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RELATIONSHIP BETWEEN THE QUANTITY AND INTENSITY OF POTASSIUM IN SOME MAIZE SOILS OF CENTRAL KASHMIR (INDIA)

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ABSTRACT

Plant K uptake depends on its intensity, capacity and removal rate of soils which can be modeled using K exchange-equilibrium obtained from quantity-intensity (Q/I) isotherms i.e. activity ratio at equilibrium (AR_e^K), labile K (K_L), potential buffering capacity ($PBC^{K)}$ and free energy change (-ΔG). These relations were studied in five major maize growing soils of district Ganderbal (Kashmir, India). AR_e^K ranged from 0.26 to 1.21 x 10^{-3} $(Mol\ L^{-1})^{0.5}$, K_L from 0.26 to 0.67 $cmol_c\ kg^{-1}$, PBC^K from 23.2 to 37.6 $cmol_c\ kg^{-1}/(Mol\ L^{-1})^{0.5}$ and -ΔG from 3.98 to 4.81 K cal $mol^{-1o}K^{-1}$. AR_e^K was found significantly correlated with clay (r = 840) and K_0 (r = 988*). Magnitude of labile K (K_L), K held on non-specific sites (K_0) and specific sites (K_X) were higher in Sumbal silty clay. The negative values of ΔG indicated that K- (Ca + Mg) exchange in all the soils was spontaneous.**

Key words: Buffering capacity, exchangeable potassium, maize, quantity/intensity parameters

INTRODUCTION

Soils of Kashmir are dominated by weathered potassium (K) bearing minerals so have high K saturation percentage (Wani, 2011). The total K in most Kashmir soils is high but only a small fraction is available to the plants (Wani and Rajkumar, 2005). For a proper appraisal of fertility status and appropriate fertilizer recommendation, it is imperative to study K-(Ca+Mg) exchange equilibria (Schneider *et al.,* 2003). Many workers independently applied the concept of activity ratio and related thermodynamic parameters to determine soil nutrient status (Ranjha *et al.,* 2001). Following the classical work of Beckett (1964), the quantity-intensity (Q/I) relationship of K has been widely promulgated to elucidate the K status and its soil availability (Wang and Scott, 2001). Q/I relationship is an effective index of mineral weathering. The changes in K availability and long range capacity to supply K to the plants could be predicted from the intensity and buffering power of K, which are directly obtained from the quantity/intensity curves of K (Beckett, 1964).

The activity ratio at equilibrium (AR_e^K) indicates the status of immediately available K, and so regulates the exchange of K^+ ions from the exchange complex to solution phase (Beckett, 1964). This ratio is the measure of intensity (I) of labile K in soil. The AR_e^K values have been used as an index of K availability (Abaslou and Abtahi, 2008). The lower portion in Q/I plot is associated with K adsorption at soil colloids (Diatta *et al.,* 2006) and is termed as labile pool of potassium (K_L). K_L

is the K exchanged by cations from colloidal surface. It is the measure of Q/I parameter and is represented by the variation from linearity of curve as it approaches an activity ratio of zero (Patra *et al.*, 2007). The quantity of K that could be held on specific sites (K_X) may be a good tool to predict K status in soils. K_X values are bound-K on specific sites on preferentially adsorbed K which had comparatively much more stronger binding energy (Sharma *et al.*, 2012). The potential buffering capacity (PBC^K) of K denotes the capacity of a soil to replenish the exchangeable K. It determines the rate of change of quantity with intensity and it represented gradient of a curve. The slope of linear part of Q/I curve is designated as potential buffering capacity of soil. It indicates the measure of the soil ability to maintain a given K activity ratio with change in the amount of K_L (Akhter and Dixon 2009). Nutrient ions are adsorbed on exchange sites on soil surface and the magnitude of energy required to remove nutrient ions from adsorption surface is known as chemical potential of ion. ΔG^0 is the measure of difference between chemical potential of K^+ and (Ca^{2+}+Mg^{2+}) and is referred to as free energy of K - (Ca + Mg) exchange. Due to less information available on K behaviour in agro-environment, the farmers often do not apply K fertilizers to soil while others blindly apply K fertilizers in quantities that lead to unsustainable crop production. In present study an attempt was made to identify different Q/I parameters and to interpret them in terms of physiochemical properties of maize soils of district Ganderbal (Kashmir).

MATERIALS AND METHODS

Five surface soil (0-15 cm) samples representing the major maize growing soils of district Ganderbal (Kashmir) were studied in 2010 at SKUAST- K, Shalimar, Kashmir (India). The soil samples were collected from the selected sites at different altitudes prior to maize sowing as per the probability soil sampling approach based on simple random sampling (Patterson and Carter 2008). The soil samples were separately processed, air-dried and ground to pass through 2 mm sieve before use. The physical and chemical characteristics of soil were determined with respect to texture, pH, clay contents, $CaCO_3$ and organic matter. The pH was determined in 1:2.5 soil-water suspension by a glass electrode, EC with the help of solu bridge conductivity meter at 25°C (Jackson, 1967) and CEC by ammonium acetate method (Lu, 1999). Particle size distribution was determined by pipette method after dispersing the soil in sodium hexametaphosphate (Gee and Bauder, 1986). Total $CaCO_3$ in soil, expressed as $CaCO_3$ equivalent, was determined by a rapid titration method (Rayment and Higginson, 1992). Organic matter was determined by wet digestion (Nelson and Sommers, 1996).

The Q/I relationship was determined as per Beckett (1964). Soil samples, 5 g each, in triplicate of each soil was equilibrated with 50 mL 0.01 M $CaCl_2$ solution, each containing 0, 5, 20, 40, 80, 100, 150 and 200 ppm K. The lab analysis was conducted under temperature of 25±1°C and $CaCl_2$ was used as background solution. Potassium was determined in the filtrate on flame photometer and Ca + Mg by titrating the filtrate with 0.01 M EDTA. Activity ratio (AR^K) i.e. intensity factor (I) of K to (Ca + Mg) was calculated from the composition of equilibrium solution.

$$AR^K = \frac{a_K}{\sqrt{a_X}} = \frac{f_K C_K}{\sqrt{f_X C_X}} = \frac{f_K C_K}{\sqrt{f_{Ca} C_{Ca} + f_{Mg} f_{Mg}}}$$

Where a_K and a_X are the activities of K and Ca + Mg. The activity coefficients were then measured as per Beckett (1964). From the plot of mean values of ΔK v/s AR^K, the Q/I parameters were obtained. Generally, the curve shows linear upper part and a curved lower part. The linear part of curve was interpolated to intersect X axis. This X axis intercept would represent the equilibrium activity ratio AR_e^K where ΔK = 0. The K_0 values were obtained by drawing a tangent from the point on Q/I curve where ΔK = 0. Labile - K (K_L) was obtained by drawing a tangent on Q/1 curve where it intercepts on X-axis and specific-K (K_X) by difference between K_L and K_0 (K_L- K_0). The potential buffering capacity was determined by dividing K_0 by AR_e^K. The difference of Gibb's free energy change of K- (Ca + Mg) was calculated from the relationship:

$$-\Delta G = {2.303RT\ log a_K}/{\sqrt{a_x}}$$

Where, R = gas constant (cal/mol); T = absolute temperature, G = free energy change (cal/mol) of K - (Ca + Mg) exchange

The necessary statistical analysis correlation and Q/I model fitting of data was conducted in SPSS 20 and Microsoft excels 2007, respectively.

RESULTS AND DISCUSSION

The soil physicochemical properties are given in Table 1. Q/I relation gives a comprehensive idea about soil K status and takes into account the activity ratio [$\frac{a_K}{\sqrt{a_X}}$] of a solution in equilibrium within a given soil to provide a satisfactory measure of K availability. Q/I relationship indicates the amount of soil K available for plant uptake during growth period. Their usefulness is based on the consistency of form and slope of quantity-intensity curves and is characteristic for each soil (Beckett, 1971). The Q/I relationship for all soil samples was characterized by an upper portion which was linear and a lower portion which was curved asymptotically towards ±ΔK axis (Fig. 1 & 2). The different Q/I parameters of potassium are given in Table 2.

Equilibrium activity ratio (AR_e^K)

The AR_e^K values in soils ranged from 0.26 x 10^{-3} to 1.21 x 10^{-3} (Mol L^{-1})$^{0.5}$ [Table 2]. The values were lower than those of Wani *et al*. (2010) for Kashmir rice soils [1.2 to 3.1 x 10^{-3} (Mol L^{-1})$^{0.5}$]. The variations could be ascribed to the differences in the concentration of equilibrating solutions, equilibration period, Ca and/or Mg contents and soil mineralogy. Smectite soil clays showed a characteristic upper linear portion at moderate value of activity ratio and a curved lower region at lower values. Illitic soil clays showed lower curved region at low values of activity ratio and linear portion at higher values while kaolinitic soil clays showed practically less curvature at lower values of activity ratio and steep linear rise at higher values (Rangel *et al.*, 2006). Beckett (1964) opined that higher AR_e^K values depict higher K ion strength in solution so that immediate available K pool will be higher. The AR_e^K showed -ve correlation with pH but +ve with exchangeable K and CEC (Table 3). It also showed significant +ve correlation with K on non-specific sites (r = 0.988*).

Labile K (K_L)

The K values in labile pool ranged from 0.26 to 0.67$cmol_c$ kg^{-1} in soils (Table 2). The higher values of K_L were found in Sumbal soil and lower values in Wangat soil. Higher values of K_L indicated the higher potential to replenish K concentration in soil solution for a longer period, resulting in a large pool of available K. The higher values of K_L may be ascribed to higher exchangeable K and soluble

Table 1: Physicochemical properties of maize growing soils of district Ganderbal (mean ± SE)

Location (soil type)	Geographic location	Altitude m masl	pH (1:2.5)	EC (dSm^{-1})	Clay (%)	Organic carbon (%)	CEC	Av-K	Ex- K
							[cmolc kg^{-1}]		
Wangat (Sandy loam)	34° 17′ 25.83′′N 74° 55′ 13.94′′E	1920	6.8±0.4	0.43±0.04	18.8±0.8	0.8±0.1	14.7±2.4	0.21±0.02	0.23±0.04
Sumbal (Silty clay)	34° 13′ 35.87′′N 75° 03′ 00.70′′E	1940	6.3±0.2	0.45±0.05	50.3±3.5	3.1±0.2	18.1±1.5	0.89±0.03	0.82±0.03
Ghund (Silty clay loam)	34° 15′ 32.00′′N 75° 05′ 29.00′′E	2020	6.4±0.3	0.44±0.05	38.4±2.8	2.7±0.1	17.5±0.6	0.71±0.05	0.45±0.06
Kulan (Silty clay loam)	34° 15′ 42.81′′N 75° 07′ 48.21′′E	2100	7.6±0.3	0.42±0.04	39.8±2.1	2.8±0.5	17.9±1.4	0.84±0.04	0.75±0.06
Gagangir (Sandy loam)	34° 18′ 02.80′′N 75° 12′ 53.79′′E	2270	7.53±0.	0.21±0.02	18.1±1.5	1.1±0.2	16.4±1.2	0.42±0.03	0.48±0.10

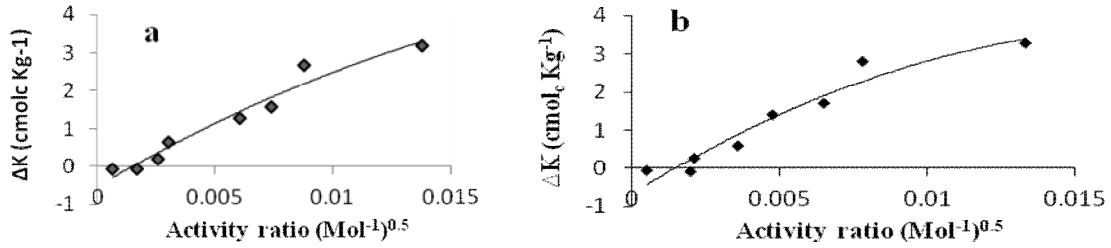

Fig. 1: Quantity/Intensity relationship of a) Wangat sandy loam and b) Kulan silty clay loam

salts and alkaline pH. In most soils under study labile K was lower than the exchangeable K content of soils (Sumbal, Ghund and Gagangir) which may be ascribed to the presence of more specific sites for K in these soils. NH^{+}_{4} could displace K^{+} from this specific sites resulting in higher exchangeable K content (Yawson *et al.,* 2011). However, in some soils (Wangat and Kulan) the value of labile K was lower than the exchangeable K indicating that the soils have high concentration of K in labile pool. Higher values of K_L may possibly be due to higher ionic strength of K in comparison to Ca^{2+} and Mg^{2+} ions in soil solution (Roy and Kumar, 1993). K_L was higher than the exchangeable K, indicating the soils have high concentration of K in labile pool. These results corroborate with the findings of Yawson *et al.* (2011).

Non-specific sites for K (K_0)

The values of non-specific K in soil ranged from 0.12 to 0.19 $cmol_c\ kg^{-1}$ (Table 2). The lower values of non-specific or immediately available K were due to greater K removal by the proceeding crops. Lowest amount of K_0 observed in these soils appears due to the predominance of illite, having high K specificity, which implied that only a small amount of K would remain in soil solution. No soil indicated much K on non-specific site, thereby revealed poor release from these soils. This is probably due to neutral to slightly acidic reaction, low base saturation and less weathered clay minerals, facilitating stronger binding of K (Wang and Scott, 2001). The K_0 showed significant correlation with exchangeable K (r = 0.879*), AR_e^K (r = 0.988*) and K_L (r = 0.803*) [Table 3]. Since K held at planar position can be easily removed, so an increase in K_0 tends to increase AR_e^K. Increased exchangeable K_0 gives rise to increase in water soluble K, which would increase AR_e^K.

Specific sites for K (K_X)

The quantity of K held on specific sites was obtained by extrapolation of Q/I curve to the ordinates. The K held on specific sites ranged from 0.11 to 0.49$cmol_c\ kg^{-1}$ (Table 2). The higher K_X values indicate higher exchange surface offering a selective or specific binding site for K^{+} and not for Ca^{2+} and Mg^{2+} and also may be due to the amount of mica present in the soil. Higher K_X than K_0 implies that labile pool of K was mainly controlled by K_X. It showed significant correlation (Table 3) with CEC (r = 0.965*) and exchangeable K (r = 0.912*) of soils which confirms the assumption that K dynamics of these soils is rather a matter of exchange reactions. Similar findings were reported by Poonia and Niederbudde (1990) who stated that K - preference for soil colloids over Ca could be a resultant of an increase/decrease in surface charge density and low/high K-specific adsorption sites.

Table 2: Q/I parameters derived to describe K dynamics in maize soils in Ganderbal (mean ± SE)

Location (soil type)	AR_e^K $(mol\ L^{-1})^{½}$ x 10^{-3}	K_L $(cmol_c\ kg^{-1})$	K_0 $(cmol_c\ kg^{-1})$	K_X $(cmol_c\ kg^{-1})$	PBC^K $(cmol_c\ kg^{-1})/(mol\ L^{-1})^{½}$	$-\Delta G^0$ K cal $mol^{-1}\ {}^0K^{-1}$
Wangat sandy loam	0.26±0.03	0.26±0.04	0.12±0.02	0.11±0.01	30.53±5.58	4.47±0.37
Sumbal silty clay	1.21±0.02	0.67±0.03	0.19±0.01	0.49±0.04	23.21±1.95	3.98±0.42
Ghund silty clay loam	0.44±0.05	0.56±0.02	0.14±0.03	0.42±0.02	36.02±3.20	4.72±0.19
Kulan silty clay loam	0.53±0.06	0.63±0.04	0.15±0.01	0.48±0.03	37.62±1.48	4.81±0.12
Gagangir sandy loam	0.33±0.02	0.45±0.03	0.13±0.01	0.39±0.02	27.22±0.39	4.67±0.06

Table 3: Correlation coefficients of various soil properties with Q/I parameters

Parameters	pH	CEC	Clay	Available K	Exchangeable K
AR_e^K	-0.529	0.679	0.840**	0.739	0.798
K_L	-0.102	0.991	0.842**	0.963*	0.964*
K_0	-0.456	0.780	0.893**	0.831**	0.879**
K_X	0.026	0.965	0.727	0.903*	0.912*
PBC^K	0.326	0.095	0.745**	0.108	-0.091
-ΔG	0.662	-0.109	-0.417	-0.109	-0.285
Parameters	AR_e^K	K_L	K_0	K_X	PBC^K
K_L	0.707				
K_0	0.988*	0.803**			
K_X	0.580	0.981*	0.687		
PBC^K	-0.513	-0.001	-0.422	0.046	
-ΔG	-0.797	-0.152	-0.695	-0.009	0.827**

*Significant at 0.05 level; **Significant at 0.01 level

Potential buffering capacity (PBC^K)

The PBC^K values ranged from 21.95 to 37.62$cmol_c$ $kg^{-1}/(MOL\ L^{-1})^{0.5}$. Higher PBC^K values suggested that the soils were highly buffered with respect to K or had high potential to replenish K in soil solution (Daitta *et al*., 2006). The low PBC^K might be due to high sand and low organic matter. The lower values of PBC^K indicate the poor ability of soil to maintain the intensity of K in soil solution for longer period when under cropping. Soils low in PBC^K would need frequent application of K fertilizers. Beckett (1964) observed that soils having low PBC^K are likely to be deficient in K under intensive cropping. The soil PBC^K showed positive significant correlation (Table 3) with clay (r = 0.754**) implying that the supplying power of soils is significant contrary to the number of accessible surface charges. Most of these charges could originate from Fe and Mn oxides, which under equilibrium state may generate additional low energetic charges responsible for K retention in these soils. In similar findings, Diatta *et al.* (2006) reported that the influence of the low organic matter content and its share in the generation of negative charges is practically marginal. Such relationships indicate that K dynamics in soils is basically subjected to interactions of several factors, of which PBC^K is a resultant.

Free energy change

The $-\Delta G^0$ ranged from 3.98 to 4.81 K cal $mol^{-1o}K^{-1}$. Negative values of free energy change indicated that K-(Ca + Mg) exchange was spontaneous. More negative values of ΔG^0 would result in more release of K (Bangroo *et al*., 2012) and less negative values of ΔG^0 indicate less bonding of K^+ ions.

Conclusion: In present study, Q/I isotherms were used to evaluate the K dynamics in five major maize growing soils of district Ganderbal (Kashmir). The soils varied appreciably in their physicochemical properties. The study revealed that higher intensity and activity leads to a lower PBC^K which is better indicator of the ability of soil to maintain K intensity.

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