RELATIONSHIP BETWEEN EXCHANGEABLE SODIUM AND SODIUM ADSORPTION RATIO IN A SOLONETZIC SOIL ASSOCIATION

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The relationship between the sodium adsorption ratio (SAR) and exchangeable sodium ratio (ESR) in a Solonetzic soil association of the Black soil zone of East-Central Alberta was examined. Highly significant correlations between ESR and SAR were determined for the A and B horizons of this soil association, although the regression equations were different for each horizon. The slope of the regression line indicated that Na was adsorbed three times more strongly, relative to Ca, in the B horizon than in the A horizon. The difference in adsorption was attributed to differences in soil properties, particularly clay and organic matter content, between the two horizons. Equations to calculate exchangeable sodium percentage (ESP) from SAR were also determined for the two horizons studied. To relate the soluble Na levels to exchangeable Na in the Duagh-Malmo soil association, appropriate equations should be used for each horizon. Also, data showed that an SAR of 3 in the B horizon corresponds to an exchangeable Ca:Na ratio of 10 that is used to differentiate Solonetzic from Chernozemic soils in the Canadian Classification System.

Key words: Solonetzic soil association, soluble-exchangeable cation ratios

[Rapport existant entre la concentration de sodium échangeable et le taux d'absorption du sodium dans une association de sols solonetziques.]

Titre abrégé: Cations solubles et échangeables dans les sols solonetziques.

On a étudié les rapports existant entre le taux d'absorption du sodium (TAS) et la concentration de sodium échangeable (CSE) dans une association de sols solonetziques de la zone des terres noires du centre est de l'Alberta. Des corrélations hautement significatives ont été établies entre le TAS et la CSE pour les horizons A et B de cette association de sols, bien que les équations de régression aient été différentes pour chacun des horizons. La pente de la courbe de régression indique une absorption du Na trois fois plus forte, par rapport au Ca, dans l'horizon B que dans l'horizon A. Cette différence d'absorption est attribuée à des différences de propriétés des sols, en particulier de la teneur en argile et en matière organique, entre les deux horizons. Des équations permettant de calculer le pourcentage de sodium échangeable (PSE) à partir du TAS ont également été établies pour les deux horizons étudiés. Pour établir un rapport entre les taux de Na soluble et de Na échangeable dans une association de sols Duagh-Malmo, il faut utiliser des équations particulières pour chaque horizon. Les résultats indiquent également qu'un TAS de 3 dans l'horizon B correspond à un taux d'échange de Ca à Na de 10, taux qui sert à différencier, dans le système de classification canadien, les sols solonetziques des sols chernozémiques.

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Mots clés: Association de sols solonetziques; rapport cations solubles/cations échangeables

It is desirable that cations adsorbed on the exchange complex of a soil be expressed by analysis of a water extract. Many studies indicate that the ratio of cations in soil solution reflect the ratio of the corresponding adsorbed cations when the two phases are at equilibrium. An equation developed by Gapon in 1933 (Bohn et al. 1979) considers that a linear relationship exists between ratios of ions in solution and the same ions on the exchange phase once the ions have been adjusted for valence. For the exchange of Ca and Na ions the form of the Gapon equation is as follows:

$$\frac{[\text{Nax}]}{[\text{Ca}_{1/2}x]} = K_{\text{G}} \frac{[\text{Na}^+]}{[\text{Ca}^{2+}]^{1/2}}$$

where the exchangeable cation concentrations are in meq/100 g of soil (x denotes exchange phase) and soluble cation concentrations are in mM/L. K_G is the Gapon exchange constant.

The exchange constant in a Na-Ca system is a reflection of the relative quantities of cations adsorbed and is related to intrinsic soil properties (Poonia and Talibudeen 1977). They found surface charge density and organic matter content significantly affected the Na-Ca exchange equilibria. Therefore, the exchange constant must be determined for soils that differ significantly in these properties.

Many equations appear in the literature based on the Gapon equation but perhaps the most widely used application is the one developed by the Staff at the U.S. Dep. Agric. Salinity Laboratory (U.S. Department of Agriculture 1954). They developed the relationship between exchangeable sodium ratio (ESR) measured in the exchange phase and sodium adsorption ratio (SAR) measured in the solution phase, namely:

 $ESR = -0.0126 + 0.01475 \text{ SAR} (r^2 = 0.852).$

The ESR was determined from the ex-

changeable Na and CEC by the following relationship:

$$ESR = \frac{ExNa}{CEC - ExNa}$$

The SAR was calculated from the concentration of cations (meq/L) in the saturated paste extract by the equation:

$$SAR = Na/\sqrt{((Ca + Mg)/2)}$$

The ESR-SAR equation was based on a collection of 59 surface soils from the Western States of the U.S.A. without consideration of differences in soil properties.

The SAR pools Ca and Mg and the ESR ignores the effects of other monovalent exchangeable ions, especially potassium (Bower 1959). Nevertheless, ESR is significantly correlated to the SAR for many soils (Bower 1959; Paliwal and Gandhi 1976; Poonia and Talibudeen 1977). The proportionality coefficient in the regression of ESR on SAR (0.01475 in the U.S. Dep. Agric. equation) corresponds to the exchange constant from the Gapon equation (K_G). Therefore, for a given set of soil properties there exists a unique function between SAR and ESR.

Although ESR has been used rather extensively, another term more commonly used during the past 10 yr in soil salinity studies is exchangeable sodium percentage (ESP). It is determined from exchangeable Na and CEC by the following equation:

$$ESP = (ExNa/CEC) \times 100.$$

However, ESP is mathematically related to ESR as follows:

$$ESP = (ESR (100))/(1 + ESR).$$

Thus, once the relationship between SAR and ESR has been determined for a soil, an estimation of ESP can be calculated (Bower 1959).

The objective of the present study was to determine the relationship between soluble and exchangeable cations in a Solonetzic soil association. Specifically a reliable estimate of ESP from the SAR of the saturated paste extract would be useful for characterization of sodic soils and provide information relative to their reclamation. Also, of importance is the relationship between SAR of the saturation extract and the ExCa:Na ratio used for classification of Solonetzic soils.

MATERIALS AND METHODS

The soils used in this study were sampled from plots on the Agriculture Canada, Solonetzic Substation at Vegreville in East-Central Alberta. The area has been mapped as a complex of Solonetzic and Chernozemic soils developed on fine-textured materials (Bowser et al. 1962). The soil series represented in the sampling area include the Duagh SiL, a Black Solonetz; the Wetaskiwin SiL, a Black Solonetz; and the Malmo SiL, an Eluviated Black Chernozem.

The Duagh soil is developed on a saline lacustrine material and the fine clay fraction consists mainly of smectite with some interstratified mica-smectite and traces of minerals with a 10-Å spacing. In the coarse clay fraction, mica and kaolinite are dominant; randomly interstratified mica-smectite is present in a moderate amount and chlorite in a trace amount (Khan and Webster 1966). The Wetaskiwin soil is developed on the same parent material and has a similar clay mineral suite. Chernozemic soils of the Alberta Parkland (Malmo could be included in this category) also have a dominance of montmorillonite in the clay fraction with major amounts of illite and minor amounts of chlorite and kaolinite (Dudas and Pawluk 1969).

Samples from the A and B horizons of the soil profiles representing the Duagh-Malmo soil association were analyzed for chemical and physical properties by methods outlined by McKeague (1978). The analyses were electrical conductivity (EC) and concentration of cations in the saturated paste extract, ammonium-acetate-extractable cations and cation exchange capacity (CEC) by the sodium acetate method. Ca, Mg, Na and K in the various extracts were determined by atomic absorption spectrophotometry.

Soil pH was measured in a 1:2.5 soil-water suspension and organic carbon content was determined by the Leco furnace method. The hydrometer method was used to determine particle size distribution with particle size classes and textural classes being defined according to guidelines of the Canada Soil Survey Committee (1978).

RESULTS AND DISCUSSION

The means and ranges of soil properties of the A and B horizons (35 samples of each) are presented in Table 1. The carbon, sand and silt contents and CEC values were significantly higher in the A horizon than in the B horizon for the 35 soil samples (P < 0.001). In contrast, the clay content, pH, SAR and EC values were significantly higher in the B horizon than in the A horizon than in the A horizon than in the B horizon than in the B horizon than in the B horizon than in the A horizon (P < 0.001).

Since the relationship between ESR and SAR is related to intrinsic soil properties (Poonia and

Table 1. Mean values and ranges for selected properties of 35 samples from a Duagh-Malmo soils complex[†]

Properties –	A horizon		B horizon	
	Mean	Range	Mean	Range
Carbon (%)	5.10	3.98-7.32	1.37	0.71-2.19
Texture	SiL	SiL	SiC	SiCL-SiC
Clay (%)	21	17-25	44	25-53
Sand (%)	16	9–23	6.	0-14
Silt (%)	63	51-70	50	43-65
pH	5.5	4.4-6.1	6.3	5.2-7.6
CEC meg/100 g	39.3	26.4-57.1	34.4	14.9-47.3
SAR	5.5	0.2~16.9	12.3	1.7-33.1
EC mS/cm	0.80	0.22-1.4	2.90	1.2-9.2

†Differences between means of A horizon and B horizon using the *t*-test were significantly different at P < 0.001 for all the properties.

Talibudeen 1977), it is expected that soils with significantly different properties will have unique relationships between the soluble and exchangeable phases. A regression analysis of ESR and SAR was conducted for the data of the A and B horizons. The regression equation for the A horizon is

$$ESR = 0.0076 + 0.0058 SAR$$
 (Fig. 1)

and for the B horizon

ESR = -0.0180 + 0.0173 SAR (Fig. 1).

The ESR is highly significantly correlated with the SAR ($r^2 = 0.902$) for both soil horizons. Since a linear relationship between ESR and SAR has previously been recognized (U.S. Dep. Agric. 1954), the high correlation was expected and compares well to other studies (Paliwal and Gandhi 1976) (Table 2).

Although both horizons have the same level of correlation between ESR and SAR, the regression equations are different. Analysis of the variance of data for the two horizons indicated that they represent two different populations (Harron 1979). Since the means of SAR for the A and B horizons are significantly different (Table 1), it is concluded that the regression equations for ESR and SAR in the A and B horizons are significantly different.

Earlier discussion suggested that the proportionality coefficients for the relationship between ESR and SAR can be compared to the exchange constant of the Gapon equation. Since the proportionality coefficient for the B horizon equation (0.0173) is almost three times the comparable value for the A horizon equation (0.0058), a unit increase in SAR will result in an increase in ESR that is three times greater in the B horizon than in the A horizon.

A significant factor accounting for the differences in proportionality coefficients is the organic matter content which is nearly four times greater in the A horizon than in the B horizon (Table 1). Poonia and Talibudeen (1977) noted a preference for Ca adsorption in upper soil horizons compared to corresponding subsoils. They attributed the differences in ion



Fig. 1. ESR as a function of SAR for the A and B horizons of the Duagh-Malmo soil complex.

Soil	Regression line	r^2	Reference	
A horizon B horizon	ESR = 0.0076 + 0.0058 SAF $ESR = -0.0180 + 0.0173 SAF$	R 0.902 R 0.902		
59 soils from Western U.S.A.	ESR = -0.0126 + 0.01475 SA	R 0.852	(U.S. Dep. Agric. 1954)	
LS SCL CL	ESR = 0.1593 + 0.0074 SAF ESR = 0.1324 + 0.0109 SAF ESR = 0.1320 + 0.0109 SAF	k 0.839 k 0.834 k 0.918	(Paliwal and Gandhi 1976)	
Above 3 soils combined	ESR = 0.1149 + 0.0109 SAF	R 0.792		

Table 2. ESR-SAR relationships for various soils

adsorption to high amounts of organic matter in the surface soils since it has been shown to have a strong preference for divalent cations, especially Ca (Salmon 1964). Because of its preferential adsorption of divalent cations, an increase in organic matter will decrease the proportionality coefficient for Na with respect to Ca and Mg.

By comparing the relationship of ESR and SAR with soils studied by other workers (Table 2), it is noticeable from the data of Paliwal and Gandhi (1976) that the amount of clay is also significant in affecting the proportionality coefficient. This coefficient of the regression line increased with increasing clay content. This trend is consistent with data for the fine-textured (SiC) B horizon of the current study. It is not possible to make comparisons with the 59 U.S. Dep. Agric. soil samples (Table 2) because the soil properties were not tabulated.

The two properties that exhibit large differences between the two horizons, i.e. clay and organic matter contents, are operating in opposite directions with respect to sodium adsorption. In the current study, the A horizon samples have higher organic matter and lower clay contents than the B horizon samples, consequently the difference in proportionality coefficients is greatly enhanced. It is apparent therefore that the ESR-SAR relationship should be determined for soils that differ significantly in clay and organic matter contents.

Since ESR and ESP are mathematically related, the latter can be expressed in terms of SAR with the same level of significance as the ESR-SAR linear regression. Therefore, ESP and SAR are highly significantly correlated through the following curvilinear relationships for the A horizon,

$$ESP = \frac{(0.0076 + 0.0058 \text{ SAR}) 100}{1 + (0.0076 + 0.0058 \text{ SAR})}$$

and the B horizon,

$$ESP = \frac{(-1.0180 + 0.0173 \text{ SAR}) 100}{1 + (-0.0180 + 0.0173 \text{ SAR})}$$

The high correlation between SAR and ESP means that 90% of the variation in exchangeable Na can be explained by the soluble cations of a water extract. The overall variation in the relationship between SAR and ESP is sufficiently small to warrant the use of the SAR of the saturated paste extract as an evaluation of the exchangeable Na level in the Duagh Solonetz and associated soils. However, the appropriate equation must be used for each horizon.

The major chemical criterion to determine whether a soil belongs to the Solonetzic Order is the ratio of exchangeable Ca to exchangeable Na (ExCa:Na). A soil that shows the characteristic Solonetzic morphology and has a ratio of ExCa:Na in the Bnt horizon of less than 10 falls in the category of the Solonetzic Order (Canada Soil Survey Committee 1978). Since it has been shown that SAR is related to exchangeable cation levels, it would be useful to determine the SAR value tha corresponds to the boundary between Solonetzic and non-Solonetzic soils. In this regard, Bresler et al. (1982) reports that although ESP was originally used as the main criterion for determining excessive Na levels in the soil, emphasis has shifted more recently to use of SAR of the extract from a saturated paste for classification purposes. The main reason given is that SAR of the saturation extract is easily determined and avoids the lengthy pro-



Fig. 2. Exchangeable Ca:Na ratio as a function of SAR for the B horizon of the Duagh-Malmo soil complex.

cedure and pitfalls associated with generating ESP data.

A log \times log transformation of the data for SAR and ExCa:Na in the B horizon results in a reasonably linear relationship. The regression of log (ExCa:Na) on log (SAR) provides the function

$$\log (ExCa:Na) = 1.645 - 1.34 \log SAR$$

which is transformed to

$$ExCa:Na = 44.2 SAR^{-1.34}$$
 (Fig. 2).

The regression equation has a high level of explained variation ($r^2 = 0.925$) which is similar to the variability in the relationship for ESP and SAR.

To separate Solonetzic from non-Solonetzic soils, the data points for the B horizons should

fall in either of the two quadrants ExCa:Na<10, or ExCa:Na>10. Since the relationship between ExCa:Na and SAR is strongly linear, an SAR value of 3 represents the same cutoff value as an ExCa:Na ratio of 10. All soils which have a SAR of less than 3 in the B horizon should belong to the non-Solonetzic soils that are represented by the Malmo series, an Eluviated Black Chernozem. The samples in the group where the SAR is greater than 3 should be from profiles that belong to the Solonetzic order represented by the Wetaskiwin and Duagh series, a Black Solodized Solonetz and Black Solonetz. respectively. This differentiation corresponds to a field inspection of the sampling sites. Therefore, for the Duagh, Wetaskiwin, Malmo soil association, a SAR of 3 in the B horizon can be considered the value which corresponds to the ExCa:Na of 10 that separates Solonetzic and Chernozemic soils.

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