Selectivity Coefficients for Calcium-Magnesium-Sodium-Potassium Exchange in Eight Soils

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Summary. The six selectivity coefficients for simultaneous Ca-Mg-Na-K exchange were calculated from soil extract cation activities and exchangeable cation concentrations for eight salt affected soils. These values were compared with selectivity coefficients calculated from solution cation concentrations and the exchangeable cations for the same soil samples. The lyotropic series for these soils in order of replaceability ease was $Na \gtrsim Mg > Ca > K$, whereas the generally accepted series is $Na > K > Mg > Ca$. The selectivity coefficient values varied between soils, but did not vary with depth in each soil. Potassium exchange selectivity coefficients have not previously been available for use in exchange models and are reported here for eight soils With these data, models can include K exchange in high K soils and soils irrigated with high K waters. Exchangeable sodium percentage (ESP) can be calculated on a programmable hand-held calculator for a soil using the chemical data and these selectivity coefficients. All ionic strength and ion pair corrections and selectivity calculations for this study were carried out on a programmable hand-held calculator.

Cation exchange selectivity coefficients have been reported for calcium-magnesium (Ca-Mg) and calcium-sodium (Ca-Na) exchange by a number of researchers and a few values have been reported for calcium-potassium (Ca-K) exchange. A partial listing and comparison of reported selectivity coefficient values for these three cation pairs are listed elsewhere (Robbins et al. 1980). In contrast to the number of values for the calcium exchange systems, magnesium-potassium (Mg-K), magnesium-sodium (Mg-Na) and sodium-potassium (Na-K) exchange selectivity coefficient values were not found in the literature. Consequently, all six selectivity coefficients are not available for comparison for a particular soil except for two soils previously described by Robbins et al. (1980). The calculation methods used to obtain selectivity coefficients are not consistent among researchers and the calculation conventions used are not always defined. The Vanselow and the Gapon convention are the two most common selectivity coefficient calculation methods and are discussed in detail by Sposito (1977). Some values have been calculated from soluble cation concentrations while others have been calculated from cation

concentrations corrected for ionic strength, ion pairing, or both. No attempt is made here to compare these calculation conventions or the analytical methods used. The purpose of this paper is to report and compare the six selectivity coefficients calculated, using cation activities for simultaneous Ca-Mg-Na-K exchange in eight salt-affected soils over a wide total soluble salt concentration range, at a variety of cation and anion compositions, and at different depths within the soil profiles with selectivity coefficients obtained from the same samples using cation concentrations.

Materials and Methods

The data required to calculate cation exchange selectivity coefficients were obtained from five salt affected soils and three normally non-saline soils that had been irrigated with salty water. Portneuf silt loam (coarse-silty, mixed, mesic, Durixerollic Calciothids) is usually·non-saline. However, samples used in this study were taken from a non-irrigated site high in salts in the lower profile and from 1.0 m deep lysimeters filled with surface soil (0–0.15 m) irrigated at a 5% leaching fraction with waters containing 15 meq $CaSO_4$, 15 meq $CaSO_4$ and 3.0 meq NaCl per l, 5.0 meq $CaCl_2$ and 5.0 meq $NaHCO_3$ per l or 3.0 meq $CaCl_2$ and 2.0 meq NaCl per l. Declo sandy loam (coarse-loamy, mixed, mesic, Xerollic Calciorthids) samples were taken from a saline-sodic field where K accounts for 30 to 60% of the soluble cations at concentrations as high as 80 meq K/l in the saturation extracts. The profile was sampled in 0.25 m increments to 1.5 m. Freedom silt loam (fine-silty, mixed, mesic, Xerollic Calciorthids) is a saline-sodic soil, sampled in 0.25 m increments to 2.0 m. These three soils were from south central Idaho. Penoyer loam (coarse-silty, mixed, calcareous, mesic, Torrifluvent) and Hunting silty clay loam (fine-silty, mixed calcareous mesic, Aquic Ustifluvent) were non-saline surface (0–0.25 cm) soils from Emery County, Utah that had been irrigated in lysimeters with waters containing various gypsum levels (15 meq/l total salts). The Penoyer soil originally contained 0.7% gypsum (Robbins et al. 1980). Raymondville sandy clay loam (fine, mixed hyperthermic Vertic Calciustolls), Rio sandy clay loam (fine, mixed, hyperthermic Typic Argiaquolls) and Willacy sandy clay loam (fine-loamy, mixed hyperthermic Udic Argiustolls) are from the lower Rio Grande Valley of Texas. These soils were selected and sampled to 1.5 m in a previous study and give a wide range of saturation extract electrical conductivity (EC) values (Carter et al. 1964).

The Freedom and Portneuf soils contained illite, kaolinite, and some poorly crystalline expandable clay minerals. Declo sandy loam contained illite and poorly crystalline expandable clay minerals. The Penoyer and Hunting soils contained illite and kaolinite type minerals in about equal quantities. The three south Texas soils contained montmorillonite, mica, and kaolinite type clay minerals. Cation exchange capacity (CEC) values for the eight soils are given in Table 1.

Cation (Ca, Mg, Na, and K) and anion (Cl, SO_4, HCO_3, and CO_3) concentrations and electrical conductivity (EC) were measured in the saturation-paste extracts. Exchangeable Na and K were determined from ammonium acetate extracts (1.0 N, pH = 7.0) (Yaalon and Koyumdjieky 1968), and exchangeable Ca and Mg were determined from sodium acetate extracts (1.0 N, pH = 8.2) (Bower et al. 1952). Saturation extract solution ionic strength was calculated from the EC (Griffin and Jurinak 1973). Cation activities were then calculated using the Davies' activity coefficient equation (Stumm and Morgan 1970), ionic strength and cation concentrations corrected for ion pair formation (Robbins et al. 1980). Ion pairs considered significant in these soils included $CaCO_3^0$, $CaSO_4^0$, $CaOH^+$, $CaHCO_3^+$, $MgCO_3^0$, $MgSO_4^0$, $MgOH^+$, $MgHCO_3^+$, $NaCO_3^-$ and $NaSO_4^-$. Two sets of selectivity coefficients were calculated for a four cation system, giving selectivity coefficient values for the six possible cation pair combinations (Tables 1 and 2). The first set was calculated using cation activities and the second set was calculated using cation concentrations.

Using the Vanselow convention which designates the anion exchange charge as −1 and the cations as reacting in molar quantities (Robbins et al. 1980; Sposito 1977), the selectivity

Table 1. Cation exchange capacity (CEC) for eight salt affected soils

Soil Depth	Portneuf	Declo	Freedom	Penoyer	Hunting	Raymond-ville	Rio	Wil-lacy
m	meq/100 g							
0 – 0.25	21	22	22	7	15	23	19	19
0.25 – 0.50	21	26	23			23	28	24
0.50 – 0.75	20	26	22			26	28	24
0.75 – 1.00	20	24	21			26	29	23
1.00 – 1.25	19	25	22			23	27	23
1.25 – 1.50	19	21	23			24	26	22

coefficients are defined as:

$$\frac{(Mg)^{0.5} X_{0.5Ca}}{(Ca)^{0.5} X_{0.5Mg}} = K_1 \qquad \frac{(Mg)^{0.5} X_K}{(K) X_{0.5Mg}} = K_4$$

$$\frac{(Na) X_{0.5Ca}}{(Ca)^{0.5} X_{Na}} = K_2 \qquad \frac{(Na) X_{0.5Mg}}{(Mg)^{0.5} X_{Na}} = K_5$$

$$\frac{(Ca)^{0.5} X_K}{(K) X_{0.5Ca}} = K_3 \qquad \frac{(Na) X_K}{(K) X_{Na}} = K_6$$

where (M) represents cation activities or concentrations, depending on calculation method and $X_{l/nM}$ represents the exchangeable ion concentration in moles per unit weight of soil where n is the cation valence. The $X_{l/nM}$ term can also represent meq per 100 g soil and will give the same numeral K_i value as will dividing the molar concentration M by n.

Results

No significant interaction was measured between total soluble salt concentration (EC) and the calculated selectivity coefficients nor between the soil solution anion composition and the calculated selectivity coefficients within a soil for eight soils used in this study when activities were used in the calculation. The variability was considerably higher for each coefficient value when concentrations were used in the calculations. Others have also shown decreased variability between selectivity coefficient values for a given soil when ionic strength and ion pairing corrections were made (Babcock and Shulz 1963; Rao et al. 1968).

All soils, except the Penoyer and Hunting soils, were sampled at various depth increments well down into the subsoil horizons. None of these soils showed any difference in the selectivity coefficient values with depth, even though the total salt concentration and ion ratios varied with depth when activities were used. When concentrations were used in the coefficient calculations there was considerable variation in the values with depth, resulting primarily from increasing $CO_3^=$, HCO_3^-, or $SO_4^=$ concentrations with depth and their ion pairing and ionic strength effects on cation activities. The variation was greatest for the equilibrium between a monovalent and a divalent cation.

Table 2. Saturation extract electrical conductivity (EC) and selectivity coefficients (with standard deviation) calculated from cation activities for eight soils

Soil	EC range mmhos cm^{-1}	K_1 (Ca-Mg)	K_2 (Ca-Na)	K_3 (K-Ca)	K_4 (K-Mg)	K_5 (Mg-Na)	K_6 (K-Na)	No. of samples
Portneuf	4.0 – 9.5	3.3±0.4	3.4±0.9	6.7±1.8	20.0±5.1	0.9 ±0.3	21.0±2.5	32
Declo	1.7 – 20.7	7.1±2.5	4.0±0.8	1.9±0.5	7.7±0.3	0.62±0.13	7.7±1.0	24
Freedom	1.5 – 40.1	3.4±1.1	4.0±1.3	3.3±1.1	3.6±0.9	1.03±0.33	13.9±2.4	38
Penoyer	3.0 – 6.2	1.4±0.2	6.4±0.7	2.8±0.3	4.2±0.3	4.3 ±0.3	18.0±0.8	8
Hunting	2.7 – 9.5	1.7±0.2	6.1±0.5	2.7±0.3	4.5±0.4	3.5 ±0.3	16.2±1.6	8
Raymondville	0.5 – 11.8	3.0±0.8	2.2±0.9	6.7±2.1	16.7±6.2	0.8 ±0.3	16.0±2.5	16
Rio	7.0 – 110.0	2.7±0.4	2.7±0.6	6.3±1.9	12.5±1.6	1.0 ±0.3	17.0±5.4	40
Willacy	0.6 – 47.4	2.8±0.8	1.9±0.9	6.3±2.0	16.7±7.1	0.7 ±0.4	14.0±3.7	112

Table 3. Selectivity coefficients calculated from cation concentrations

Soil	K_1 (Ca-Mg)	K_2 (Ca-Na)	K_3 (K-Ca)	K_4 (K-Mg)	K_5 (Mg-Na)	K_6 (K-Na)
Portneuf	3.0±0.6	2.0±0.6	9.5± 2.8	31.8±12.2	0.6±0.3	21.4±2.7
Declo	6.3±2.7	2.0±0.8	4.9± 2.7	21.90± 8.9	0.3±0.2	8.1±1.1
Freedom	3.1±1.4	1.9±1.4	6.9± 3.8	20.2±13.1	0.6±0.1	14.4±3.1
Penoyer	1.3±0.3	3.1±1.4	11.2± 4.4	18.8± 6.1	1.3±0.3	18.6±1.1
Hunting	1.6±0.3	3.2±1.5	10.8± 5.1	19.36± 5.9	1.2±0.4	16.8±1.8
Raymondville	2.8±1.1	0.4±0.2	46.0±12.0	133.0±33.0	0.2±0.1	16.8±3.1
Rio	2.7±0.9	0.5±0.3	41.0±15.0	88.0±27.0	0.4±0.2	17.3±6.1
Willacy	2.6±1.2	0.3±0.2	38.0±16.0	127.05±35.0	0.3±0.2	14.7±5.1

When activities were used in the calculations, the Mg-Ca selectivity coefficient was lower for Declo sandy loam and higher for Penoyer and Hunting soils than for the other four soils, but the overall differences were small (Table 2). These values were similar to most values reported in the literature (Robbins et al. 1980). The Ca-Na selectivity coefficient was slightly more variable but similar or lower than values reported elsewhere. The Ca-K selectivity coefficient is even more variable and tends to increase as the exchangeable potassium ratio increases. This agrees with the findings of Udo (1978). The Mg-K selectivity coefficient is highly variable among soils and tends to increase as the exchangeable potassium ratio increases. With the exception of the Penoyer and Hunting soils the Mg-Na selectivity coefficients are near unity. The K-Na selectivity coefficient is variable and is highest for Portneuf silt loam which had the lowest exchangeable potassium ratio, and is lowest for Declo which had the highest exchangeable potassium ratio. The variability in the selectivity coefficients involving K could also result partially from K-clay mineral interactions. Potassium was preferentially held over the other three cations, Ca was next and Na and Mg varied, depending on the soils.

Comparing the calculation method results showed that the selectivity coefficients calculated from cation concentrations were always more variable between soils and with depth than the values calculated with cation activities (Tables 2 and 3). The Ca-Mg and Na-K coefficients showed the least variability as would be expected since the ionic strength and ion pairing effect would be similar between Ca and Mg and between Na and K. In the heterovalent coefficients the ionic strength and ion pairing effects would be greater for the divalent ion than the monovalent ion, resulting in wider differences between the two calculation methods and in greater variability with depth resulting from concentration increases in the ion pair forming anions and total salt concentration increases.

Discussion

The data presented here (Table 2) gives the six selectivity coefficients with their standard deviation for simultaneous Ca-Mg-Na-K exchange in eight salt affected soils over a wide EC range. This allows selectivity coefficient comparison between the several cation pairs in a soil as well as coefficient value comparisons between the eight soils and comparison between values calculated with cation concentration (Table 3) and activities.

It is not the intent of this presentation to quantify all aspects of exchange in a four cation system, but rather to show the similarities and differences in selectivity coefficients in systems with solution concentration, ionic strength, anion mixes, clay mineralogies, exchangeable cation ratio and soil depth differences. By using cation activities, differences resulting from ionic strength, ion pairing and anion differences were eliminated from the selectivity coefficient values. Differences arising from clay mineralogy were not separated out here even though other workers have shown differences in many cases (Dolcater et al. 1968).

The sodium adsorption ratio (SAR) has been used to predict the potential sodium hazard in soils and the potential adverse effect of high sodium in irrigation water in relation to the calcium plus magnesium concentration in these systems

(U.S. Salinity Lab Staff). The SAR has traditionally been defined as:

$$\text{SAR} = \text{Na} \left[\frac{\text{Ca} + \text{Mg}}{2} \right]^{-0.5} \quad \text{or} \quad \text{SAR} = [\text{Na}] ([\text{Ca}] + [\text{Mg}])^{-0.5}$$

where the values without brackets represent sodium, calcium, and magnesium concentrations in meq/l units and the square bracketed values represent mM/l units. This SAR relationship is still being used in many soil chemistry models because data similar to those in Table 1 have not been available. This definition suggests that the Mg-Ca selectivity coefficient is unity and that the Ca-Na and Mg-Na selectivity coefficients are equal. Neither of these assumptions hold for the eight soils studied. In the past, Ca and Mg concentrations have been combined into a single value for physical and chemical evaluations in high salt and sodium affected soils. This has resulted because they are both divalent alkali earth metals and they were usually determined and reported as a single value by the versenate method which does not distinguish between the two. The Mg-Ca selectivity coefficients vary from 0.14 to 0.69 with the average being 0.38 (Table 1). The Ca-Na coefficient varies between 1.7 to 6.5 times higher than the Mg-Na coefficient. The values from Declo sandy loam suggest that Na is even more tightly bound than Mg while Ca is much more tightly bound than Na. For Penoyer loam, Ca and Mg are more tightly bound than Na and there is not as great a Ca-Mg preference as in the other seven soils. This definition also does not account for K effect on the Na exchange relationship in the soil system. Care should also be used in predicting Na reclamation of a soil like Declo sandy loam from data obtained from a soil like Penoyer loam or Hunting silty clay using an irrigation water or material that contains a significant proportion of Mg in relation to Ca, since the Ca-Mg relationships are different.

These data produce the lyotropic series, $\text{Na} \gtreqqless \text{Mg} > \text{Ca} > \text{K}$ in order of relative ion replaceability ease. The series $\text{Na} > \text{K} > \text{Mg} > \text{Ca}$ as given in soil text books (Bohn et al. 1979; Buckman and Brady 1969) shows K as being easier to exchange than Ca and Mg whereas our data show it to be the least easily exchanged. These data were developed from simultaneous exchange coefficients in soils while the $\text{Na} > \text{K} > \text{Mg} > \text{Ca}$ series was developed by comparing NH_4 or K exchange equilibria with the other cations on montmorillonite and were then ranked according to the relative replacement ease by NH_4 or K.

Potassium has usually been ignored in salt affected soils. In some instances such as the Declo soil or irrigation water containing as much as 15 meq K/l (Smith and Hayden 1980), K concentrations are high enough that it must be considered in controlling soil salinity. The K exchange values shown, also suggest that for high K soils or irrigation waters, K exchange should also be considered in estimating the exchangeable sodium percentage on the soil exchange complex, because K will more readily replace Na than will Ca or Mg.

In a soil system containing Ca, Mg, Na, and K the cation exchange capacity (CEC) can be defined as:

$$\text{CEC} = X_{\text{Na}} + X_{\text{K}} + X_{0.5\,\text{Mg}} + X_{0.5\,\text{Ca}} \tag{1}$$

where Na, K, etc. are the mmoles of cation on the cation exchange. Again using the Vanselow convention (Sposito 1977), by rewriting the selectivity coefficients

designated a K_2, K_5, and K_6 in terms of the exchangeable cation in the numerator, substituting the results into equation (1) and factoring X_{Na} from each term, the CEC becomes:

$$CEC = X_{Na} \left[1 + \frac{K_2 (Ca)^{0.5}}{(Na)} + \frac{K_5 (Mg)^{0.5}}{(Na)} + \frac{K_6 (K)}{(Na)} \right] \qquad (2)$$

which can then be substituted into:

$$ESP = 100 \frac{X_{Na}}{CEC}$$

The X_{Na} terms cancel and ESP can be calculated from solution activities and the appropriate selectivity coefficients by:

$$ESP = 100 \, (Na) \left[(Na) + K_2 (Ca)^{0.5} + K_5 (Mg)^{0.5} + K_6 (K) \right]^{-1} \qquad (3)$$

Values for K_2 are available in the literature for many soils and soil minerals, but the only values available for K_5 and K_6 known (Table 1) to the authors are reported here. These data show that there is as much as a 3-fold difference between the K_2 and the K_5 selectivity coefficients for a given soil, indicating that Ca and Mg do not respond equally to Na exchange. These data also show that the relative K preference is 8 to 21 times that of Na and according to equation (3), should be considered when K concentration in the soil solution makes up an appreciable fraction of the soluble cations. In cases where irrigation waters contain appreciable K concentrations, the ESP will not equal the value from conventional ESP-SAR relationships, but can be calculated from irrigation water data and the selectivity coefficients.

All calculations for this study were carried out on a hand-held programmable calculator, making this approach adaptable to field use.

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