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## Organic Matter and Salt Concentration Effect on Exchange Selectivity Coefficient in Calcareous Soils

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**Abstract:** Three calcareous soils were taken to investigate the effect of salt concentration and organic matter on their exchange selectivity coefficients. In homoivalent exchange ( $K^+$ - $Na^+$ ) all the three soils showed an increase in the values of selectivity coefficient with increasing salt concentration and organic matter. The maximum value of  $K_k$  was observed at 4.00% level of organic matter and 2:1 salt concentration. In case of heterovalent exchange ( $K^+$ - $Ca^{2+}$ ) there was also an increasing trend in Kerr ( $K_k$ ) Vanselow ( $K_v$ ) and Gapon ( $K_g$ ) selectivity coefficients values with the increase in salt concentration and organic matter. Moreover the results indicated preferential adsorption of  $K^+$  over  $Na^+$  in case of homoivalent exchange and  $Ca^{2+}$  over  $K^+$  in case of heterovalent exchange.

**Key words:** Calcareous soils, homoivalent, heterovalent, cation exchange, organic matter, salt concentration, cation exchange capacity

### Introduction

Knowledge of cation exchange chemistry provides valuable clues about plant nutrient deficiencies, toxicity and about exchangeable sodium. Kerr (1928), Vanselow (1932) and Gapon (1933) used concentration of cations mole fraction and activities respectively for the soluble cations while studying the cation exchange equilibria in soils. The value of  $K_k$  increased with an increase in organic matter. The soils show preferential adsorption of  $K^+$  over  $Na^+$  and  $Ca^{2+}$  over  $K^+$  (Zia *et al.*, 1999). The value of exchange selectivity coefficients increased with an increase in pH and organic matter in both the soils (Samin *et al.*, 1999). The present project was planned to determine the suitability of existing cation equilibria in calcareous soils of Pakistan and cation selectivity of different soils.

### Materials and Methods

Three calcareous soil samples of different soil texture varying in clay and carbon contents belonging to different soil series, soil A-"Rasulpur soil B-"Kotli and soil C- "Hafazabad" series. Various Physico-chemical properties of the soil samples (1) pHs, (2) electrical conductivity (ECe), (3) soluble ions (4) exchangeable cation, (5) sodium adsorption ratio (SAR), (6) exchangeable sodium percentage (ESP), (7) cation exchange capacity (CEC), (8) lime and (9) organic matter were determined by standard methods (Anonymous, 1954; Moodie *et al.*, 1959). Particle size was determined by Bouyoucos hydrometer method (Bouyoucos, 1962). Then 5 gm of each soil sample was treated with 1N  $NH_4Cl$  solution to remove all the cations present in soils after drying, grinding and sieving the soil samples. After washing with 95% ethanol the soils were made homoionic by saturating with 1N KCl. The excess of KCl was removed by washing the samples with ethanol.

The equilibrium suspensions were prepared by shaking  $K^+$  saturated soil with different salt concentrations 1:1, 1:2 and 2:1 for homoivalent (KCl: NaCl) and 1:1, 1:2 and 2:1 for heterovalent (KCl:  $CaCl_2$ ) for half an hour respectively. These were then allowed to stand overnight and centrifuged. The equilibrium extract was analyzed for Ca, K and Na by standard methods.

The exchangeable bases were determined using IN  $CH_3COONH_4$  (pH 7.0) as extratants by centrifuging the suspensions and analyzing the supernatants.

To study the effect of organic matter soil samples were mixed

with well decomposed organic matter to get three levels of organic matter i.e., original, 2.00% and 4.00%. The remaining process was carried out in the same way as to estimate the effect of salt concentration. The data obtained was analyzed by the ANOVA techniques following complete randomized design (CRID) with two factors (Steel and Torrie, 1992).

### Results and Discussion

The results of physico-chemical analysis (Table 1) showed that soil A sandy loam soil B clay and soil C is loamy clay with organic matter 0.67, 0.531 and 0.81% with pH 7.8, 8.5 and 7.50 and CEC 11.13 16.11 and 12.08  $cmol_c Kg^{-1}$  respectively.

**Homoivalent system:** In homoivalent the  $K^+$ - $Na^+$  exchange (1:1, 1:2 and 2:1 KCl: NaCl) the value of  $K_k$  increased by increasing the salt concentration. In the present investigation the  $K_k$  value ranged from 0.374 to 3.818 (Table 2). The value of  $K_k$  is markedly increased with 1:2 and 2:1  $K^+$ - $Na^+$  exchange as compared to the 1:1  $K^+$ - $Na^+$  exchange. The three soils showed preferential adsorption of  $K^+$  over the  $Na^+$  and is in accord with the concept that most important factor in determining the relative extent of adsorption and desorption of given ion is its valency, within a given valency series the degree of replaceability of an ion decreases as its hydrated radius increases (Neilson *et al.* 1972). In case of organic matter, the value of  $K_k$  increase with an increase in organic matter (Table 3). The  $K_k$  value of all the three soils showed similar trend but soil A sowed maximum adsorption at 2% level as compared to 4% level. The increase in Kerr coefficient indicates that  $Na^+$  was easily replaced by  $10^+$  as the quantity of organic matter increased. The difference in behaviour of three soils could be due to difference in CEC of three soils. External sites are easily accessible to all competing cations for adsorption while internal sites are accessible only to the cations with their hydrated sizes compatible to the cations with the geometry of exchange sites (Mehta *et al.*, 1983; Poonia *et al.*, 1986). By increasing the organic matter contents, the internal exchange sites are increased which lead to higher preference for  $K^+$  in all the three soils. By increasing the organic matter the negative charges increases CEC also increases which leads to the increase in adsorption of  $K^+$  over  $Na^+$  (Murtaza 1997; Chaudhry *et al.*, 1999; Samin *et al.*, 1999).

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Table 1: Physical and chemical characteristics of soils

Properties		Soil A	Soil B	Soil C
Saturation percentage (%)		29.95	30.30	42.67
Ph <sub>e</sub>		7.8	8.5	7.50
Ec <sub>e</sub>	dSm <sup>-1</sup>	3.39	0.95	4.47
TSS	meL <sup>-1</sup>	33.9	33.9	9.5
Soluble cations				
Na <sup>+</sup>	m mol <sub>c</sub> L <sup>-1</sup>	17.05	3.35	27.50
K <sup>+</sup>	m mol <sub>c</sub> L <sup>-1</sup>	0.53	0.379	1.5
Ca <sup>2+</sup> + Mg <sup>2+</sup>	m mol <sub>c</sub> L <sup>-1</sup>	18.3	3.6	9.03
SAR	(mmol <sub>c</sub> L <sup>-1</sup> ) <sup>1/2</sup>	5.63	2.37	12.94
Soluble anions CO <sub>3</sub> <sup>-2</sup>				
HCO <sub>3</sub> <sup>-1</sup>	m mol <sub>c</sub> L <sup>-1</sup>	Absent	0.25	Absent
CF <sup>-1</sup>	m mol <sub>c</sub> L <sup>-1</sup>	2.5	2.5	6.0
SO <sub>4</sub> <sup>-2</sup>	m mol <sub>c</sub> L <sup>-1</sup>	24.3	2.0	20.01
SO <sub>4</sub> <sup>-2</sup>	m mol <sub>c</sub> L <sup>-1</sup>	7.7	1.4	18.9
Exchangeable cations				
Na <sup>+</sup>	m mol <sub>c</sub> L <sup>-1</sup>	0.49	0.65	3.09
K <sup>+</sup>	m mol <sub>c</sub> L <sup>-1</sup>	0.264	0.283	0.57
Ca <sup>2+</sup> + Mg <sup>2+</sup>	m mol <sub>c</sub> L <sup>-1</sup>	10.37	7.39	9.23
ESP	%	4.47	7.79	25.75
BCSP	%	100.00	99.99	100.00
CEC	cm mol <sub>c</sub> kg <sup>-1</sup>	11.13	16.11	12.08
Lime	%	3.10	1.59	4.20
Organic matter	%	0.67	0.531	0.81

Table 2: Effect of organic matter on Ic in K<sup>+</sup> - Na<sup>+</sup> exchange in soils

Soil	Treatment	Levels	Equilibrium solution			Exchangeable bases			Equilibrium constant K <sub>k</sub>
			K <sup>+</sup> MeL <sup>-1</sup>	N <sup>+</sup> MeL <sup>-1</sup>	K <sup>+</sup> / Na <sup>+</sup>	Kx me 100 g <sup>-1</sup>	Nax me 100 g <sup>-1</sup>	(Nax) (Kx)	
A	O.M	0.67%	42.80	52.60	0.81	7.68	21.15	2.75	2.23
		2%	67.18	62.74	1.07	7.73	33.32	4.321	4.61
		4%	81.02	72.78	1.113	20.49	42.45	2.07	2.31
B	O.M	0.53%	91.28	76.52	1.19	7.76	5.3	0.68	0.809
		2%	87.44	95.73	0.913	17.06	15.36	0.900	0.822
		4%	89.22	103.94	0.868	27.99	29.73	1.06	0.91
C	O.M	0.81%	65.63	86.95	0.75	9.55	4.77	0.499	0.374
		2%	53.58	87.88	0.95	13.85	33.7	2.43	2.30
		4%	106.6	93.20	1.14	24.06	50.44	2.09	2.390

M = Organic matter

Table 3: Effect of salt concentration on K in K<sup>+</sup>-Na<sup>+</sup> exchange in soils

Soil	Treatment	Levels	Equilibrium solution			Exchangeable bases			Equilibrium constant K <sub>k</sub>
			K <sup>+</sup> meL <sup>-1</sup>	N <sup>+</sup> meL <sup>-1</sup>	K <sup>+</sup> / Na <sup>+</sup>	Kx me 100 g <sup>-1</sup>	Nax me 100 g <sup>-1</sup>	(Nax) (Kx)	
A	SC	1:1	300.84	721.72	0.4168	14.52	43.48	2.99	1.25
		1:2	42.80	52.60	0.81	7.68	21.15	2.75	2.23
		2:1	524.74	310.136	1.69	20.52	46.37	2.259	3.82
B	SC	1:1	91.28	76.516	1.19	7.76	5.3	0.68	0.809
		1:2	338.45	689.8	0.490	21.36	42.04	1.968	0.964
		2:1	524.78	321.73	1.63	23.81	52.17	2.191	3.57
C	SC	1:1	65.63	86.95	0.75	9.55	4.77	0.499	0.374
		1:2	246.15	539.10	0.465	17.09	40.58	2.37	1.102
		2:1	572.6	373.9	1.53	19.65	46.37	2.35	3.605

SC = Salt concentration

**Hstsvolent System:** The effect of salt concentration on K<sup>+</sup>-Ca<sup>2+</sup> exchange equilibria showed that by increasing the salt concentration there was an increase in selectivity coefficients K<sub>k</sub>, K<sub>v</sub> and K<sub>G</sub> values. (Table 4, 5). All the three soils showed preferential adsorption of Ca<sup>2+</sup> over K<sup>+</sup>. This selectivity for Ca<sup>2+</sup> over K<sup>+</sup> is in accord with concept that in heterovalent system the preferentially adsorbed cation are those with high charge density per unit surface area. (Overbeek, 1952). Moreover Neilson *et al.* (1972) stated that divalent ions, in general are retained more strongly than

monovalent ions wherever trivalent ions are unreplaceable by an equivalent amount of KCl.

By increasing the organic matter contents the values of selectivity coefficients K<sub>k</sub>, K<sub>v</sub> and K<sub>G</sub> increase. The soils showed minimum preferential adsorption of Ca<sup>2+</sup> over K<sup>+</sup> at 2% level and maximum at 4% level of organic matter. By increasing the organic matter the CaX<sub>2</sub>/KX ratios increase which is indication of preferential adsorption of Ca<sup>2+</sup> over K<sup>+</sup>. Organic matter in soils has been known to result in a greater preference for CO<sup>+</sup> than do the clay minerals (Black, 1968).

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Table 4: Effect of organic matter on  $K_e$ ,  $K_v$  and  $K_y$  in  $K^+$ - $Ca^{+2}$  exchange in soils

	Soil								
	A				B			C	
	O.M. Levels (%)				O.M. Levels (%)			O.M. Levels (%)	
	0.67	2	4	0.531	2	4	0.81	2	4
Equilibrium solution									
$K^+$ (meL <sup>-1</sup> )	101.27	258.40	226.96	150.56	313.00	311.75	311.78	207.06	280.30
$Ca^{+2}$ (meL <sup>-1</sup> )	7166.60	9733.30	9400.00	8700.00	9516.60	9266.64	96333.00	7300.00	8066.60
$Ca^{+2}$ (mmolL <sup>-1</sup> )	3583.30	4866.60	4700.00	4356.00	4758.13	4633.33	4816.65	3550.00	4633.30
$(K^+)/2/Ca^{+2}$	2.85	13.72	10.95	50.19	20.60	20.97	20.17	11.75	17.33
Exchangeable bases									
$K^+/Ca^{+2}$	1.69	3.70	3.31	1.60	4.58	4.57	4.49	3.42	4.16
$K \times me$ 100 g <sup>-1</sup>	4.65	6.64	6.75	8.58	16.64	13.65	14.56	7.57	9.02
$Cax_2$ me 100 g <sup>-1</sup>	7.66	11.00	9.33	7.00	10.33	9.66	11.60	10.83	11.20
$Cax_2/[kx]^2$	0.56	0.249	0.412	0.066	0.037	0.51	0.05	0.188	0.138
$Cax_2/[Kx]$	1.65	1.66	1.96	0.82	0.62	0.70	0.80	1.43	1.24
Equilibrium constants									
$K_e$	474.00	1514.40	2273.4	309.00	353.00	521.00	462.20	748.16	965.60
$K_v$	5834.90	24714.00	32032.2	4798.00	9520.40	12144.50	12091.10	13713.70	19524.40
$K_c$	2.74	6.12	6.50	1.13	2.33	3.19	3.59	4.96	5.15

Table 5: Effect of organic matter on  $K_e$ ,  $K_v$  and  $K_y$  in  $K^+$ - $Ca$  exchange in soils

	Soil								
	A				B			C	
	O.M. Levels (%)				O.M. Levels (%)			O.M. Levels (%)	
	0.67	2	4	0.531	2	4	0.81	2	4
Equilibrium solution									
$K^+$ (meL <sup>-1</sup> )	101.27	663.24	1145.30	150.57	639.31	733.33	311.75	729.06	799.60
$Ca^{+2}$ (meL <sup>-1</sup> )	7166.60	13620.80	43500.00	8700.00	10216.60	31751.00	9633.30	60334.60	65000.00
$Ca^{+2}$ (mmolL <sup>-1</sup> )	3583.30	6810.40	2175.00	4350.00	5108.30	15875.50	4816.65	30187.30	32500.00
$(K^+)/2/Ca^{+2}$	2.85	66.54	38.86	5.19	80.60	54.00	20.17	17.61	44.30
Exchangeable bases									
$K^+/Ca^{+2}$	1.69	8.00	7.765	1.69	8.94	7.41	4.49	4.19	6.65
$K \times (me)$ 100 g <sup>-1</sup>	4.85	23.07	23.07	8.53	23.07	29.05	14.56	33.33	26.49
$Cax_2$ (me 100 g <sup>-1</sup> )	7.66	8.16	8.55	7.00	4.50	7.66	11.60	29.33	16.156
$Cax_2/[kx]^2$	0.56	0.0115	0.0112	0.096	0.0025	0.495	0.065	0.026	0.023
$Cax_2/[Kx]$	1.65	0.35	0.37	0.82	0.19	0.26	0.80	0.87	0.60
Equilibrium constants									
$K_e$	474.00	826.50	2464.50	309.00	767.30	1032.16	462.20	478.47	911.13
$K_v$	5834.90	24158.50	77925.90	479.80	21164.58	378905.00	12091.10	2966.50	38856.13
$K_c$	2.74	2.80	2.90	1.31	1.74	1.92	3.59	3.69	4.05

Particularly hydrous mica like clays (Bohn *et al.*, 1985 which is dominant mineral in Pakistan soils. In heterovalent ( $K^+$ - $Ca^{+2}$ ) exchange both soils showed an increased in Kerr, Vanselow and Gapon selectivity coefficients with an increase in organic matter and pH showing greater affinity for  $Ca^{+2}$  than for  $K^+$  (Zia *et al.*, 1999).

From the above discussion it can be concluded that In homoivalent exchange soils showed greater selectivity of  $K^+$  over  $Na^+$  by increasing the salt concentration and organic matter.

In heterovalent exchange soils showed greater selectivity of divalent cation over monovalent cations by increasing organic matter and salt concentration.

Selectivity coefficients used for both homoivalent exchange ( $K^+$ - $Na^+$ ) and heterovalent exchange ( $K^+$ - $Ca^{+2}$ ) equilibria not remained constant at different levels of organic matter and salt concentration.

Kerr, Vanselow and Gapon's equations were found better to predict the  $K^+$ - $Na^+$  and  $K^+$ - $Ca^{+2}$  exchange equilibria in soils of Pakistan.

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