Agropedology 2009, 19 (2), 106-111

K – Ca exchange equilibria in some Inceptisols of southern Karnataka

B. C. DHANANJAYA AND R. ANANTHANARAYANA

Department of Soil Science and Agricultural Chemistry, Agriculture College,
UAS Campus, GKVK, Bangalore–560065, India

Abstract : Exchange equilibria involving K and Ca were studied in some Inceptisols of southern Karnataka. The soils were dominant in Kaolinite clay and differing in their clay content, organic carbon and cation exchange capacity (CEC). Preferential K adsorption was observed on all the soils. The exchange isotherms, selectivity co-efficients and ΔGr^0 indicated K selectivity relative to Ca, the selectivity was higher at lower K saturation and decreased to a rather constant value with increasing K saturation. The decrease in the selectivity co-efficients with increase in K saturation was in the order of $K_V > K_N > K_G$ which was due to the difference in the forms of the cation exchange equations. The observed K affinity in these soils is attributed to high surface charge density of dominant kaolinitic clay and K specific adsorption sites provided by the organic matter. The decreasing K preference with increasing K saturation is due to the decrease in the binding energy of the K adsorption sites.

Additional key words: *Selectivity co-efficients, ΔGr^0 of K-Ca exchange, K saturation, kaolinitic soils*

Introduction

Acid soils in high rainfall areas suffer from the deficiency of nutrients. It is, therefore, of great importance to study the exchange equilibria involving relevant cations in such soils to understand the nutrient leaching phenomenon and correct their deficiency. Potassium (K) and calcium (Ca) are some of the cations that have undergone the most extensive testing in soil systems in terms of solution – exchange phase interaction (Beckett 1964). Both the cations are important for proper nutrition of plants. In acid soils, these cations are lost through leaching under the influence of heavy rainfall. The exchange equilibria among various cations, especially K and Ca, are useful in explaining the interaction between the solid and solution phases of soils for these cations and understanding their leaching and adsorption behaviour in these soils. Although cation exchange equilibria of these acid soils with variable charge is known, yet in view of the fundamental importance of such information, cation exchange equilibria involving K and Ca were studied in some selected Inceptisols of southern Karnataka.

Materials and Methods

Four surface soil samples (0 to 15 cm) representing Inceptisols were collected from various locations falling under different agro-climatic zones of southern Karnataka. Hassan coming under the southern transition zone, Thirthahally under the hilly zone and Kumta and Gundmi under coastal zone receive annual rainfall of 700 to 1800 mm, 1500 to 3800 mm and 3000 to 4500 mm, respectively (Dhanorkar and Ananthanarayana 2002). Important physico-chemical characteristics of the soils were determined as per the standard procedures (Baruah and Barthakur 1998) (Table 1). The dominant clay mineral in these soils is Kaolinite and the surface charge density (SCD) determined on the basis of the X-ray diffractometry (Ananthanarayana and Ravindra 1998) is also given in table 1.

Exchange equilibria study

An attempt was made to study exchange equilibria involving K-Ca in agricultural soils by adopting the procedure as outlined by Mehta *et al.* (1983). For this, the soils were made homoionic with Ca by repeated washings with 1*N* $CaCl_2$. The soils were then made chloride free by repeated washings with distilled water and methanol. The samples so prepared were air dried, ground and passed through 60 mesh sieve and used.

Two gm of Ca saturated soil sample was taken in 50 ml. centrifuge tubes and equilibrated with 1:10 soil-solution ratio with mixed chloride solutions of K and Ca (K + Ca), at a constant electrolyte concentration of 10 meL^{-1}. The equivalent ion fractions of K in the solution varied from 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 me L^{-1}. The soil suspensions were shaken for one hour and equilibrated in a BOD incubator for 24 hours. Then, they were centrifuged and the supernatant was filtered. In the filtrate, Ca and K were estimated by versenate titration and flame photometry, respectively.

The data obtained was fitted into adsorption isotherms. The exchange reaction between K and Ca is represented as :

$$Ca - X + 2K \longleftrightarrow 2K - X + Ca^{2+}$$

where, X is the exchanger phase

Selectivity co-efficients were determined using the following exchange equations:

$K_N = (E_K)^2/E_{Ca} \times (aCa)/(aK)^2$ (Gaines and Thomas 1953)

$K_G = (E_K)^2/E_{Ca} \times (aCa)/(aK)^2$ (Gapon 1933)

$K_V = (E_{MK})^2/E_{MCa} \times (aCa)/(aK)^2$ (Vanselow 1932)

where, E_{Ca} and E_K are the equivalent fractions [cmol (p^+) kg^{-1}] and E_{MCa} and E_{MK} mole fractions (mol 100 g^{-1}) of Ca and K on the soil exchange complex, aCa and aK are the activities of the Ca and K (mol L^{-1}) in the equilibrium solution, K_N, K_G and K_V are the thermodynamic, Gapon's and Vanselow's selectivity coefficients, respectively.

The standard free energy change for the reaction (ΔGr^0) is calculated as follows.

$$\ln K = -(Z_K - Z_{Ca}) + \int_0^1 \ln K_N \,.\, D E_K$$

$$\Delta Gr^0 = -RT \ln K$$

where, R is gas constant, and T is absolute temperature

Results and Discussion

Physico-chemical characteristics

The physico-chemical properties of the experimental soils are presented in table 1. The texture of soils was sandy loam in Thirthahally and Gundmi soils and sandy clay loam in Hassan soil and loamy sand in Kumta soils. The clay content was highest (32.4%) in Hassan soils followed by that in Thirthahally (18.6%) and Gundmi (18.0%) soils. Lowest clay (14.1%) was observed in Kumta soil. The SCD was highest 2.71 meq cm^{-2} in Kumta soil and varied a little among other soils (ranging between 1.90 to 1.97 meq cm^{-2}). According to Ananthanarayana and Ravindra (1998), Kaolinite was the dominant clay mineral in these soils. Soil pH was acidic ranging from 4.64 to 6.05 and organic carbon content varied from medium to high status in these soils. High organic carbon content of 15.7 g kg^{-1} was noticed in Kumta soil followed by Hassan soil (10.1 g kg^{-1}) mainly due to differences in the management practices under varied land use systems. The free Fe and Al oxides contents were high due to the higher solubility of Fe and Al in these soils. The CEC was quite high [22.10 cmol (p^+) kg^{-1}] in Hassan soil and it varied between 10.30 and 12.40 cmol (p^+) kg^{-1} in the remaining soils. The low CEC values are also ascribed to acidic parent material and low exchangeable bases, which are leached due to high rainfall. The exchangeable Al content was higher in Gundmi soil (0.35 cmol (p^+) kg^{-1}) followed by Thirthahally, Hassan and Kumta soils.

Table 1. Physicochemical characteristics of the soils

Location	Clay (%)	Textural class	SCD* (meq m^{-2})	Sesquioxides (%)		pH	Organic carbon (g kg^{-1})	CEC	Exch. Al
				Fe_2O_3	Al_2O_3			[cmol (p^+) kg^{-1}]	
Hassan	32.4	scl	1.95	2.98	0.08	6.05	10.1	22.10	0.15
Thirthahally	18.6	sl	1.90	2.33	0.17	5.47	7.4	10.30	0.25
Kumta	14.1	ls	2.21	4.28	0.13	5.19	15.7	11.20	0.15
Gundmi	18.0	sl	1.97	3.24	0.04	4.64	6.2	12.40	0.35

** SCD: Surface Charge Density*

Cation exchange equilibria studies

Exchange isotherms

The exchange isotherms for K on all the soils (Fig. 1) show the relationship between the equivalent fraction of K in the equilibrium solution (C_K) and that on the adsorbed phase (Q_K). With the increase in the K concentration in the equilibrium solution (C_K/C_O), the equivalent fraction of K on the exchange sites (Q_K/Q_O) also increased. The normalized exchange isotherms showed non-preferential exchange in these soils. It is very clear from the exchange isotherms that, at very low K concentration in the equilibrium solution (up to 20% K saturation), the adsorption isotherms for all the soils were very close to the diagonal at lower K saturation and with increasing K saturation, they moved closer to the diagonal. This indicates that K is selectively preferred at lower K saturation and the selectivity decreased with increasing K saturation of the equilibrium solution. The reason is that, when K saturation increases, more of the K^+ ions will be held on the planar surfaces of the clay minerals and the affinity for K^+ by the specific sites decreases. Delvaux et al. (1989) reported similar observations for acid kaolinitic soils from Cameroon.

The isotherms were below the diagonal after 20 percent K saturation in soils from Hassan, Thirthahally and Gundmi and after ten percent K saturation in soil from Kumta, and with increasing levels of K saturation, the isotherms moved closer and below the diagonal. This suggests decreased K selectivity and increased Ca preference by all the soils.

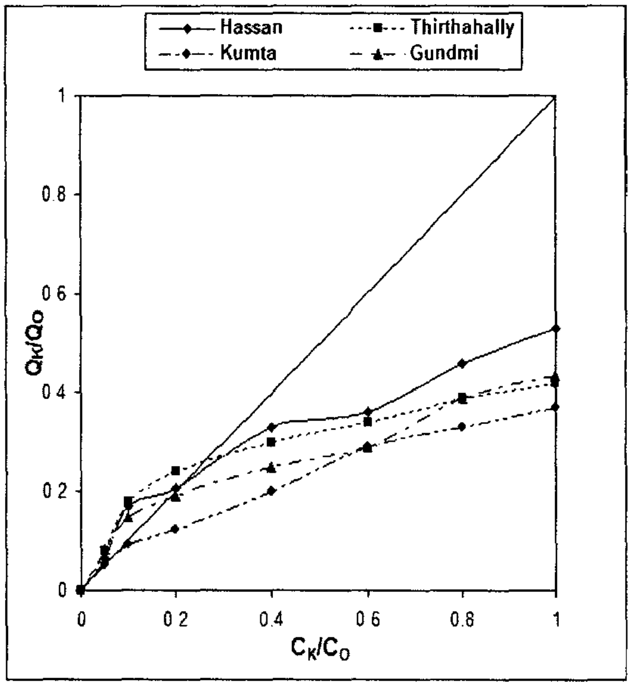

Fig. 1. K exchange isotherm for some Inceptisols of Southern Karnataka

Selectivity coefficients and standard free energy change

The data on selectivity co-efficients (K_N, K_G and K_V) and standard free energy change ($\Delta Gr°$) of the K-Ca exchange are presented in table 2. It is clear from the table that the values were different for different soils, being higher at lower K saturation (up to 20 % K saturation) and decreasing thereafter with increasing K saturation of the equilibrium solution. In all the soils, the pattern of variation of these parameters with K saturation was similar, being high at low K saturation and decreasing to approximately a constant value with increasing K saturation. The high values (>1) of selectivity coefficients (K_N, K_G and K_V) and negative

Table 2. Calculated values of selectivity co-efficients (K_N, K_G and K_V) and standard free energy change (ΔGr^0) for the K-Ca exchange on Inceptisols

[K Saturation (%)	K_N ($mol^{-1}L$)	K_G ($mol^{-1/2}L^{1/2}$)	K_V ($mol^{-1}L$)	ΔGr^0 (Kcal mol^{-1})
Hassan Soil: Typic Dystrustepts, Land use: Wetland rice				
5	642.86	25.54	2534.49	-3.83
10	360.97	19.21	1412.63	-3.49
20	293.27	17.49	1126.58	-3.37
40	242.92	16.26	899.03	-3.25
60	223.01	15.86	801.00	-3.20
80	165.00	13.80	582.35	-3.03
100	151.61	13.46	521.63	-2.98
Thirthahally Soil: Fluventic Haplustepts, Land use: Arecanut plantation				
5	885.61	30.03	3480.68	-4.02
10	521.74	23.11	2040.69	-3.71
20	246.91	16.01	952.38	-3.26
40	190.27	14.30	711.97	-3.11
60	123.23	11.64	452.06	-2.85
80	82.49	9.59	299.03	-2.61
100	62.70	8.42	224.71	-2.45
Kumta Soil: Typic Dystrustepts, Land use: Cultivated rice fallow				
5	277.42	16.74	1098.95	-3.33
10	230.88	15.33	907.21	-3.22
20	160.65	12.88	622.51	-3.01
40	97.17	10.13	369.11	-2.71
60	85.67	9.63	318.66	-2.64
80	78.11	9.30	284.86	-2.58
100	73.02	9.11	260.88	-2.54
Gundmi Soil: Typic Dystrustepts, Land use: Cultivated rice fallow				
5	348.21	18.76	1377.85	-3.47
10	285.60	17.07	1120.18	-3.35
20	158.93	12.82	615.85	-3.00
40	190.27	14.30	711.97	-3.11
60	95.33	10.19	352.69	-2.70
80	91.05	10.09	329.56	-2.67
100	82.76	9.74	293.76	-2.62

ΔGr^0 values for all the soils suggested a higher K selectivity over Ca over the entire range of K saturation. This indicates the involvement of forces other than long-range electrostatic forces.

The values of these parameters decreased with increased K saturation, the magnitude of decrease being varied for different soils. The decreasing values of all the parameters suggest the preferential selectivity of Ca over K with increasing K saturation. The decrease in K selectivity is due to decrease in the binding energy of the K adsorption sites (Ogwada and Sparks 1986). Mehta *et al.* (1983) also reported similar results from their studies.

The decrease in the selectivity coefficients with increase in K saturation was in the order of $K_V > K_N > K_G$, which was due to the difference in the forms of the cation exchange equations. The differences among these coefficients were higher at lower K saturation levels. Das *et al.* (1995) reported similar observations in K-Ca exchange for acid soils of Orissa.

Multiple regression analysis indicated that clay and organic carbon are the dominant factors, respectively, influencing the selectivity coefficients and the standard free energy change, respectively. The observed higher K selectivity coefficients at lower K saturation might be attributed to the higher amounts of organic matter in the surface soils. Organic matter influences K-selectivity by increasing the internal-external surface area/exchange sites giving rise to increase in the preferential sites for K relative to Ca as also reported by Poonia and Niederbudde (1990). The experimentally observed K preference in relation to organic matter would be a resultant to this effect.

The large and negative ΔGr^0 values suggest K preference by the dominant kaolinite clay due to specific interactions of the cation with the edge sites of the clay. The large SCD associated with edge sites of the kaolinite clay would tend to create exergonic values for the exchange of such cations. The smaller hydration size of K ions relative to Ca might also be a reason for its higher selectivity.

Levy et al. (1988) also reported that the high SCD of kaolinite coupled with low energy of adsorption of water on K would enhance dehydration of K and result in an increase in the affinity for K compared to Ca. The K selectivity is also attributed to the 2:1 impurities in the clay fraction. Thus, it is very difficult to explain the K preference of the soil exclusively on the basis of clay mineralogy since detailed information on surface properties of their individual clay minerals is also needed. Dhanorkar and Ananthanarayana (2002) also reported the presence of 2:1 impurities like vermiculite and illite in the clay fraction of these acid soils.

Conclusion

High K preference exhibited by the experimental soils indicated strong K retention and less leaching. At low K saturation levels, the release of K from the solid to solution phase will be difficult due to the specific adsorption of K on soil exchange sites. Consequently, the low available K content of these soils emphasizes the need for application of higher doses of potassic fertilizers than the recommended levels to build a satisfactory concentration of K in soil solution to meet the immediate requirement of the growing crop.

References

Ananthanarayana, R. and Ravindra, M.R. (1998) Soil Acidity and Liming in Karnataka. Technical Bulletin, Department of SS & AC, UAS, GKVK, Bangalore

Baruah, T.C. and Barthakur, H. P. (1998) Methods of Soils and Plant Analysis, Vikas Publications, New Delhi

Beckett, P.H.T. (1964) Potassium calcium exchange equilibria in soils: Specific adsorption sites for potassium. Soil Science **97,** 376-383

Das, P.K., Patra, R.K., Acharyya, N. and Sahu, G.C. (1995) K-Ca exchange characteristics in an Alfisol and Inceptisol of Orissa. Journal of the Indian Society of Soil Science **3,** 587-589

Delvaux, B., Dufey, J.E., Vielvoye, L. and Herbillon, A.J. (1989) Potassium exchange behaviour in a weathering sequence of volcanic ash soils. Soil Science Society of America Journal **53,** 1679-1684

Dhanorkar, B.A. and Ananthanarayana, R. (2002) Clay mineralogy of typical acid soils of Karnataka. Technical Bulletin, Department of SS & AC, UAS, GKVK, Bangalore

Gaines, G.L. and Thomas, H.C. (1953) Adsorption studies on clay minerals. I. A formulation of the thermodynamics of exchange adsorption. Journal of Chemical Physics **212,** 714-718

Gapon, E.N. (1933) On the theory of exchangeable adsorption in soils. Journal of General Chemistry USSR **3,** 144-152

Levy, G.J., Van Der Watt, H.V.H., Shainberg, I. and Du Pleiss, H.M. (1988) K-Ca and Na-Ca exchange on Kaolinite and Kaolinitic soils. Soil Science Society of America Journal **52,** 1259-1264.

Mehta, S.C., Poonia, S.R. and Pal, R. (1983) Exchange equilibria of K versus Ca and Na in soils from a semi-arid region of India. Soil Science **135,** 214-220

Ogwada, R.A. and Sparks, D.L. (1986) Use of mole or equivalent fractions in determining thermodynamic parameters for potassium exchange in soils. Soil Science **141,** 268-273

Poonia, S.R. and Niederbudde, E.A. (1990) Exchange equilibria of potassium in soils, V. Effect of natural organic matter on K-Ca exchange. Geoderma **47,** 233-242

Vanselow, A.R. (1932) Equilibrium of the base exchange reactions of bentonites, permutites, soil colloids and zeolites. Soil Science **33,** 95-113

Received : December 2005 *Accepted : May 2009*