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Organic Matter and Salt Concentration Effect on Cation Exchange Equilibria in Non-calcareous Soils

Imrana Naseem and Haq Nawaz Bhatti

Department of Chemistry, University of Agriculture, Faisalabad-380410, Pakistan

Abstract: Studies were conducted to investigate the effect of organic matter and salt concentration on cation exchange equilibria in non-calcareous soils. Various physico-chemical properties like pHs, ECE, soluble ions, exchangeable cations, ESP, SAFI, lime and organic matter were determined. In homovalent (K^+ - Na^+) exchange, the values of K_k increased with increasing organic matter. The results of three levels of salt concentration indicated that equal concentration of both the salts showed less coefficient values as compared to 1:2 K^+ - Na^+ concentration, but this coefficient values markedly increased by 2:1 K^+ - Na^+ concentration. In heterovalent (K^+ - Ca^{2+}) exchange, selectivity coefficients showed an increase with increasing organic matter, while in case of salt concentration, 2:1 ratio had marked effect on K_k , K_v and K_G values.

Key words: Cation exchange equilibria, homovalent, heterovalent, non-calcareous soils, selectivity coefficients, organic matter, salt concentration

Introduction

Cation exchange in soil is the second most important phenomenon in nature, it is important in sustaining soil fertility, in causing and correcting soil acidity and alkalinity, in altering soil physical properties and as a mechanism in purifying or altering percolating water. Calcium and sodium are the major competing cations in normal and salt affected soils. Various equations have been proposed to study the non-exchange equilibria in soils. Kerr (1928) used concentration in place of their activities and was followed for homovalent cation exchange only. Vanselow (1932) used mole fraction in place of activities of cations and this equation holds good for both homovalent and heterovalent cation exchange. Gapon (1933) used concentration for adsorbed cations and activities for the soluble cations. The current study was planned to investigate the effect of organic matter and salt concentration on monovalent-monovalent (K^+ - Na^+) and monovalent-divalent (K^+ - Ca^{2+}) exchange in non-calcareous soils of Pakistan.

Materials and Methods

Three non-calcareous soil samples varying in clay and carbon contents belonging to different soil series (Soil A-Gujrawala soil series, soil B-Wazirabad soil series and soil C-Pindorian soil series) were collected. The pH of soil saturation electrical conductivity (ECE), soluble ions, exchangeable cations, sodium adsorption ratio (SAR), exchangeable sodium percentage (ESP), basic cation saturation percentage (BCSP) and cation exchange capacity (CEC) were determined by standard methods (Richards, 1954). 250 gm of each soil were saturated with 1N NH_4Cl and allowed to stand overnight. Five gram of soil was taken for three replications of each treatment. The soil was washed with 95% ethanol and made homoionic with K using 1N KCl solution and excess KCl solution was washed with 95% ethanol. The equilibrium suspensions were prepared by shaking K^+ saturated soil with a desired salt concentration 1:1, 1:2 and 2:1 (KCl-NaCl) for homovalent and 1:1, 1:2 and 1:1 (KCl- $CaCl_2$) for heterovalent for half an hour respectively. It was taken allowed to stand overnight and centrifuged. This equilibrium extract was analyzed for Na, K and Ca by standard methods. Exchangeable bases were determined using 1N CH_3COONH_4 (pH 7.0) as extractants by centrifuging the suspensions and analyzing the supernatant.

To study the effect of organic matter, soils were mixed with well decomposed organic matter to get three levels of organic matter

i.e. original, 2 and 4%. The remaining process was carried out in the same as to estimate the effect of salt concentration. The mineralogical analysis of soil samples was also done. The data obtained was analyzed by ANOVA technique in completely randomized design with two factors (Steel and Torrie, 1992).

Results and Discussion

The physico-chemical analysis (Table 1) of the soils revealed that CEC of soil A is 11.13 $cmol_c kg^{-1}$, soil B is 5.91 $cmol_c kg^{-1}$ and that of soil C is 6.17 $cmol_c kg^{-1}$ with 0.46, 0.37 and 0.38% organic matter respectively.

Homovalent Exchange: The K^+ - Na^+ exchange were studied on three non-calcareous soil at three different levels of organic matter i.e. original, 2 and 4%. The selectivity coefficient K_k values ranged from 0.200 to 0.809 (Table 2). In all the three soils, the values of K_k increased with increasing organic matter. There is a little change in K_k values for soils B and C, but for soil A K_k values marked increase with increasing organic matter. This difference of K_k values in all the three soils could be due to difference in CEC of the soils. CEC of soil A is higher than soil B and C. As organic matter increases, the surface charge density increases, which ultimately increases the CEC of the soils, increase in CEC increased the adsorption of K^+ (Murtaza, 1997). The increase in the values of K_k indicates that Na^+ was replaced by K^+ as greater as the quantity of organic matter increased, showing preferential adsorption of K^+ over Na^+ . It was also noted that soils high in organic carbon, such as soil A, has higher preference for K^+ than the soils low in organic carbon such as soils B and C (Mehta *et al.*, 1983; Poonia *et al.*, 1986) Table 2 indicates that equal concentration of both the salts showed less coefficient values as compared to 1:2 K^+ - Na^+ concentration, but this coefficient values markedly increase by 2:1 K^+ - Na^+ concentration. This increase in K_k values for 2:1 K^+ - Na^+ concentration in all the three soils indicates that by doubling the concentration of KCl solution than NaCl there was greater the number of exchangeable K^+ , therefore sodium was much replaced by potassium. The most important factor determining the relative extent of adsorption or desorption of given ion is its valence. The above results are in accord with Neilson *et al.* (1972) whom studied the diffuse double layer and stated that within a given valence series, the degree of replaceability of an ion decreases as its hydrated radius increases. As we already know that the hydrated size of K^+ is small as compared to Na^+ . The selectivity of K^+ over Na^+ is in

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Table 1: Physics-chemical characteristics of soils

Soil characteristics	Soil A (Gujrawala soil series)	Soil B (Wazirabad soil series)	Soil C (Pindorian soil series)
Clay %	33.00	10.25	17.00
Texture class	Slit clay loam	Loamy sand	Sandy loam
pHs	7.70	7.74	8.95
Ece (dSm ⁻¹)	1.08	0.98	0.65
TSS (meL ⁻¹)	10.8	9.60	6.5
SAR(mmolL ⁻¹) ^{1/2}	2.06	1.82	1.25
Exchangeable cations			
Na ⁺ (cmol kg ⁻¹)	0.498	0.437	0.40
K ⁺ (cmol kg ⁻¹)	0.26	0.391	0.43
Ca ²⁺ + Mg ²⁺ (cmol kg ⁻¹)	10.37	5.08	5.34
ESP (%)	4.47	7.39	6.4-5
ECE cmol kg ⁻¹	11.13	5.91	6.17
BCSP (%)	100.00	100.00	100.00
Lime (%)	Absent	Absent	Absent
Organic carbon (%)	0.26	0.21	0.22
Organic matter (%)	0.46	0.37	0.38

Table 2: Organic matter and salt concentration effect on K⁺-Na⁺ exchange in soils

Soil	Trt.	Levels	Equilibrium solution			Exchangeable bases			Equilibrium constant
			K ⁺ (meL ⁻¹)	Na ⁺ K ⁺ (meL ⁻¹)	KX Na	NaX (me 100 g ⁻¹)	$\frac{[NaX]}{[KX]}$ (me 100 g ⁻¹)	K _k	
A	O.M	Control (0.46%)	60.47	64.33	0.939	11.68	5.35	0.458	0.430
		2.00%	65.59	66.94	0.979	29.74	19.05	0.633	0.649
		4.00%	59.155	68.68	1.007	18.93	14.75	0.779	0.784
A	Salt conc.	1:1	60.47	64.33	0.939	11.68	5.35	0.456	0.430
		1:2	239.30	618.8	0.46	15.70	26.06	1.659	0.753
		2:1	434.17	275.34	1.576	17.67	27.90	1.587	2.50
B	U.M	Control (0.37%)	50.28	62.604	0.803	10.92	9.533	0.872	0.700
		2.00%	62.01	74.777	0.829	21.50	20.112	0.935	0.775
		4.00%	59.96	69.66	0.861	4.77	4.886	0.940	0.809
B	Salt conc.	1:1	59.96	69.66	0.1361	4.77	4.486	0.940	0.809
		1:2	370.92	750.56	0.494	8.26	30.408	3.637	1.796
		2:1	643.66	350.59	1.542	11.74	29.684	2.52	3.90
C	O.M	Control (0.36%)	68.67	50.65	1.128	34.603	6.144	0.178	0.200
		2.00%	62.01	59.99	1.033	13.237	3.456	0.561	0.269
		4.00%	60.47	50.43	1.199	44.051	10.752	0.244	0.292
	Salt conc.	1:1	62.01	59.99	1.033	13.237	3.456	0.261	0.259
		1:2	352.127	594.158	0.592	10.24	28.798	2.616	1.548
		2:1	407.676	292.731	1.392	10.24	25.34	2.474	3.443

Table 3: Organic matter and salt concentration affect on K⁺-Ca²⁺ exchange in soils

Soil	Trt.	Levels	Equilibrium solution					Exchangeable bases			Equilibrium constant			
			K ⁺ (meL ⁻¹)	Ca ²⁺ (meL ⁻¹)	Ca ²⁺ (mmolL ⁻¹)	$\frac{[K^+]^2}{[Ca^{2+}]}$	$\frac{K^+}{\sqrt{Ca^{2+}}}$	KX me 100 g ⁻¹	$\frac{CaX_2}{(me 100 g^{-1})}$	$\frac{[CaX_2]}{[KX]^2}$	$\frac{CaX_2}{KX}$	K _k	K _k Me 100 g ⁻¹	K _c
Soil A	O.M	0.46%	315.36	10075	5.037.5	13.74	4.44	12.032	17	0.117	1.412	1.097	87.034	6.269
		2.00%	258.96	11000	5500	12.192	3.49	21.76	43	0.090	1.976	2.309	71.041	6.686
		4.00%	371.77	10200	5100	21.10	5.20	16.256	36	0.132	2.153	3.577	183.34	11.195
Soil A	O.M	1:1	760.683	93750	46875	12.24	3.513	14.102	9.00	0.045	0.638	0.555	12.821	2.241
		1:2	1692.308	60000	30000	95.46	9.77	16.666	4.33	0.015	0.259	1.431	30.036	2.530
		2:1	315.36	10075	5037.5	19.74	4.44	12.032	17.00	0.117	1.412	2.309	67.034	6.269
Soil B	O.M	0.37%	325.62	9600	1750	22.32	4.72	5.832	9	0.283	1.596	6.316	02.415	01.142
		2.00%	407.67	9900	4950	33.57	5.79	10.388	28	0.213	2.216	7.150	238.581	12.842
		4.00%	366.65	9775	4887.5	27.50	5.24	6.784	22	0.478	3.242	13.14	378.365	16.988

Table 3 Continue.....

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Soil	B												
Trt.	O.M												
Levels	1:1	760.68	122500	612.60	9.44	3.07	9.828	8.66	0.089	0.881	0.840	15.520	2.704
	1:2	325.62	9500	4750	22.32	4.72	5.632	9	0.283	1.698	6.316	92.415	6.412
	2:1	1735.04	61666.66	30833.33	97.63	9.88	5.128	3.33	0.126	0.649	12.30	199.48	7.542
Soil	C												
Trt.	O.M												
Levels	0.38%	346.135	10600	5300	22.60	4.75	14.646	17	0.081	1.175	1.83	57.57	5.581
	2.00%	320.49	9950	4975	20.64	4.54	7.160	14	0.272	1.953	5.61	118.752	8.866
	4.00%	466.64	10425	5212.5	41.77	6.46	9.725	20	0.211	2.055	8.81	281.90	13.275
Soil	C												
Trt.	O.M												
Levels	1:1	1034.18	11000	5500	19.44	4.40	8.974	3.00	0.037	0.334	0.719	8.609	1.469
	1:2	1529.91	545133.33	32291.66	72.48	8.51	13.247	4.00	0.022	0.301	1.694	27.49	2.561
	2:1	320.49	9950	4976	2084	4.54	7.168	14.00	0.0272	1.953	6.61	118.752	8.866

Table 4: Mineralogical analysis of soils

Minerals identified	Minerals Formula
Quartz	SiO ₂
Albite	NaAlSi ₃ O ₈
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂
Clinochlore	(Mg ₅ Al)(Si,Al) ₄ O ₁₀
Clinochlore ferroan	(Mg,Al) ₅ (Si,Al) ₄ O ₁₀
Halite potassium	KO.2NaO.8Cl
Halite	NaCl
Illite	KO.7Al ₂ (Si,Al) ₄ O ₁₀
Gypsum	CaSO ₄ .2H ₂ O
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄
Dolomite	CaMg(CO ₃) ₂

accord with the concept that in homovalent systems, the preferentially adsorbed ion is usually the ion with the smaller hydrated radius (Helfferich, 1962).

Heterovalent Exchange: Organic matter has favourable effect on K⁺-Ca²⁺ exchange. The results of present study revealed that the values of K_k, K_v and K_G increase as organic matter increases (Table 3). The increase in CaX₂/KX ratio with increasing organic matter indicates the preferential adsorption of Ca²⁺ over K⁺. Organic matter in soils has been known to result in a greater preference for Ca²⁺ than do the clay minerals. All the soils and showed greater preference for Ca²⁺ over K⁺ in small quantity at 2% level and more at 4% level.

The selectivity for the divalent cations Ca²⁺ over K⁺ can be explained on the basis of organic matter role as shown by Ca²⁺ ions because of their divalent nature are preferentially adsorbed cations then those of K⁺ particularly on easily accessible sites. In case of salt concentration, in all the three soils, the values obtained for K_k, K_v and K_G indicated a very large selectivity for Ca²⁺ over K⁺ (Table 3). By increasing salt concentration the CEC also increases which increases the adsorption of Ca²⁺ over K⁺. Thus increase in CEC can be best explained as in accord with Overbeek (1952) who stated that soil colloids of high charge

density, that is of high charge or CEC per unit of surface area, generally have the greatest preference for high charged cations. The preferential adsorption of Ca²⁺ over K⁺ is also in accord with Neilson *et al.* (1972) whom reported that divalent ions in general are retained more strongly than are monovalent ions, trivalent ions are retained even more strongly unreplaced by an equivalent amount of KCl.

Mineralogical Analysis of Soil Samples: The mineralogical analysis (Table 4) of three soil samples showed that all the soils contained almost the same Minerals and the intensity of quartz was high in all the three soils.

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