

# Studies on Ca-Mg and Ca-Na Exchange in Fine Textured Soils

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## ABSTRACT

Studies were conducted to investigate the effect of pH and organic matter on cation exchange equilibria in fine textured soils, varying in clay contents, organic carbon and textural class. Various physico-chemical properties of both the soils were determined. In  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  exchange the values of selectivity coefficients increased within an increase in pH and organic matter in both the soils. Kerr, Vanselow and Gapon exchange coefficients were calculated. In  $\text{Ca}^{2+}$ - $\text{Na}^+$  exchange for both the soils the replacement of  $\text{Ca}^{2+}$  over  $\text{Na}^+$  decreased and hence the values of  $K_K$ ,  $K_V$  and  $K_G$  also decreased with an increase in pH and organic matter.

**Key Words:** Cation exchange; Adsorption; pH; Organic matter; Fine textured soil

## INTRODUCTION

Soil being negatively charged help to retain cations due to which leaching loss is reduced thus maintaining plants over longer periods. Knowledge of cation exchange chemistry provides valuable clues about plant nutrient deficiencies, toxicity and about exchangeable sodium. A number of equations have been used with different assumptions to express cation exchange equilibria in soils. Kerr (1928) used concentration of cations in place of their activities for homoivalent cation exchange. Vanselow (1932) used mole fraction of cations which hold good for both homoivalent as well as heteroivalent cation exchange. Whereas, Gapon (1933) used concentration for adsorbed cations and activities for soluble cations. However, various factors like pH, organic matter, concentration of cation, soil CEC and temperature etc. could alter the exchange coefficients of these equations i.e. spatial variability. Keeping this in view, the current study was planned to investigate the effect of pH and organic matter on divalent-monovalent ( $\text{Ca}^{2+}$ - $\text{Na}^+$ ) and divalent-divalent ( $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ ) exchange in soils of Pakistan.

## MATERIALS AND METHODS

Two soil samples one clay loam (soil A, Gujranwala soil series) and other silty clay loam (soil B, Kotli soil series) both having fine texture were collected. Both the soil samples were processed and analyzed by methods of U.S. Salinity Laboratory Staff (USSLS, 1954) and Moddie *et al.* 1954 (Table I). Particle size analysis was made by Bouyoucos hydrometer method (Bouyoucos, 1962) and for textural class International Textural Triangle was followed.

Both the soil samples were treated with  $\text{NH}_4\text{Cl}$  solution to remove all the cations present in the soils. After three washings with ethanol soil samples were made homoionic with  $\text{CaCl}_2$  solution. For homoivalent exchange, adsorbed Ca was replaced with  $\text{CaCl}_2$  :  $\text{MgCl}_2$  (1:1) solution while for heteroivalent exchange treated the Ca-saturated samples with  $\text{CaCl}_2$ : $\text{NaCl}$  (1:1) solution. The pH levels for soil A were 7.85 control  $8.0 \pm 1.0$  and  $9.0 \pm 1.0$  while these were 8.05 (control),  $7.0 \pm 1.0$  and  $9.0 \pm 1.0$  for soil B. Organic matter was 1.22% (control) in soil A and 1.24% (control) in soil B. To get organic matter (2 & 4%) over and above the control value, well rotten farmyard manure was added in both the soils. pH was maintained by using NaOH and HCl. Desorbed cations were determined in the filtrates. Following equations were tested by calculating the exchange coefficients:

### 1. Kerr equation

a. For divalent-monovalent exchange

$$K_K = \frac{[\text{NaX}]^2[\text{Ca}^{2+}]}{[\text{CaX}][\text{Na}^+]^2} = \frac{(\text{NaX})^2(\text{Ca}^{2+})}{(\text{CaX})(\text{Na}^+)^2}$$

b. For divalent-divalent exchange

$$K_K = \frac{[\text{MgX}][\text{Ca}^{2+}]}{[\text{CaX}][\text{Mg}^{2+}]} = \frac{(\text{MgX})(\text{Ca}^{2+})}{(\text{CaX})(\text{Mg}^{2+})}$$

### 2. Vanselow equation

a. For divalent-monovalent exchange

$$K_V = \frac{[\text{NaX}]^2(\text{Ca}^{2+})}{[\text{CaX}][\text{NaX} + \text{CaX}](\text{Na}^+)^2}$$

b. For divalent-divalent exchange

$$K_v = \frac{[MgX](Ca^{2+})}{[CaX](Mg^{2+})}$$

### 3. Gapon equation

a. For divalent-monovalent exchange

$$K_g = \frac{[NaX](Ca^{2+})^{0.5}}{[CaX]^{0.5}(Na^+)}$$

[ ] = Concentration of cations; ( ) = Activity

The data obtained were analyzed by the ANOVA technique following completely randomized design with two factors (Steel & Torrie, 1992).

## RESULTS AND DISCUSSION

Soil analysis showed (Table I) that CEC of soil A was greater than that of soil B, perhaps due to slightly higher organic matter in the former soil. Otherwise, there is no obvious reason for this higher CEC because in soil A Mica is dominant while in soil B Montmorillonite is dominant in the clay fractions (Anonymous, 1986).

**Ca<sup>2+</sup>-Mg<sup>2+</sup> exchange.** In divalent-divalent exchange under different soil conditions the selectivity coefficient K<sub>K</sub> values range from 2.56 to 32.11 (Table II). An increase in pH and organic matter increased the K<sub>K</sub> of

soil A more than that of soil B because soil B has low CEC than soil A. In both the soils, an increase in pH and organic matter increased the CEC indicating greater replacement of Ca<sup>2+</sup> with Mg<sup>2+</sup> which is in accord with the concept that in homovalent system the preferentially adsorbed ion is usually the ion with smaller hydrated radius (Helfferich, 1962).

**Table I. Physico-chemical characteristics of soils**

Soil characteristics	Gujranwala soil series	Kotli soil series
Clay %	42	33
Textural class	Clay loam	Silty clay loam
pH <sub>c</sub>	7.85	8.05
EC <sub>e</sub> (dSm <sup>-1</sup> )	0.94	0.62
TSS (mmol <sub>c</sub> L <sup>-1</sup> )	9.4	6.2
SAR (mmol L <sup>-1</sup> ) <sup>1/2</sup>	3.89	2.47
Exchangeable cations		
Na <sup>+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	5.05	3.32
K <sup>+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	0.38	0.38
Ca <sup>2+</sup> + Mg <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	9.00	6.85
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	14.43	10.52
ESP %	1.73	3.42
Organic carbon %	1.00	0.70
Organic matter %	1.74	1.22

The selectivity coefficient values difference in both the soils could be due to low CEC of soil B compared to soil A. The increase in pH and organic matter may have increased CEC more for soil A than soil B. The low CEC soils are easily accessible to the cations with greater hydrated radii compared to high CEC soils to become neutral.

**Table II. pH and organic matter effects on Ca<sup>2+</sup>-Mg<sup>2+</sup> exchange in soils**

Trt.	Soil	Levels	Equilibrium solution			Adsorbed bases			Equilibrium constant
			Ca <sup>2+</sup> (me L <sup>-1</sup> )	Mg <sup>2+</sup> (me L <sup>-1</sup> )	Ca <sup>2+</sup> /Mg <sup>2+</sup>	CaX me 100g <sup>-1</sup>	MgXme 100g <sup>-1</sup>	MgX/CaX	
pH	A	7.85 (control)	725.00	275.00	2.63	1.90	13.00	6.84	17.9
pH	A	8	1000.00	650.00	1.54	1.17	16.20	13.80	21.3
pH	A	9	975.00	525.00	1.85	1.60	22.00	13.70	25.5
pH	B	7	1250.00	750.00	1.66	2.50	4.00	1.60	2.56
pH	B	8.05 (control)	1400.00	450.00	3.11	4.00	10.00	2.50	7.77
pH	B	9	700.00	300.00	2.33	2.20	14.00	6.36	14.83
OM	A	Control	725.00	275.00	2.63	1.19	13.00	10.92	28.71
OM	A	2%	875.00	425.00	2.05	1.50	23.50	15.66	32.11
OM	A	4%	1200.00	800.00	1.50	1.30	42.00	23.30	35.46
OM	B	Control	1400.00	450.00	3.11	4.00	10.00	2.50	7.75
OM	B	2%	1200.00	900.00	1.33	2.50	18.00	7.20	9.57
OM	B	4%	1650.00	450.00	3.66	3.30	12.00	3.60	13.30

Trt.=Treatment; OM=Organic matter

**Table III. Effect of pH and organic matter on Ca<sup>2+</sup> Na exchange in soil**

Trt.	Soils	Levels	Equilibrium solution		Adsorbed bases		Equilibrium constants		
			Na <sup>+</sup> mel L <sup>-1</sup>	Ca <sup>2+</sup> mel L <sup>-1</sup>	NaX me 100g <sup>-1</sup>	CaX me 100g <sup>-1</sup>	Kerr	Vanselow	Gapon
pH	A	7.85 (control)	860.00	775.00	7.39	12.00	0.0047	0.000242	0.0198
pH	A	8	747.82	850.00	3.91	20.00	0.0011	0.000046	0.0074
pH	A	9	656.52	1075.00	1.304	12.55	0.00033	0.000023	0.00025
pH	B	7	423.26	725.00	12.20	6.00	0.100	0.0054	0.129
pH	B	8.05 (control)	401.73	600.00	8.47	12.20	0.02	0.0010	0.04
pH	B	9	425.62	675.00	9.56	18.00	0.018	0.00068	0.032
OM	A	Original	860.00	775.00	7.39	11.00	0.0051	0.000277	0.021
OM	A	2%	675.65	1125.00	6.21	16.00	0.0050	0.00022	0.019
OM	A	4%	712.17	1150.00	5.26	18.20	0.0034	0.000183	0.0137
OM	B	Original	401.73	600.00	8.40	11.00	0.0237	0.00122	0.046
OM	B	2%	602.60	650.00	5.70	14.00	0.0041	0.00020	0.0172
OM	B	4%	598.04	525.00	5.20	18.00	0.0021	0.00009	0.0110

Trt.=Treatment; OM=Organic matter

**Ca<sup>2+</sup> - Na<sup>2+</sup> exchange.** In the present study the K<sub>V</sub> values in divalent-monovalent exchange under different soil conditions range from 0.00023 to 0.000277 for soil A and from 0.00009 to 0.0054 for soil B (Table III). In Ca<sup>2+</sup> - Na<sup>+</sup> exchange, as pH increased (7.00 to 9.00), the values of selectivity co-efficient K<sub>K</sub>, K<sub>V</sub> and K<sub>G</sub> decreased as the increase in pH is considered to give additional negative charge resulting in higher CEC. Higher CEC favors high selectivity of Ca<sup>2+</sup> showing preferential adsorption of Ca<sup>2+</sup> over Na<sup>+</sup>. Increase of pH increased Ca<sup>2+</sup> preference over Na<sup>+</sup> (Pratt *et al.*, 1962). Specificity of adsorption of Ca<sup>2+</sup> vs Na<sup>+</sup> might be related to the chemical values of negative charge on some of the exchanges in soil as well as to the surface charge density.

The selectivity co-efficient K<sub>K</sub>, K<sub>V</sub> and K<sub>G</sub> decreased with an increase in organic matter. Organic matter increased the CEC of both the soils which ultimately increased the preference of Ca<sup>2+</sup> vs Na<sup>+</sup>. The high CEC and organic matter attracts strongly the polyvalent cations that reduces their replacement by low valents like Na<sup>+</sup> (Rangasamy & Olsson, 1991).

In equilibrium solution of Ca and Na, both the soils showed preference for Ca adsorption. This selectivity of Ca over Na may be attributed to the research that organic matter in soils have been known to result in great preference for Ca<sup>2+</sup> than do clay minerals (Black, 1968).

## CONCLUSIONS

It is concluded from above results that K<sub>K</sub> value for Ca<sup>2+</sup>-Mg<sup>2+</sup> exchange differ not only from treatment to

treatment but also from soil to soil having different properties. Moreover, in Ca<sup>2+</sup>-Na<sup>+</sup> exchange, the K<sub>K</sub>, K<sub>V</sub>, and K<sub>G</sub> values decreased with an increase in pH and organic matter showed preference of Ca<sup>2+</sup> over Na<sup>+</sup>.

## REFERENCES

- Anonymous, 1986. Profile description, analytical data and on site discussion. pp. 66-250. *Proc. XII Int. Forum on Soil Taxonomy and Agri. Technology Transfer* (2nd Vol.) October 9-23, Lahore, Pakistan.
- Black, C.A. 1968. *Soil Plant Relationship*. John Willey and Sons, New York, USA.
- Bouyoucos, G.J., 1962. Hydrometer method improved for making particle size analysis of soils. *Agron. J.*, 54: 464-5.
- Gapon, E.N., 1933. On the theory of exchange adsorption in soils. *J.Gen. Chem. (U.S.S.R)*, 3: 144-63.
- Helfferich, F. 1962. *Ion Exchange*. McGraw-Hill Book Company Inc., New York, USA.
- Kerr, H.W., 1928. The identification and composition of the soil alumino silicate active ion base exchange and oil acidity. *Soil Sci.*, 26: 385-98.
- Moodie, C.D., H.W. Smith and R.A. McCreey, 1959. *Laboratory Manual for Soil Fertility*. State college of washington, Mineograph, Pullman, Washington, DC., USA. pp. 31-9.
- Pratt, P.F., L.D. Whitting and B.L. Grover, 1962. Effect of pH on Na-Ca exchange equilibria in soils. *Soil Sci. Soc. Amer. Proc.*, 26: 227-30.
- Rangasamy, P. and K.A. Olsson, 1991. Sodcity and soil structure. *Aust. J. Soil Res.*, 29: 935-52.
- USSLS, 1954. *Diagnosis and Improvement of Saline and Alkali Soils*. U.S. Deptt. Agri. Hand Book, 60. Washington, DC, USA.
- Vanselow, A.P., 1932. Equilibria of base exchange reactions of bentonites, permutites, soil colloids and zeolites. *Soil Sci.*, 35: 95-113.

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