Effect of Exchangeable Sodium on Soil Electrical Conductivity-Salinity Calibrations¹

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ABSTRACT

This study was undertaken to ascertain if soil sodicity significantly influences soil electrical conductivity (σ_a) – salinity calibrations. Laboratory columns of Fallbrook (Typic Haploxeralfs) and Yolo (Typic Xerorthents) soils were adjusted to various levels of salinity and sodicity by leaching them with solutions varying in electrical conductivity (σ_w) and sodium adsorption ratio (SAR); then σ_a was measured using four-electrode techniques. Calibrations obtained between σ_w and σ_a over the σ_w range 2 to 20 were compared at different levels of SAR ranging between 0 to 80 or 400. The calibrations between σ_w and σ_a were found to be insignificantly influenced by variations in SAR over the range studied. Normal variations in the exchangeable Na contents of typical saline, arid-land soils should not cause any serious misdiagnosis of soil salinity based on measurements of bulk σ_a and use of σ_w - σ_a calibrations.

Additional Index Words: soil sodicity, earth resistivity, sodium adsorption ratio.

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HEORY AND INSTRUMENTATION for measuring soil Lelectrical conductivity (σ_a) have been substantially advanced since 1971 when σ_a was first shown applicable to the determination of soil salinity in the field (Rhoades and Ingvalson, 1971). Theories of the measurement and interrelations among the various soil parameters involved have been described, improved instrumentation and circuitry have been developed, and commercial units are available for measuring σ_a using four-electrode, electromagnetic induction and time domain reflectrometry methodology. It has been shown that σ_a and soil salinity, in terms of the electrical conductivity of the soil solution (σ_w) or of the soil extract (σ_e), are closely related. Accurate and simple methods have been developed for calibrating soil salinity and σ_a . Methods for predicting such calibrations have also been developed. Applications of the method for measuring, mapping, and monitoring field salinity, detecting the presence of a shallow water table, detecting saline seeps, determining leaching fraction, and scheduling and controlling irrigations have been developed and demonstrated. Reviews of much of the above are given elsewhere (Rhoades, 1976, 1978, 1985; Rhoades and Corwin, 1984; Rhoades and Oster, 1985).

The following equation(s) of Rhoades et al., (1976) has been shown to be valid for saline soils:

$$\sigma_{\rm a} = [\sigma_{\rm w}\Theta]T + \sigma_{\rm s},$$
 [1]

$$T = a\Theta + b, [2]$$

where Θ is volumetric soil water content, σ_w is electrical conductivity of the soil water, σ_s is apparent electrical conductivity of the solid phase (primarily due to surface conductance and exchangeable cations), and T is a transmission coefficient (pore geometry factor of value ≤ 1) which is linearly dependent upon Θ (when Θ is greater than some minimum; Θ_t) with a and b

being empirical parameters appropriate for the particular soil. This relation has been found to describe observed data quite well, except where σ_w and Θ are atypically low for arid soils. Under such conditions the σ_a - σ_w relation becomes curvilinear at σ_w levels of less than about 4 dS m⁻¹ (or at σ_e levels of less than about 2 dS m⁻¹) depending on soil clay content and soil type (Shainberg et al., 1980; Nadler and Frenkel, 1980; Nadler 1982).

From the above, it may be assumed that surface conductance is generally insignificant relative to σ_w in moist, saline soils and should not interfere seriously in their σ_a - σ_w calibrations. But little data are available to establish limits in this regard. Likewise, little data are available to establish the specific influence of exchangeable sodium on the σ_a - σ_w relation. One would expect σ_s to increase with exchangeable sodium, especially as σ_w is reduced and the outward extent of the double layer influence is increased. On the other hand, as double-layer effects are manifested, reductions in pore geometry could occur with clay swelling; hence, T could be simultaneously reduced. Thus the two processes—increase in σ_s and decrease in T—could be offsetting, or at least partially so.

Early unpublished attempts of the second author to evaluate the influence of exchangeable sodium percentage (ESP) on σ_a - σ_w relations yielded inconsistent, inconclusive results. In a subsequent attempt (Shainberg et al., 1980), some hint of an ESP effect was evidenced but the variability of the data limited its conclusiveness. This study was undertaken using improved techniques and more critical methods of statistical analysis in an attempt to gain more conclusive data and to establish the influence, if any, of ESP on σ_a - σ_w calibrations and the conditions under which ESP might produce a misdiagnosis of salinity level from σ_a measurements.

MATERIALS AND METHODS

The electrical conductivities of two California soils, Fallbrook-B (USSL soil no. 3677; fine-loamy, mixed thermic Typic Haploxeralfs) and Yolo (USSL soil no. 3416; fine-silty, mixed, nonacid, thermic Typic Xerorthents) were studied as a function of exchangeable sodium percentage (as deduced from the sodium adsorption ratio, SAR = Na⁺/[(Ca²⁺ + Mg²⁺)/2]^{1/2}, where the solute concentrations are expressed in mmol_c L⁻¹) and pore solution electrical conductivity. Some properties of these soils are given in Table 1. The Yolo soil is dominated by montmorillonitic clay while the Fallbrook soil is dominated by kaolinitic clay; thus, surface conductance and clay swelling effects would be more likely to occur with the Yolo soil.

Seven columns of Fallbrook soil and 14 columns of Yolo soil were prepared by packing approximately 300 g of <2

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Table 1. Characteristics of soils.

	Mechani	ical comp	positions		Dominant		
Soil type	Sand	Silt	Clay	CEC	clay type		
		-g kg-1-		mmol (+) kg-1			
Fallbrook-B (no. 3566)	630	210	160	169	kaol., mont., mica		
Yolo (no. 3416)	380	350	270	223	mont., mica		

mm air-dried soil into plastic cylinders (5.1-cm diam by 8cm length) at average bulk densities (\pm 0.5%), of 1.35 kg m⁻³ (Yolo) or 1.31 kg m⁻³ (Fallbrook). For both the Fallbrook and Yolo soils, a set of seven columns were prepared in which the soil was constrained to prevent expansion through swelling (see Fig. 1). In addition, another set of seven columns was prepared for the Yolo soil in which the soil was unconstrained, but was kept fully saturated during the experiment. This was facilitated by placing a stopper in the top of the column through which a tube was inserted to permit water flow. Eight electrodes were inserted through the cylinder walls at intervals of about 1.8-cm around the middle perimeter of the soil column. Groups of any four neighboring electrodes were used as a four-electrode array; the outer two were used as current electrodes and the inner two as potential electrodes. By rotating the connections, five independent measurements of σ_a were made for any treatment using a Bison Model 2350A Earth Resistivity Meter.³ The appropriate cell constants were obtained by calibration using solutions of known σ_w -SAR values covering the ranges used in the experiment. These solutions included the following concentrations, in mmol_c L⁻¹: 200, 160, 120, 80, 60, 40, and 20 and SAR values: 0, 10, 20, 30, 40, 80 and infinity (i.e., pure NaCl solution). The solutions were prepared from sodium and calcium-chloride salts.

The objective of the study was to compare σ_a - σ_w calibrations at various levels of ESP(SAR) to see if ESP affected the calibrations of the two soils. To accomplish this objective, an attempt was made to keep water content as constant as possible. The following procedure was carried out with the above objective in mind. The air in the soil columns was replaced with CO₂ to prevent air entrapment during saturation of the soils, since removal of air during leaching can cause errors in the measurement of σ_a (Frenkel et al., 1983). The soils were then saturated with the highest concentration solution of the appropriate SAR treatment. This leaching was continued using the same solution until the $\sigma_{\rm w}$ of the effluent no longer changed and was essentially that of the influent (treatment) solution. At this time, five measurements of σ_a were made and a sample of the final effluent was analyzed for Na⁺, Ca²⁺, Mg²⁺ concentrations, and σ_w . Also, the weight of each "constrained" column, which had been previously tared, was measured so that the value of Θ could be determined and checked for constancy. The height of each "unconstrained" column was measured to determine how much expansion had occurred through swelling. Subsequently, leaching was reinitiated using a solution of the same SAR, but of the next lower concentration. A series of such successive equilibrations were carried out until the permeability of the soil column became limiting.

RESULTS AND DISCUSSION

The experimental results are shown in Fig. 2 and 3 for the Fallbrook and Yolo constrained soils, respectively. Since there were no significant differences in the results obtained for the Yolo soil in the uncon-

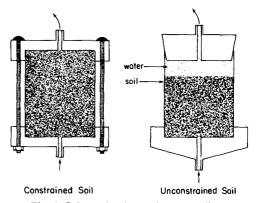
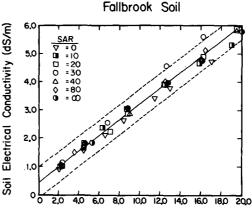


Fig. 1. Schematic of experimental cells.



Electrical Conductivity of the Water (dS/m)

Fig. 2. Relationship between Fallbrook soil electrical conductivity (σ_n) , and the electrical conductivity (σ_w) , and sodium adsorption ratio (SAR) of the soil water.

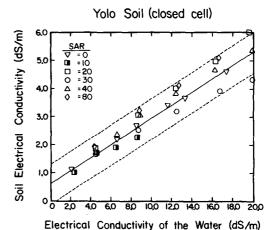


Fig. 3. Relationship between Yolo soil electrical conductivity (σ_n) and the electrical conductivity (σ_w) and sodium adsorption ratio (SAR) of the soil water.

strained and constrained columns (swelling occurring in the unconstrained soil columns was in the order of 5 to 10% in magnitude), only the constrained data are given. Changes in Θ in the constrained columns, as determined from the weight measurements, were < 1%. There is no obvious or marked effect of ESP(SAR) on σ_a for these soils, within the limits of the accuracy of measurements and experimental conditions. The fact that separate columns were used for each SAR

³ The citation of particular products is for the convenience of the reader and does not imply any particular endorsement by the USDA or its agents.

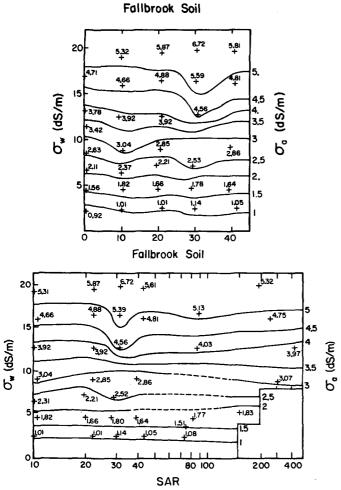


Fig. 4. Relations between Fallbrook soil electrical conductivity (σ_a) and the electrical conductivity (σ_w) and sodium adsorption ratio (SAR) of the soil water for the ranges of SAR of 0 to 40 (a) and 10 to 400 (b).

treatment is one cause of the observed variation. It would have been preferable to use one column for each value of $\sigma_{\rm w}$ and to successively vary SAR, but this was impractical because of the very long time required to achieve ESP-SAR equilibration. Furthermore, the differential leaching that would be required at the different levels of concentration to achieve such equilibration would likely also create differences between columns and errors at least as great as those observed in this experiment. Part of the observed variation was related to errors in determining the actual values of ESP(SAR) existing in the middle of the soil column at the time σ_a was measured. This results from release of low amounts of Ca2+ and Mg2+ by mineral dissolution (which is ongoing in the columns during the leaching-equilibration process) which reduces the SAR values from those of the applied waters. The magnitude of error associated with this phenomenon is greatest where SAR is high and σ_w is low in the influent because, under these conditions, an increase of a few mmol(+) L^{-1} of $Ca^{2+} + Mg^{2+}$ substantially alters the SAR of the influent solution. On the other hand, $\sigma_{\rm w}$ is not so markedly affected because the total amount of electrolyte added to the solution is small. Since the SAR value of the effluent did not attain that

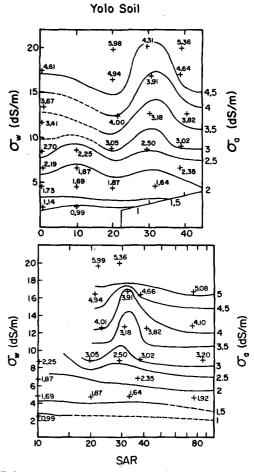


Fig. 5. Relations between Yolo soil electrical conductivity (σ_n) and the electrical conductivity (σ_w) and sodium adsorption ratio (SAR) of the soil water for the ranges of SAR 0 to 40 (a) and 10 to 80 (b).

of the influent even after extensive leaching, the average of the influent and effluent solutions was used to represent SAR of the pore solution, except for the SAR infinity treatment (pure sodium chloride solution). In this case, the SAR of the effluent was used.

The experimental data are plotted in Fig. 4 and 5 in terms of $\sigma_a = f(SAR)$ to further aid in the evaluation of the influence of ESP on σ_a and $\sigma_a = f(\sigma_w)$ relations. The data over the SAR range of 0 to 40 are shown in Fig. 4a as linear plots; the wider SAR range of 10 to 400 are shown in Fig. 4b as semilog plots. These data show that there is no structure or trend in the σ_a values relative to SAR(ESP). The isolines of σ_a are essentially parallel to the SAR axis at any fixed value of σ_w , except for Yolo soil at SAR 30. This discrepancy is likely an artifact of column preparation, since the "effect" diminished with increased leaching and did not occur at other levels of SAR. These figures show that σ_a is clearly dominated by σ_w .

Two statistical approaches were undertaken in an attempt to more precisely evaluate the relative influences of σ_w and SAR on σ_a . Because of the uncertainty regarding the accuracy of SAR, these analyses were made twice—once for the range of SAR <45 and again using all SAR values. For one analysis, the structural model given in Kendall and Stuart (1973) was fol-

Table 2. Statistical parameters obtained in multilinear statistical analyses.

	Regression values†			Standard errors‡			Test value§	
Soil type	$X_i\left(\sigma_{\mathbf{w}}\right)$	X, (SAR)	Int.	$X_i(\sigma_{\mathbf{w}})$	X2 (SAR)	Int.	X_2 (SAR)	df¶
Fallbrook (all SAR data) Yolo (closed cell, SAR < 45) Yolo (open cell, SAR < 45)	0.281 0.236 0.261	0.00009 0.0013 -0.0017	0.408 0.602 0.577	0.0067 0.015 0.017	0.00054 0.005 0.003	0.078 0.171 0.103	0.026 0.055 0.312	39 23 12

- \dagger Magnitudes of the multilinear regression coefficients for $\sigma_{\rm w}$ and SAR and the intercept values.
- \ddagger Standard errors of the multilinear regression coefficients of σ_w and SAR and the intercept values.
- § The test statistic is approximately distributed as F(1, df).

¶ Degrees of freedom for the test statistic.

lowed using the measured values of σ_a , σ_w , and SAR as estimates of their real values, i.e.,

$$\sigma_{ai} = X_i + Y_i + \gamma_i$$

$$\sigma_{wi} = X_i + \epsilon_i,$$

$$SAR_i = Y_i + \delta_i,$$

where X_i and Y_i are the actual values of σ_{w_i} and SAR_i and γ_i , ϵ_i and δ_i are the errors in σ_{ai} , σ_{wi} and SAR_i, respectively. The calculation procedure was developed by Fuller (1975) and Hidiroglou et al. (1980) and requires knowledge of the covariance error matrix and the covariances of the dependent variable for each error. The errors γ and ϵ were found to be normally distributed with means of 0 and to have variances of 0.031 and 0.15, respectively. The δ errors had a mean of 0 and a variance of 1.79 [53 degrees of freedom (df)) for the data limited to SAR < 45. When all values of SAR were included, the variance of δ increased sharply to a value of 2.25 (61 df). The errors γ and ϵ appeared to be independent of σ_a and of each other. Errors associated with column packing differences could not be established, and variations related to differences in initial dry soil bulk densities and to differences in water contents were not significant.

The results of the multilinear regression statistical analyses are given in Table 2 in terms of the coefficients of $X(\sigma_w)$ and Y(SAR), the regression intercepts (I), the standard errors of the coefficients and intercepts, the test values for the hypothesis that the coefficient of SAR is zero, and the df for the various data sets. The values of the SAR coefficients are very low (hence, they should have very little effect on σ_a) and are not statistically significant at the 5% level.

Results of simple (least squares) linear regression analyses of $\sigma_a = f(\sigma_w)$ and $\sigma_w = f(\sigma_a)$ for the Fallbrook and Yolo soils using data covering all SAR values are given in Table 3. These results show that σ_a and σ_w are highly correlated, irrespective of SAR.

Errors involved in measurements of σ_a , σ_w , and SAR under laboratory-controlled conditions exceed, and preclude, the detection of any influence of SAR on σ_a - σ_w relations. It is concluded that variations in the exchangeable sodium contents of typical saline, arid land soils should not cause any serious misdiagnosis of soil

Table 3. Least squares linear regression analyses.

Soil type		Linear	regression	Coefficient of	
	Function	Slope	Intercept	correlation	
Fallbrook (all SAR data)	$\sigma_{\mathbf{a}} = \mathbf{a}\sigma_{\mathbf{w}} + b$ $\sigma_{\mathbf{w}} = \mathbf{a}\sigma_{\mathbf{a}} + b$	0.280 3.494	0.422 -1.266	0.9895	
Yolo (all SAR data)	$ \sigma_{\mathbf{a}} = \mathbf{a}\sigma_{\mathbf{w}} + \mathbf{b} \\ \sigma_{\mathbf{w}} = \mathbf{a}\sigma_{\mathbf{a}} + \mathbf{b} $	0.235 3.909	0.687 -1.854	0.9597	

salinity based upon measurements of soil σ_a and use of σ_a - σ_w or σ_a - σ_e field calibrations.

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