Relation Between pH_c and Sodium Adsorption Ratio (SAR) and an Alternative Method of Estimating SAR of Soil or Drainage Waters[1]

D. L. Suarez[2]

ABSTRACT

The relation between the sodium adsorption ratio (SAR) and pH_c derived here predicts SAR of the drainage water (SAR_{dw}) better than existing empirical equations. Inaccuracies in SAR estimates from the new relationship can be anticipated by the extent to which the derived conditions are valid. Empirical equations provide no understanding of why they are sometimes inaccurate. Due to the relative insensitivity of SAR to calcium concentrations, SAR predictions of most drainage waters (where $Ca \simeq \frac{1}{2} HCO_3$) are satisfactory when the Ca concentration of the drainage water is assumed to be constant at any fixed P_{CO_2}. Prediction of SAR in drainage or soil water in the absence of gypsum precipitation requires knowledge of P_{CO_2}, irrigation water composition, HCO_3/Ca ratio, and the leaching fraction. SAR_{dw} can be simply and accurately calculated from the derived equation and a table accounting for ionic strength and HCO_3/Ca ratio.

Additional Index Words: water quality, irrigation, sodic soils.

THE SODIUM ADSORPTION RATIO (SAR)[3] of soil and drainage waters is a common index of the suitability of a water for irrigation or the environmental consequence of irrigation. Since the SAR of drainage water is a valuable measure of the maximum SAR within the root zone, empirical equations have been developed to predict drainage water SAR based on leaching fraction (LF)[4] and chemical composition of the irrigation water.

The objective of determining SAR is usually to predict the exchangeable sodium percentage (ESP) of a soil. The SAR expression implicitly assumes that calcium and magnesium have equal selectivity for exchange. Also, the exchange phase composition is fixed by the total concentrations of the exchangeable ions rather than their activities. Despite these simplifications, the SAR expression can predict ESP for a range of solution compositions and concentration. The statistical fit shown in *USDA Handbook 60* (U.S. Salinity Laboratory Staff, 1954), where ESP $= -0.0126 + 0.01475$ SAR, is usually adequate ($r^2 = 0.852$). For greater accuracy, each soil and water type should be calibrated. The prediction of SAR in the soil solution is discussed below.

The prediction of Bower et al. (1968) for the SAR of drainage water, SAR_{dw}, is

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[3] SAR $= Na/(Ca + Mg)^{1/2}$ where concentrations are expressed in mmol/liter.
[4] LF $=$ fraction of irrigation water that leaves the root zone as drainage water.

$$SAR_{dw} = (1/LF)^{1/2} \cdot SAR_{iw} \ (1 + 8.4 - pH_c^*) \quad [1]$$

where

$$pH_c^* = (pK_2' - pK_c') + p(Ca + Mg) + pAlk; \quad [2]$$

pK_2' and pK_c' are the negative logarithms of the second dissociation constant of carbonic acid and the solubility constant of calcite, respectively (corrected for ionic strength); and pAlk is the negative logarithm of the alkalinity. Equation [1] attempts to correct SAR_{dw} for leaching fraction and $CaCO_3$ precipitation-dissolution, and assumes that the drainage water pH is 8.4 and that Mg precipitates along with Ca as a carbonate. This relationship overpredicted SAR_{dw} in lysimeter experiments; Rhoades (1968) modified the expression to

$$SAR_{dw} = \frac{y^{(1 + 2 LF)}}{(LF)^{1/2}} \cdot SAR_{iw} \left(1 + (8.4 - pH_c^*)\right) \quad [3]$$

where y is a constant, usually 0.65 in value. Although described as a mineral weathering parameter, y is an empirical curve-fitting constant. Since the original equation was empirical, any inadequacy in predicting SAR_{dw} cannot be anticipated.

The following derivation shows how SAR_{dw}, irrigation water compositions, pH_c, and LF are theoretically interrelated. The SAR-pH_c relationship developed here is different than the Bower et al. (1968) or Rhoades (1968) equation; it is simpler and more accurately predicts SAR_{dw}.

THEORY

We assume ion exchange equilibrium (or steady state) has been achieved and that magnesium carbonate does not precipitate, i.e., Na and Mg are concentrated in direct proportion to 1/LF. Magnesium precipitates in irrigated soils only under agriculturally unusual conditions (Suarez, 1975). In contrast, Ca does not increase in direct proportion to 1/LF but is instead controlled by a $CaCO_3$ solid phase. From the definition of SAR and LF, and at steady state,

$$SAR_{dw} = \frac{Na_{iw}/LF}{\{(Mg_{iw}/LF) + Ca_{eq}\}^{1/2}} \quad [4]$$

where Ca_{eq} is the Ca concentration in millimoles per liter in equilibrium with a $CaCO_3$ solid phase at the bottom of the root zone. To solve for SAR_{dw}, Ca_{eq} must be calculated for the appropriate CO_2 concentration. This Ca value is not easily estimated and its calculation can be complex.

Combining the equilibrium expression for calcite solubility with the second dissociation constant of carbonic acid yields

$$[H^+] = \frac{K_2}{K_{sp}}[Ca^{2+}] \ [HCO_3^-] \quad [5]$$

where brackets denote activities, $K_{sp} = 10^{-8.47}$ (Jacobson and Langmuir, 1974), and $K_2 = 10^{-10.33}$ (Harned

and Scholes, 1941). This equation gives the pH of calcite-saturated solutions (pH_{eq}).

Equation [5] can calculate the pH that a soil water at calcite equilibrium would have if P_{CO_2} were adjusted such that Ca and CO_3 had not precipitated or dissolved as evapotranspiration concentrated the irrigation water in the rootzone. For the ideal system where $\gamma = 1$, and there is no complexing, Eq. [5] can be written

$$H = \frac{K_2}{K_{sp}} \cdot \frac{Ca_{lw}}{LF} \cdot \frac{HCO_{3lw}}{LF},$$ [6a]

where Ca_{lw} and HCO_{3lw} are the concentrations of Ca and HCO_3 in the irrigation water, assuming all carbonate alkalinity as HCO_3. In contrast to Eq. [5], Eq. [6a] represents the hypothetical pH obtained by increasing P_{CO_2} without any precipitation.

Similarly

$$pH_i = pK_2 - pK_{sp} + p\frac{Ca_{lw}}{LF} + p\frac{HCO_{3lw}}{LF},$$ [6b]

where pH_i is the pH of the soil water necessary to prevent calcite precipitation or dissolution. Equation [6] is equivalent to Eq. [2], except that Eq. [2] considers Mg as precipitating with Ca as a carbonate and Eq. [2] considers the concentration of the irrigation water uncorrected for LF.

Rearranging Eq. [5], assuming no complexation and that $\gamma = 1$,

$$\frac{Ca^2}{H} \cdot \frac{HCO_3}{Ca} = \frac{K_{sp}}{K_2},$$ [7]

then

$$2\, pCa_{eq} - pH_{eq} = p\left(K_{sp}(Ca/HCO_3)_{eq}K_2\right)$$ [8]

and

$$2\, pCa_i - pH_i = p\left(K_{sp}(Ca/HCO_3)_iK_2\right).$$ [9]

It follows that

$$Ca_{eq} = Ca_i/(10^{-(pH_i - pH_{eq})/2}),$$ [10a]

where Ca_{eq} is the Ca concentration of the water at the bottom of the root zone at calcite equilibrium; pH_{eq} is its pH at the fixed CO_2 level (that of the drainage water); Ca_i is the Ca concentration the water would have if precipitation or dissolution did not occur (Ca_{lw}/LF); and pH_i is the pH necessary to prevent dissolution or precipitation of $CaCO_3$ (with P_{CO_2} adjusted to achieve that pH).

Equation [10a] holds for any solution in which $(HCO_3/Ca)_{eq} \sim (HCO_3/Ca)_i$. If $Ca_i = Ca_{lw}/LF$, then

$$Ca_{eq} = \frac{Ca_{lw}}{LF \cdot 10^{-(pH_i - pH_{eq})/2}}.$$ [10b]

If the P_{CO_2} necessary to prevent precipitation equals the actual P_{CO_2}, then $pH_i = pH_{eq}$ and $Ca_{eq} = \frac{Ca_{lw}}{LF}$.

Finally, substitution of Eq. [10b] into Eq. [4] yields

$$SAR_{dw} = \frac{\dfrac{Na_{lw}}{LF}}{\left(\dfrac{Mg_{lw}}{LF} + \dfrac{Ca_{lw}}{LF \cdot 10^{-(pH_i - pH_{eq})/2}}\right)^{1/2}}.$$ [11]

A comparable expression can be derived for SAR_{dw} and the pH_c of the irrigation water (rather than pH_i of the drainage water.) Using the pH_c expression as did Bower et al. (1968) in Eq. [2] (except without Mg precipitation), then

$$SAR_{dw} = \frac{\dfrac{Na_{lw}}{LF}}{\left(\dfrac{Mg_{lw}}{LF} + \dfrac{Ca_{lw}}{10^{-(pH_c - pH_{eq})/2}}\right)^{1/2}}.$$ [12]

Equation [12] is the theoretical relationship between pH_c and SAR and can adequately predict SAR_{dw} while Eq. [1] does not. Also Eq. [11] and [12] are valid for any HCO_3/Ca ratio.

Solving Eq. [11] and [12] for SAR_{dw} require pH_{eq} which depends on the HCO_3/Ca ratio in solution and P_{CO_2}. Equation [1] assumes $pH_{eq} = 8.4$. For solutions with an equilibrium pH of 8.4, Eq. [12] accurately predicts SAR_{dw} while Eq. [1] does not, as will be shown.

Rather than choose an arbitrary value for pH_{eq} it is preferable to solve pH_{eq} for a set of reasonable conditions. For the solution where $Ca = HCO_3/2$, substituting that into Eq. [5] gives

$$K_2[HCO_3^-]^2/2[H^+] = K_{sp}.$$ [13]

Combining the solubility equation of CO_2 in water with the first dissociation constant of carbonic acid yields

$$[HCO_3^-] = K_1 P_{CO_2} K_{CO_2}/[H^+].$$ [14]

Combining Eq. [13] and [14] yields

$$pH_{eq} = 10 \exp -\left(\frac{K^2_{CO_2}\, K^2_1\, P^2_{CO_2}\, K_2}{2\, K_{sp}}\right)^{1/3}$$ [15a]

with values of K_{CO_2} and K_1 given by Harned and Davis (1943). Equation [15a] could be formulated for any other HCO_3/Ca ratio by substituting that ratio for the value (2) in the denominator, i.e.,

$$pH_{eq} = 10 \exp -\left(\frac{K^2_{CO_2}\, K^2_1\, P^2_{CO_2}\, K_2}{(HCO_3/Ca)\, K_{sp}}\right)^{1/3}.$$ [15b]

The pH_{eq} can now be solved for any value of P_{CO_2} and HCO_3/Ca ratio. The root zone CO_2 concentration is properly considered an external independent variable, not substantially affected by mineral dissolution and precipitation, but the result of a balance between CO_2 production by plant roots and microbial respiration vs. diffusion to the atmosphere. The prediction of the Ca concentration of any saturated solution cannot be done without knowing the P_{CO_2}. Proper application of the pH_c concept thus requires a P_{CO_2} assumption since we cannot predict pH_{eq} without it. The derived Eq. [11] is more accurate if we calculate pH_{eq} taking into account the water's HCO_3/Ca ratio and P_{CO_2} from Eq. [15b] rather than using a fixed pH_{eq}. This eliminates the advantage of using pH_c, as Ca_{eq} can be directly estimated from the same variables. This derivation is shown below.

Combining the $CaCO_3$ solubility equation with the first and second dissociation constants of carbonic acid yields

$$\frac{[H_2CO_3]}{[HCO_3^-]^2}\frac{K_1K_{sp}}{[Ca^{2+}]} = K_2. \qquad [16]$$

If we substitute the constant for the solubility of CO_2 into Eq. [16] we obtain

$$(K_1\ K_{sp}\ K_{co_2}\ P_{co_2}/K_2) = [Ca^{2+}]\ [HCO_3^-]^2. \qquad [17]$$

This is a general condition, valid for any solution in equilibrium with any $CaCO_3$ solid phase (of given K_{sp}).

If we substitute $HCO_3^- = 2\ Ca^{2+}$ into Eq. [17] we obtain

$$[Ca^{2+}]^3 = (K_1\ K_{sp}\ K_{co_2}\ P_{co_2})/\ 4\ K_2. \qquad [18]$$

When Eq. [18] is solved for Ca, in millimoles per liter and the Ca value substituted into Eq. [4], then

$$SAR_{dw} = \frac{Na_{lw}/LF}{\left\{(Mg_{lw}/LF) + 9.33\ (P_{co_2})^{1/3}\right\}^{1/2}}. \qquad [19]$$

This expression is much simpler than either Eq. [11] or [12] and quite accurate. Even if the assumption ($HCO_3 = 2\ Ca$) is not reasonable, SAR will still be adequately predicted by Eq. [19], due partly to the insensitivity of SAR to the Ca concentration. As will be shown, Eq. [19] is preferable to the assumption of a fixed value for pH_{eq} of 8.4. The assumption ($HCO_3 = 2\ Ca$) is not the only possibility because Eq. [18] and [19] can also be generalized for any HCO_3/Ca ratio.

The general form of Eq. [18] is $Ca^{2+}_{eq} = (P_{co_2})^{1/3} \cdot$ constant, where the constant depends on K_1, K_{sp}, K_{co_2}, and K_2 (all of which are fixed) and the HCO_3/Ca coefficient

$$Ca^{2+}_{eq} = \left(\frac{K_1\ K_{sp}\ K_{co_2}}{K_2\ (HCO_3/Ca)^2\ \gamma_{Ca}\gamma^2_{HCO_3}}\right)^{1/3}$$

$$\times\ (P_{co_2})^{1/3} = \frac{X}{10^3} \cdot (P_{co_2})^{1/3}. \qquad [20]$$

Table 1 lists the X values for Ca in millimoles per liter. The values of the activity coefficients γ_{Ca} and $\gamma^2_{HCO_3}$, were calculated by means of an extended Debye-Huckel equation. Since $Ca_{eq} = X \cdot P_{co_2}^{1/3}$, this value, when inserted into Eq. [4], yields

$$SAR_{dw} = \frac{Na_{lw}/LF}{\left\{(Mg_{lw})/LF + X\ (P_{co_2})^{1/3}\right\}^{1/2}}. \qquad [21]$$

This equation should be accurate because it properly considers LF, activity coefficients, P_{co_2}, and the HCO_3/Ca ratio.

Calculations and Evaluation of SAR_{dw} Expressions

The best procedure to evaluate the accuracy of SAR_{dw} equations is to compare the predicted SAR_{dw} for different water types and leaching fractions against computer model predictions. This is justified because all the expressions attempt to account for $CaCO_3$ precipitation, which the program does precisely, correcting for activity coefficients and complexing. Because of the nonsteady-state conditions encountered in field measurements, it is not desirable to evaluate a derived or empirical expression on limited field data. Use of field data alone have resulted in correlations which do not have general validity but fit only that particular water type, leaching fraction, or P_{co_2}. As a point of reference, a comparison will be made between the computer program and data obtained from a lysimeter experiment.

The leaching fractions listed in Table 2, Col. 1, were achieved in the lysimeter experiment of Oster and Rhoades (1975). The leaching fractions marked with an § § are those that result in gypsum in addition to $CaCO_3$ precipitation. Compositions of the eight western rivers used for irrigation are given in Rhoades et al. (1973). Listed in Table 2, Col. 2, are the SAR measured by Oster and Rhoades (1975) on the drainage waters from their lysimeters after several years of irrigation. The soil P_{co_2} in the lower quarter of their lysimeters averaged 0.13 atm. In Col. 3 is the SAR

Table 1—X values calculated from Eq. [20] for various HCO₃/Ca ratios and ionic strength.

| HCO₃/Ca | Ionic strength | | | | | | | | | | | | | | |
	0.001	0.005	0.01	0.02	0.03	0.04	0.05	0.07	0.1	0.15	0.2	0.25	0.3	0.4	0.5
0.1	73.4	79.6	84.1	90.0	94.4	97.9	101.0	106.0	112.0	120.0	125.0	130.0	133.0	139.0	144.0
0.2	46.2	50.1	53.0	56.7	59.5	61.7	63.6	66.8	70.5	75.3	78.8	81.7	84.0	87.7	90.4
0.3	35.3	38.2	40.4	43.3	45.4	47.1	48.5	51.0	53.8	57.5	60.1	62.3	64.1	67.0	69.0
0.4	29.1	31.6	33.4	35.7	37.5	38.9	40.1	42.1	44.4	47.4	49.6	51.5	52.9	55.3	57.0
0.5	25.1	27.2	28.8	30.8	32.3	33.5	34.5	36.3	38.3	40.9	42.8	44.3	45.6	47.6	49.1
0.6	22.2	24.1	25.5	27.3	28.6	29.7	30.6	32.1	33.9	36.2	37.9	39.3	40.4	42.2	43.5
0.7	20.1	21.7	23.0	24.6	25.8	26.8	27.6	29.0	30.6	32.7	34.2	35.4	36.4	38.1	39.2
0.8	18.3	19.9	21.0	22.5	23.6	24.5	25.2	26.5	28.0	29.9	31.3	32.4	33.3	34.8	35.9
0.9	17.0	18.4	19.4	20.8	21.8	22.6	23.3	24.5	25.9	27.6	28.9	30.0	30.8	32.2	33.2
1.0	15.8	17.1	18.1	19.4	20.3	21.1	21.8	22.8	24.1	25.8	26.9	27.9	28.7	30.0	30.9
1.5	12.1	13.1	13.8	14.8	15.5	16.1	16.6	17.4	18.4	19.7	20.6	21.3	21.9	22.9	23.6
2.0	9.96	10.8	11.4	12.2	12.8	13.3	13.7	14.4	15.2	16.2	17.0	17.6	18.1	18.9	19.5
2.5	8.58	9.31	9.84	10.5	11.0	11.5	11.8	12.4	13.1	14.0	14.6	15.2	15.6	16.3	16.8
3.0	7.60	8.24	8.71	9.33	9.78	10.1	10.5	11.0	11.6	12.4	13.0	13.4	13.8	14.4	14.9
3.5	6.86	7.44	7.86	8.42	8.82	9.15	9.44	9.91	10.5	11.2	11.7	12.1	12.5	13.0	13.4
4.0	6.27	6.80	7.19	7.70	8.07	8.37	8.63	9.06	9.57	10.2	10.7	11.1	11.4	11.9	12.3
4.5	5.80	6.29	6.65	7.12	7.46	7.74	7.98	8.38	8.85	9.45	9.88	10.2	10.2	11.0	11.3
5.0	5.41	5.86	6.20	6.63	6.96	7.22	7.44	7.81	8.25	8.81	9.21	9.55	9.83	10.3	10.6
6.0	4.79	5.19	5.49	5.87	6.16	6.39	6.59	6.92	7.30	7.80	8.16	8.46	8.70	9.09	9.37
7.0	4.31	4.68	4.95	5.30	5.56	5.77	5.95	6.24	6.59	7.04	7.36	7.63	7.85	8.20	8.45
8.0	3.95	4.29	4.53	4.85	5.09	5.28	5.44	5.71	6.03	6.44	6.74	6.98	7.18	7.50	7.73
9.0	3.65	3.96	4.19	4.48	4.70	4.88	5.03	5.28	5.57	5.95	6.23	6.46	6.64	6.94	7.15
10.0	3.41	3.69	3.90	4.18	4.38	4.55	4.69	4.92	5.20	5.55	5.80	6.02	6.19	6.46	6.66

predicted by a computer program which corrects for ionic strength and complexing and uses the apparent solubility value of $10^{-8.0}$, the ion activity product of $CaCO_3$ for groundwaters beneath irrigated lands (Suarez, 1977). The SAR predicted in Col. 4 represents the SAR_{dw} calculated with the equation of Bower et al. (1968), i.e., Eq. [1]. The expression $pK_2' - pK_c'$ necessary to solve for SAR_{dw} was determined by the following corrected equation, following Bower et al. (1965):

$$pK_2' - pK_c' = a + 0.059$$

$$\times \left(\frac{4(\mu)^{1/2}}{1 + 2(\mu)^{1/2}} + \frac{(\mu)^{1/2}}{1 + 1.45(\mu)^{1/2}} \right), \quad [22]$$

where a is 2.027. The ionic strength (μ) was estimated by the relationship

$$1,000 \ \mu = 1.3477 \ C + 0.5355, \quad [23]$$

where C is millimoles cation charge per liter (Bower et al., 1965). The sum of the cation charges of the drainage water was approximated by dividing the sum of the cation charge of the irrigation water by the LF. The pH_c value was determined with Eq. [2], only omitting the Mg term. The SAR predicted in Col. 5 is based on calculations using Eq. [3] (Rhoades, 1968), with a "y" value of 0.65 and $pK_2' - pK_c'$ "a", and pH_c as given above. The SAR values in Col. 6 were calculated with Eq. [11]. The apparent solubility value of $10^{-8.0}$ was used in place of K_{sp} of cal-

cite in Eq. [15a]. The calculated value of pH_{eq} was 6.68 for the lysimeter P_{CO_2} (0.13 atm). Column 7 represents the solubility of $CaCO_3$ (with a solubility of $10^{-8.0}$) corrected for complexing and ionic strength at $P_{CO_2} = 0.13$ atm. This value can be obtained from Eq. [19] if it is corrected for ionic strength. Column 8 was calculated, using Eq. [23] to estimate ionic strength, reading off the appropriate X value in Table 1 and substituting into Eq. [21].

The determined values of SAR_{dw} shown in Table 2, Col. 2, are fairly accurately predicted by the computer-calculated values in Table 2, Col. 3. It is not certain that the drainage waters were at steady state. There might still have been some Ca-Mg ion exchange, and fluctuations in P_{CO_2} and LF are to be expected. All subsequent comparisons are best made with respect to the program-generated values. The SAR_{dw} calculated with the Bower equation (Eq. [1] of this paper) shown in Table 2, Col. 4, predicts SAR_{dw} for Feather River water reasonably well but overpredicts SAR_{dw} for all other waters by a factor of about 2 to 2.5, with a mean absolute error of 9.10. A regression equation could be fitted to the data; SAR_{dw}, however, could just as easily be regressed to SAR_{iw} directly. The overprediction would be even greater if Mg was added to the pH_c calculation (as in Eq. [2]), as per Bower et al. (1968). The Rhoades equation, incorporating the additional y parameter, adequately predicts SAR_{dw} as shown in Table 2, Col. 5. There is some underprediction for Feather River water and

Table 2—Comparison of SAR of drainage waters from lysimeter experiment (Oster and Rhoades, 1975) to SAR calculated using predictive equations.

River water	1 LF	2 SAR measured†	3 SAR prog‡	4 SAR Bower§	5 SAR Rhoades¶	6 SAR Eq. [11]#	7 SAR Ca=6.45 mM††	8 SAR Eq. [21]‡‡
Feather	0.102	1.43	0.70	0.54	0.45	0.78	0.68	0.82
	0.199	0.65	0.37	0.39	0.30	0.44	0.37	0.47
	0.309	0.49	0.24	0.31	0.22	0.30	0.24	0.32
Grand	0.328	11.5	9.24	21.4	10.7	9.36	7.80	10.3
Missouri	0.275	4.7	3.08	6.93	3.75	3.20	3.48	3.21
	0.341	3.4	2.59	6.22	3.18	2.69	2.90	2.72
	0.088	6.7	7.18	12.3	7.78	7.49	8.23	7.56
Salt	0.168	13.9	16.1	30.0	17.1	16.1	17.7	16.8
	0.305	10.9	9.85	22.3	11.3	10.0	10.7	10.4
Colorado	0.086	5.6	6.58§§	11.6	7.35	6.63	7.42	6.71
	0.192	3.7	3.47§§	7.78	4.49	3.81	4.38	3.78
	0.304	2.6	2.55	6.18	3.24	2.70	3.13	2.69
Sevier	0.107	14.8	16.7	32.2	21.4	16.4	16.8	16.6
	0.222	10.9	10.4	22.3	15.4	10.4	10.6	10.9
	0.320	9.0	8.07	18.6	10.3	8.19	8.31	8.39
Gila	0.112	22.6	23.3§§	48.3	29.9	25.3	19.0	25.4
	0.230	16.1	14.7	33.7	18.8	15.5	18.4	15.4
	0.296	13.5	12.5	29.7	15.7	12.9	15.5	12.8
Pecos	0.099	12.8	14.4§§	25.3	15.6	13.5	15.9	13.1
	0.211	8.4	8.48§§	17.4	9.71	8.01	10.2	7.70
	0.320	6.3	6.16§§	14.1	7.19	5.95	7.83	5.63
Error¶¶				9.10	1.81	0.32	1.23	0.50

† Measured SAR of drainage water (Oster and Rhoades, 1975).

‡ SAR determined by program with P_{CO_2} = 0.13 atm.

§ SAR determined by Eq. [1] of this report (Bower equation) and equations similar to Eq. [2] without the Mg term.

¶ SAR calculated from irrigation water using equation of Rhoades (1968), (Eq. [3] of this report) and an equation similar to Eq. [2] without the Mg term.

SAR calculated from Eq. [11] and [15a], assuming apparent IAP = $10^{-8.0}$ (Suarez, 1977).

†† SAR calculated assuming Ca of the drainage water = 6.45 mM and $SAR_{dw} = (Na_{iw})/\{(Mg_{iw}/LF) + 6.45\}^{1/2}$.

‡‡ SAR calculated from Eq. [21] with X values determined from Table 1 and P_{CO_2} = 0.13 atm.
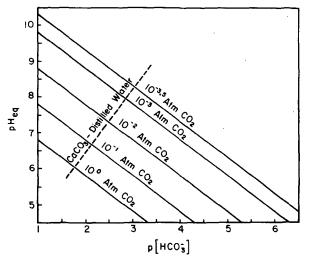
§§ Gypsum and $CaCO_3$ precipitated.

¶¶ Mean absolute difference between computer model and other methods.
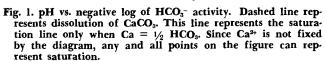
overprediction for all other waters. The mean absolute error was 1.81. The overprediction would also be greater if the Mg term were included in the pH$_c$ calculation. Table 2, Col. 6 was calculated with Eq. [11], the pH-SAR equation derived in this paper. It predicts SAR very well using the same terms as the Bower equation (except that pH$_{eq}$ = 6.68, derived from Eq. [15a] rather than pH$_{eq}$ = 8.4) without additional fitting parameters. The mean absolute error was only 0.32. The values calculated in Table 2, Col. 7, represents the Ca value of 6.45 substituted into the simple SAR expression. Despite lack of correction for ionic strength of the individual solutions and the assumption that HCO$_3$ = 2Ca, the mean absolute error was only 1.23. The data in Table 2, Col. 8, were calculated from Eq. [21]; calculation of SAR was very accurate with a mean absolute error of 0.50.

Substantial errors in predicting Ca result in only modest errors in predicting SAR. For example, if the Ca concentration of Gila drainage water at LF = 0.230 is one-half the actual value (8.75 instead of 17.5 mM), then the SAR increases from 14.7 to 17.4 or an error of 18%. If we assume Ca in the drainage water is zero, the SAR increases to 22.6. For numerous waters, the empirical equations gave SAR values greater than those obtained assuming Ca was zero. At constant SAR, the Ca term becomes less important as salinity increases due to the square root term. The sensitivity of SAR to Ca also decreases as Mg/Ca increases.

Of the 21 waters examined, six precipitate gypsum. This is not typical of arid land irrigation waters, but these waters have been included as a test of the conditions under which the equations can be used. Obviously, a model that considers CaCO$_3$ precipitation alone cannot yield accurate predictions of Ca in a CaCO$_3$-gypsum–controlled system, and none of the equations presented would be useful in a pure Ca-Na-SO$_4$ system. For waters that precipitate CaCO$_3$ and gypsum, a CaCO$_3$ model alone will usually predict SAR quite well. The reasons are twofold: (i) relative insensitivity of SAR to Ca concentration, especially at high salinity (discussed above); and (ii) the interaction of CaCO$_3$ and gypsum precipitation. If gypsum precipitation is not considered, CaCO$_3$ precipitation is overestimated for waters that precipitate gypsum (gypsum precipitation removes Ca and SO$_4$ which allows more HCO$_3$ to stay in solution). The CaCO$_3$ overestimate does not completely compensate for gypsum precipitation but usually equals a substantial portion of it. The data in Table 2 show that Eq. [21], as expected, is not as accurate for waters that precipitate gypsum and CaCO$_3$ as compared to those that precipitate only CaCO$_3$. The mean absolute difference between the program and Eq. [21] was 0.86 for the six gypsum precipitating waters vs. 0.50 for all the samples.

The low accuracy of the Bower equation stems from two difficulties: (i) the form of the SAR-pH relationship used; and (ii) the choice of a fixed pH$_{eq}$ and specifically pH$_{eq}$ as 8.4. This 8.4 value is very close to the pH of a pure calcite solution, when HCO$_3$ = 2Ca at P$_{co_2}$ of $10^{-3.5}$ (atmospheric CO$_2$ pressure). However, due to the form of the equation, it will not accurately predict SAR when HCO$_3$ = 2Ca and P$_{co_2}$ equals $10^{-3.5}$. Also, the appropriate pH$_{eq}$ for a P$_{co_2}$

Fig. 1. pH vs. negative log of HCO$_3^-$ activity. Dashed line represents dissolution of CaCO$_3$. This line represents the saturation line only when Ca = $\frac{1}{2}$ HCO$_3$. Since Ca^{2+} is not fixed by the diagram, any and all points on the figure can represent saturation.

of 0.13 atm (P$_{co_2}$ of the lysimeter expriment) is 6.68 when HCO$_3$ = 2 Ca. The determination of pH$_{eq}$, necessary for proper use of the pH$_c$ concept, is dependent on the solution composition, leaching fraction, and P$_{co_2}$.

The necessity of considering P$_{co_2}$ and determining the HCO$_3$/Ca ratio is evident from Fig. 1. All points on the figure can represent calcite equilibrium, since we have one variable [Ca^{2+}] which is not specified. The solubility of CaCO$_3$ in distilled water is given by the dashed line. Any point on the line when HCO$_3$ = 2Ca defines the system (i.e. P$_{co_2}$, pH, HCO$_3$, and Ca). If HCO$_3$/Ca is not given, the system is not defined when other salts in addition to CaCO$_3$ are present. If we calculate pH$_c$ and want to determine equilibrium (pH$_{eq}$), we still have two degrees of freedom, since P$_{co_2}$ and Ca or HCO$_3$ must still be specified. At atmospheric P$_{co_2}$, for any solution with a pH above 8.4, HCO$_3$/Ca ratios exist which result in CaCO$_3$ equilibrium, supersaturation, and undersaturation. Thus, pH$_c$ values below 8.4 need not indicate supersaturation or a tendency towards precipitation as assumed in the Bower equation.

In the absence of precise P$_{co_2}$ data, it is certainly better to estimate P$_{co_2}$ based on soil type, soil moisture content, and crop than to make no assumption and leave one degree of freedom in the solubility relations. That P$_{co_2}$ need not be precisely known is evident by examining the exponent terms in Eq. [21]. If it is known that the P$_{co_2}$ is very low (near that of the atmosphere) the equations developed here will adequately account for this change if some rough estimate of P$_{co_2}$ is made. In contrast, the empirical equations would not be adequate at low P$_{co_2}$ even with a regression equation, unless the regression equation were determined for samples at the same P$_{co_2}$. A similar problem is encountered with waters of different HCO$_3$/Ca ratios. By examining Eq. [1] or Eq. [3], it is not clear how a change in P$_{co_2}$ or HCO$_3$/Ca would alter the coefficients of a regression equation. Use of Eq. [21] properly requires that we know the final HCO$_3$/Ca ratio of the drainage water. It is apparent that using the HCO$_3$/Ca ratio the drainage water would have

if no precipitation or dissolution occurred, is often a reasonable estimation of the actual HCO_3/Ca ratio. It should be noted that the use of a constant value of Ca_{eq} at a given P_{CO_2} (as per Table 2, Col. 6) is often sufficient; it is not, however, much more difficult to use Table 1 and Eq. [21].

Use of these equations is not restricted to drainage water. If the term analogous to leaching fraction is known for any other point in the soil, the SAR at that point can be calculated, with the appropriate P_{CO_2} value by using Eq. [21] and Table 1. Also, if the drainage water leaving the root zone enters an environment of different fixed P_{CO_2} (open system), we assume that the SAR will adjust accordingly. Simple predictions are not possible if the waters undergo chemical reactions below the root zone since closed-system CO_2 conditions may prevail. In those instances, we would need to know the total mass of inorganic carbon present as CO_2 and the water content.

SAR of Surface Soil Water

In many instances, the SAR of the near-surface soil environment is needed. The suitability of a water for irrigation, for example, often depends on its potential for causing surface crusting and reduced infiltration rates. The near-surface soil environment is usually characterized by a P_{CO_2} level slightly above atmospheric and a salinity level slightly above that of the applied irrigation water. Most irrigation waters from surface sources in arid areas are calcite supersaturated but at a level of saturation where precipitation is negligible. For such conditions, the SAR of the irrigation water per se will be a suitable indicator of the resultant near-surface soil water SAR (and ESP) under steady-state conditions. Bingham et al. (1979) found good agreement between SAR_{iw} and ESP of the top 0.3 m of a soil irrigated with four different waters. Although the exchangeable-Na percentages were very low (<5), the results are consistent with the above reasoning and with computer model predictions. If irrigation is infrequent or nonuniform, or both, near-surface SAR's will be greater than predicted, as will salinity. In those instances, a reasonable estimate of near-surface soil water SAR may be obtained by allowing for concentration of the applied water. Use of ground water for irrigation (especially irrigation drainage water) will usually result in large degrees of supersaturation after degassing of CO_2. For these waters, the appropriate P_{CO_2} value should be chosen (e.g. $P_{CO_2} = 7 \times 10^{-4}$ atm) and SAR surface calculated by Eq. [21] and Table 1. In this instance, use of irrigation water SAR values would be expected to underpredict surface SAR, and thus surface-ESP values.

If the irrigation water is substantially undersaturated with respect to calcite, which is quite unusual, then the SAR of the irrigation water will again not be a good predictor of surface-soil water SAR and ESP. Assuming calcite or Ca containing silicates are present, these waters will dissolve Ca. In this instance, assuming a LF of 1.0, a P_{CO_2} of 7×10^{-4} atm, and an IAP value of $10^{-8.0}$, Ca will equal 0.955 mM for a pure $CaCO_3$-water system. Substitution of this value into Eq. [4] results in an expression for estimating near-surface soil water SAR. Alternatively, Table 1 and Eq. [23] can be used either with the irrigation waters-HCO_3/Ca ratio or, if the water is very under-

saturated, with the HCO_3/Ca ratio of 2. These expressions yielded SAR estimates comparable to the computer model, when tested with the data of Schroer (1970). Consequently, the high degree of correlation between surface ESP and SAR reported by Oster and Schroer (1979) also exists with these equations. With these data, irrigation water-SAR did not correlate well with surface ESP, because the prepared irrigation waters were at widely varying levels of calcite undersaturation. This is not typical of most irrigation waters in arid lands and SAR of surface-derived irrigation water will generally be a good predictor of near-surface soil ESP.

CONCLUSION

The derived pH_c-SAR equation predicts SAR_{dw} better than existing empirical equations. Proper application of the pH_c concept requires that we calculate pH_{eq}, taking into account the HCO_3/Ca ratio and P_{CO_2}. This eliminates the advantage of using pH_c as Ca can be directly estimated and SAR calculated using Eq. [21] and Table 1. This equation is more accurate and easier to use than existing equations for calculating SAR in soil and drainage waters. Satisfactory results can be obtained with rough estimates of P_{CO_2}, as SAR is not very sensitive to P_{CO_2}. Under saline conditions and with Mg/Ca ratios > 1, SAR is not particularly sensitive to the concentration of Ca. This explains why fair predictions of Ca will result in good SAR predictions. For calculation of soil water SAR at the surface, it is usually best to estimate SAR surface from the irrigation water SAR, or if it is a ground water, make some correction for degassing and $CaCO_3$ precipitation.

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