

ESTIMATION OF GAPON EXCHANGE COEFFICIENT FOR DIFFERENT TEXTURED SOILS AND LANDFORMS OF PUNJAB, PAKISTAN

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Cation exchange equilibria involving Ca^{2+} - Na^+ and Na^+ - Ca^{2+} ion pairs was investigated to calculate the Gapon exchange coefficient for sodication and desodication on different textured soils belonging to various landforms of Punjab, Pakistan. The soils were made homoionic with Ca^{2+} or Na^+ as index cation in varying cationic concentrations (0, 2, 4, 8, 12, 16 and 20 mmol L^{-1}) and then desorbed with other cation at the same respective electrolyte concentration. The Gapon exchange coefficient (K_G) was determined for two reactions, i.e. sodication and desodication, designated as K_{GS} and K_{GD} , respectively. The values of K_{GS} and K_{GD} gradually increased with an increase in the concentration of Na^+ or Ca^{2+} as index cation, but the K_{GD} values were found higher than that of the K_{GS} showing preferential adsorption of Ca^{2+} over Na^+ , i.e. the rate of desodication (Na^+ - Ca^{2+}) was more as compared with the sodication (Ca^{2+} - Na^+), possibly due to Na^+ saturation of soils and greater hydrated size of Na^+ . The sodication and desodication rates in soils at various electrolyte concentrations observed in relation to various textured soils showed more sensitivity of fine textured soils to saline-sodic irrigation waters as compared to coarse textured soils particularly at higher concentrations of index cations. The values of K_{GS} and K_{GD} correlated statistically with CEC and clay percentage of soils, which indicates that reclamation of higher CEC saline-sodic soils are more efficient with the application of external Ca source (CaCl_2 in this study) than the coarse textured soils (loamy sand soils).

Keywords: Gapon exchange coefficient, sodication, desodication.

INTRODUCTION

Soils being negatively charged adsorb and exchange cations. The cation exchange sustain availability of plant nutrient cations. The study of cation exchange equilibria involving Na^+ and Ca^{2+} could be useful in the prediction of their accumulation in the adsorption complex and leaching in to the deeper layers, i.e. sodication and desodication of soils.

Under arid and semi-arid climates, evapotranspiration causes concentration of soil solution and upon achieving the solubility limits, CaCO_3 precipitation takes place leading to the preponderance of Na^+ in soils which is conducive to soil sodication. Thus prediction of sodication or desodication is important for such situations. In Pakistan, more than 0.55 million tubewells are pumping out about 55 MAF water of which 70-80% is saline-sodic or sodic. Excess of sodium in irrigation waters could promote sodication of soils which may induce soil dispersion and structural breakdown resulting in decreased water transmission through soils, soil crusting, poor seedling emergence and reduced soil aeration. All the processes adversely affect the crops, mainly through reduced water availability to crops.

A number of equations (Kerr, 1928, Vanselow, 1932 and Gapon, 1933) have been proposed with different assumptions and all these equations have merits, demerits and usually are site-specific and derived for soils outside Pakistan.

Among these equations the Gapon equation is the simplest and user friendly. Basically, it was designed to predict soil sodication (Ca - Na exchange) by a Russian scientist, Gapon. Major feature of the Gapon equation is that it considers the concentrations rather than activities for soluble ions and writing mass action equation with chemically equivalent quantities both on colloid exchange sites and adsorbed cations. The Gapon exchange equation is commonly employed to study heterovalent exchange reactions. The Gapon cation exchange selectivity coefficient is simply the rate of Na^+ adsorption or soil sodication:

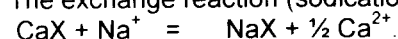
$\text{CaX} + \text{Na}^+ \rightleftharpoons \text{NaX} + 1/2\text{Ca}^{+2}$
 $K_G = \frac{[\{\text{NaX}\} (\text{Ca}^{+2})^{1/2}]}{[\{\text{CaX}\} (\text{Na}^+)]}$, where Ca^{2+} and Na^+ are expressed in mmol L^{-1} while CaX and NaX as cmol_c kg^{-1} soil.

Under arid climatic conditions of Pakistan, irrigation of crops is imperative for which the use of brackish water is not only practiced rather it is on an increase. As a result by now, salt-affected area is about 6.67 mha in Pakistan (Khan, 1998). In these soils, sodicity predominates and their reclamation efforts are necessary to sustain the irrigated agriculture. Under these circumstances, the prediction of sodication and desodication process is quite useful to devise management and reclamation strategies to sustain the irrigated agriculture. Since the studies pertaining to the quantitative determination of K_G have been conducted for soils in countries other than Pakistan, the present studies were designed to estimate K_G for sodication and desodication of soils of different landforms within Punjab province.

MATERIALS AND METHODS

Soil samples in bulk were collected from different landforms in a cross section fashion from River Ravi to the Syed Wala town and Chiniot town near River Chenab. These bulk samples were ground to pass through 2 mm sieve and stored. Out of these soil samples collected from various landforms (recent, subrecent and old river terraces) of Punjab, only 5 g material was made homoionic with Ca^{2+} as index cation by saturating with 33 mL in $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution thrice followed by three ethanol washings through centrifugation at 1000 RPM for 5 minutes. The Ca^{2+} saturated soil samples in triplicate, were then treated with NaCl solutions having different concentrations (0, 2, 4, 8, 12, 16, and 20 mmol L^{-1}).

The exchange reaction (sodication) equation was:

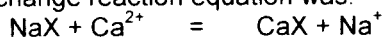


The K_{GS} for this sodication reaction was determined by the following formula:

$$K_{\text{GS}} = \frac{[\{\text{NaX}\} (\text{Ca}^{2+})^{1/2}]}{[\{\text{CaX}\} (\text{Na}^+)]}$$

After each washing with 33 mL, the filtrate was analyzed for Ca^{2+} by titration with EDTA (U.S. Salinity Lab. Staff, 1954). Then the same soil samples were given three washings with ethanol to remove excess Na^+ from solution phase. These soil samples were then treated thrice with different (0, 1, 2, 4, 6, 8, and 10 mmol L^{-1}) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solutions.

The exchange reaction equation was:



The K_{GD} was determined by the formula:

$$K_{\text{GD}} = \frac{[\{\text{CaX}\} (\text{Na}^+)]}{[\{\text{NaX}\} (\text{Ca}^{2+})^{1/2}]}$$

The filtrates were analyzed for Na^+ by Jenway PFP-7 flame photometer using sodium filter. The soluble cations were expressed as mmol L^{-1} and adsorbed cations as $\text{cmol}_c \text{ kg}^{-1}$ soil. The data obtained were computed statistically following simple regression and correlation of soil properties (CEC, % clay) with K_{GS} and K_{GD} , adsorption or desorption of Na^+ with concentrations of electrolytes applied (Steel and Torrie, 1980).

RESULTS AND DISCUSSIONS

The physical and chemical properties (Table 1) of soils were determined to correlate the properties with K_{GS} and K_{GD} . The results (Table 2 and 3) showed that the rate of desorption of adsorbed cation was maximum in the first washing which further decreased in second and third washings. Amrhein and Suarez (1991) reported similar experimental results regarding Na^+ - Ca^{2+} exchange. The smaller value of K_{GS} and K_{GD} reported for the control treatment might be due to the dilution factor (Eaton and Sokoloff, 1935) as there was no electrolyte in the washing solution in this treatment.

The data regarding K_{GS} and K_{GD} for seven soils at different concentrations of Na^+ (Table 2) or Ca^{2+} (Table 3) in the equilibrating solution showed a similar pattern. The values of K_{GS} and K_{GD} gradually increased with an increase in the concentration of Na^+ or Ca^{2+} as index cations. But the magnitude of K_{GS} and K_{GD} for different soils did not differ much especially at higher concentrations. Similar results were reported by Kachoui et al. (1996). They worked on three soils and computed the K_{G} values for sodication at different threshold electrolyte concentrations (TEC) of 25-500 $\text{mmol}_c \text{ L}^{-1}$. The results revealed an increase in K_{G} with an increase in TEC and Na^+ saturation of soils. The increase in K_{G} was from 0.012 (L mmol^{-1})^{1/2} at 25 $\text{mmol}_c \text{ L}^{-1}$ TEC to 0.023 (L mmol^{-1})^{1/2} at 500 $\text{mmol}_c \text{ L}^{-1}$ TEC.

The sodication and desodication rates were correlated with different soil textures and CEC of soils in our investigations. The coarse textured soils (loamy sand) at same electrolyte concentration showed lower rate of sodication and desodication compared to that in fine textured soils (clay and loam). This could be attributed to more clay percentage and high CEC of soils having fine textures which promoted the rate of cation exchange. Indirectly, this indicates that fine textured saline-sodic soils, if provided with Ca^{2+} source, will be reclaiming at a faster rate and less chances of leaching of the applied Ca^{2+} .

Sodication

The fundamental chemical reaction is:

$\text{CaX} + \text{Na}^+ = \text{NaX} + 1/2\text{Ca}^{2+}$, solution cations were expressed as mmol L^{-1} and adsorbed ones as $\text{cmol}_c \text{ kg}^{-1}$ soil.

The K_{GS} values computed for Ca-Na exchange (sodication) for all the concentrations of Na as index cation (0, 2, 4, 8, 12, 16 and 20 $\text{mmol}_c \text{ L}^{-1}$) against 7 soils are shown in Table 2. For the control, the values of K_{GS} were less as compared with the other concentrations applied and were lower for loamy sand soils (Soil 1, 2 and 7) with the highest for clayey soil (Soil 4). This indicates that the values of K_{GS} are positively correlated with the clay contents and CEC. The clay fraction is main site for cation exchange in these soils, since organic matter was low (0.3 to 0.6 %). This inference is of practical significance under the agro-climatic conditions of the irrigated Indus Plains. In the Indus Plains, ground waters have high SAR / RSC and these waters can be relatively better for irrigating coarse textured than the fine textured soils. Such observations were also recorded by Pratt and Grover (1964). The K_{GS} values increased as the Na^+ concentration in leaching solution increased but the rate of change in K_{GS} decreased with an increase in concentration of Na^+ as the index cation (Table 2).

Desodication

The fundamental exchange reaction is:

$\text{NaX} + 1/2\text{Ca}^{2+} = \text{CaX} + \text{Na}^+$, soluble cations expressed as mmol L^{-1} and adsorbed ones as $\text{cmol}_c \text{kg}^{-1}$.

The values of K_{GD} for Na-Ca exchange (desodication) at various cation concentrations for different soil samples are given in Table 3. The values of K_{GD} obtained for the control showed a similar trend as was in sodication (K_{GS}), i.e. the K_{GD} values were higher for fine textured (clay) and lower for coarse textured soils (loamy sand). The K_{GD} values ranged from 0.0169 to 0.147 with control treatment for the test soils. The important difference in desodication (Table 3) and sodication (Table 2) was that the K_{GD} values were higher in desodication than the K_{GS} during sodication.

The K_{GD} values increased further with an increase in concentration of Ca^{2+} , with a maximum rate of desorption of Na^+ at $12 \text{ mmol}_c \text{L}^{-1}$ for coarse textured soils and at $20 \text{ mmol}_c \text{L}^{-1}$ for fine textured soils. This trend of Na-Ca exchange is of practical importance in reclamation of saline-sodic and sodic soils which proceeds by increasing Ca^{2+} on the exchange complex at the expense of Na^+ and removal of desorbed sodium along with the soluble salts in infiltrating water out of the root zone (Ghafoor et al., 1988, Ghafoor and Salam., 1993). The rate of increase in K_{GD} values

during desodication was high compared to the K_{GS} values.

The K_{GD} values correlated with CEC of soils which confirmed the effect of higher CEC for preferred adsorption of divalents (Ca^{2+}) over monovalents (Na^+). The regression equations and correlation coefficients between K_{GD} and soil properties (% clay and CEC) in table 4 are statistically significant.

CONCLUSIONS

It is inferred from the results that K_{GS} and K_{GD} value increased with an increase in concentration of index cation but the rate of increase in K_{GS} and K_{GD} decreased at higher concentrations of index cation. Moreover, the coarse textured soils showed lower rate of adsorption and desorption of index cations even at their higher concentrations of index cations (16 and 20 mmol L^{-1}) than the fine textured soils. This showed sensitivity of clay soils to saline-sodic irrigation water than loamy sand soils which remained unaffected at higher concentrations of Na^+ and Ca^{2+} ions. The regression equations and correlation coefficients between K_{GS} or K_{GD} (sodication and desodication, respectively) and soil properties (% clay and CEC) were statistically significant showing better exchange of cations at higher clay percentage and CEC.

Table 1. Physical and chemical properties of soils used for investigations

Characteristics	Unit	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7
Sand	%			56.0	51.6	55.2	73.8	75.0
Silt	"	14.0	11.6	28.0	8.2	20.0	6.4	12.6
Clay	"	7.6	13.2	16.0	40.2	24.8	19.8	12.4
Textural class	—	Loamy sand	Loamy sand	Loam	Clay	Sandy clay loam	Sandy loam	Loamy sand
pH _s	-	6.8	7.0	7.4	7.8	7.3	7.1	6.9
EC _e	dS m ⁻¹	0.6	0.7	0.6	1.1	0.8	0.6	0.7
SAR	-	1.4	0.6	1.1	0.9	1.3	0.8	0.8
CEC	$\text{cmol}_c \text{kg}^{-1}$	4.5	6.7	8.3	15.0	9.2	7.3	6.1
ESP	%	1.8	1.4	1.5	1.2	1.7	1.3	3.0
Organic matter	"	0.2	0.2	0.3	0.6	0.3	0.3	0.2
Lime	"	0.9	1.3	1.1	1.0	0.7	0.8	0.6

Table 2. The $K_{\text{GS}} (\text{L mmol}^{-1})^{1/2}$ values for Ca-Na exchange (sodication)

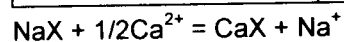
Na^+ added (mmol L^{-1})	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Mean
0	0.019	0.058	0.029	0.153	0.111	0.071	0.054	0.070
2	0.381	0.329	0.359	0.214	0.271	0.299	0.335	0.312
4	0.415	0.373	0.392	0.313	0.367	0.377	0.394	0.375
8	0.438	0.409	0.437	0.388	0.418	0.426	0.436	0.421
12	0.457	0.435	0.453	0.422	0.440	0.445	0.454	0.443
16	0.466	0.449	0.463	0.440	0.445	0.468	0.462	0.456
20	0.470	0.461	0.469	0.445	0.450	0.465	0.467	0.461
Mean	0.378	0.359	0.371	0.339	0.357	0.364	0.371	



$$K_{\text{GS}} = \{[\text{NaX}] (\text{Ca}^{2+})^{1/2}\} / \{[\text{CaX}] (\text{Na}^+)\}$$

Table 3. The K_{GD} values ($L\ mmol^{-1}$)^{1/2} for Na-Ca exchange (desodication)

Ca ²⁺ added ($mmol\ L^{-1}$)	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Mean
0	0.016	0.033	0.021	0.147	0.067	0.045	0.048	0.053
2	1.713	1.570	1.652	1.165	1.526	1.571	1.612	1.544
4	1.769	1.670	1.761	1.455	1.651	1.675	1.701	1.668
8	1.860	1.765	1.852	1.701	1.782	1.803	1.821	1.797
12	1.875	1.820	1.871	1.792	1.841	1.865	1.877	1.848
16	1.890	1.860	1.892	1.835	1.874	1.891	1.907	1.878
20	1.910	1.881	1.900	1.861	1.903	1.915	1.921	1.898
Mean	1.576	1.514	1.564	1.422	1.520	1.537	1.555	



$$K_{GD} = \{[CaX] (Na^{+})\} / \{[NaX] (Ca^{2+})^{1/2}\}$$

Table 4. Computation of regression equations and correlation coefficients

Sr.No.		Regression	Correlation (r)
1	K_{GS} Vs % Clay (Sodication)	$y = -0.003x + 0.932$	0.846**
2	K_{GD} Vs % Clay (Desodication)	$y = -0.004x + 1.598$	0.736*
3	K_{GS} Vs CEC (Sodication)	$y = -0.007x + 0.420$	0.582*
4	K_{GD} Vs CEC (Desodication)	$y = -0.018x + 1.660$	0.697*

x = % clay and CEC, y = K_{GS} or K_{GD}

** Significant at 1 % level of probability

* Significant at 5 % level of probability

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