of CEC is necessary to achieve optimal fertiliser application rates in heavy clay Vertosols soils. For soils with similar CECs the addition of K fertiliser can increase K availability (both ArK and exchangeable K) producing increased dry matter production in soils with low exchangeable K levels.

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تأثير السعة التبادلية للايونات الموجبة على جاهزية البوتاسيوم للنبات في الترب

الطينية الثقيلة

حسين خضير عباس العزاوي

الملخص

ان هدف هذه الدراسة ان تفهم جاهزية البوتاسيوم للنبات الذرة الصفراء كدلالة لتجهيز البوتاسيوم في الترب الطينية الثقيلة (VERTOSOL) . ثلاثة تراكيز من البوتاسيوم (صفر، 100، 200) ملغم/كغم اضيفت بشكل كلوريد البوتاسيوم الى اثنتا عشر تربة VERTOSOL ملدة ثلاثة ايام.

تراكيز الايونات الموجبة القابلة للتبادل حصل عليها قبل وبعد الترشيح مع 18 مل من محلول كلوريد الكالسيوم CaCl_2 (تركيز 0.0025m . نسبة فعالية K activity ratio) ازدادت بعد اضافة سماد البوتاسيوم وهذه الزيادات تفاوتت بين انواع الترب طبقاً للاختلاف في قيم (CEC) وكمية البوتاسيوم القابل للتبادل الاولية في التربة. وجدت علاقة بين CEC وسعة البفر المختتملة للبوتاسيوم PBCK وكانت الترب ذات القيم العالية من PBCK لها قدرة عالية جداً على حفظ تراكيز البوتاسيوم من النضوب بينما الترب ذات القيم الواطنة من PBCK تؤشر على الحاجة لاضافة سماد K باستمرار.

بيت الدراسة ان القيم العالية PBCK كانت مرتبطة بالتراب ذات القيم العالية لا CEC والقيم الواطنة لا PBCK كانت مرتبطة بالتراب ذات القيم الواطنة لا CEC .

هذه الادلة كانت لها نتائج لاستعمال اضافة سماد K في زراعة الذرة الصفراء. نوعين من الترب ال (vertosol) استخدمت لزراعة نباتات الذرة الصفراء مع اضافة الجرع السمادية (صفر، 50، 100 ، 200، 400) ملغم/كغم من سماد البوتاسيوم (KCL) لفترتين حش . امتصاص K في الجزء الخضري ازداد معنوياً مع زيادة اضافة سماد البوتاسيوم.

انتاج المادة الجافة للجزء الخضري في التربة ذات المستوى العالي من البوتاسيوم القابل للتبادل الاولى لم تتأثر باضافة سماد البوتاسيوم بينما النباتات التي زرعت في الترب ذات المستوى المنخفض من الـ K اشارت الى زيادة المادة الجافة للجزء الخضري في فترة الحصاد الثانية .

تركيز البوتاسيوم العالي للنباتات التي زرعت في الترب ذات التركيز العالي من الـ K اشارت الى ان جاهزية البوتاسيوم ليست عامل محدد لنمو الجزء الخضري.