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Quality of Percolating Waters

I. Properties of Deep Substrata Materials in the West Side of the San Joaquin Valley, California

L. D. Doneen

II. A Computer Method for Predicting Salt Concentrations in Soils at Variable Moisture Contents

> K. K. Tanji, G. R. Dutt, J. L. Paul, and L. D. Doneen

III. The Quality of Waters Percolating through Stratified Substrata, as Predicted by Computer Analyses

K. K. Tanji, L. D. Doneen, and J. L. Paul



The San Luis Project, a major new unit in the Central Valley Project, is currently under construction. It will transport Feather River water to the west side of the San Joaquin Valley. The State of California Water Plan envisions a program of cyclic use of ground water during periods of deficiency, and storage of excess surface water when supplies are plentiful. Recharge of underground storage basins will involve the percolation of water through substrata, and the quality of the percolating water will be influenced by salts present in the substrata.

A series of papers in this issue present a method of predicting the quality of percolating waters in substrata (Part III), utilizing field data obtained from substrata profiles in the west side of the San Joaquin Valley (Part I). Theoretical considerations and approximations (Parts II and III) are formulated in the computer programs, for calculating simultaneously the major physicochemical reactions that occur during recharge.

THE AUTHORS:

- L. D. Doneen is Professor of Water Science, and Irrigationist in the Experiment Station, Davis.
- K. K. Tanji is Laboratory Technician IV, Department of Water Science and Engineering, Davis.
- G. R. Dutt was formerly Assistant Research Irrigationist, Davis. He is now Associate Professor, Department of Agricultural Chemistry and Soils, University of Arizona, Tucson.
- J. L. Paul is Assistant Professor of Landscape Horticulture, and Assistant Horticulturist in the Experiment Station, Davis.

II. A Computer Method for Predicting Salt Concentrations in Soils at Variable Moisture Contents^{1,2}

INTRODUCTION

THE CHEMICAL characteristics of the solution phase in a soil-water system are usually determined by analyses for solute species in the extract. Many different methods are available for obtaining soil solutions, among them the saturation extract (Richards, 1954), the 1:1 soil-water extract, and pressure methods (Richards, 1941; Eaton, Harding, and Gauge, 1960).

The effect of moisture content on the concentration and composition of solutes in extracts has been qualitatively studied by Reitemeier (1946). Heretofore, the most nearly accurate measure of soluble soil salts has been obtained by pressure, displacement, or suction methods, at prevailing moisture contents of the material studied, and measurement of salts in the extract. At soilmoisture suctions greater than 1 bar, however, the soil solution obtained is generally insufficient for detailed characterization unless large samples are used. A technique for quantitatively converting soil-salt data obtained at higher moisture contents (by saturation or 1:1 extract methods) to soil salts present under actual field-moisture conditions is necessary in order to predict the dynamic changes occurring in soil-water systems.

By utilizing existing principles of the solubility and dissociation of salts (Glasstone, 1946) and cation exchange (Krishnamoorthy, Davis, and Overstreet, 1949), it is possible to calculate the theoretical concentrations of components in a soil-salt system at a given water content. The calculations involved in solving the theoretical concentration of ion species are necessarily lengthy due to the simultaneous reactions occurring in the system (Dutt and Doneen, 1963). The computation can be made very rapidly, however, with electronic computers, by employing iteration methods.

The purpose of this publication is to present a computer method for predicting the equilibrium salt concentrations in a soil-soil solution-gypsum system at any given moisture content from extract data obtained initially at a different moisture content.

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THEORETICAL CONSIDERATIONS

The equilibrium relationships for the solubility of $CaSO_4 \cdot 2H_2O$ in soil solutions and the simultaneous exchange of Ca^{++} , Mg^{++} , and Na^+ between the solution and adsorbed phases of these ions at a given moisture content have been developed by Dutt (1962) and Dutt and Doneen (1963) for computer programming. Dutt's program has been extended to allow for the prediction of equilibrium concentrations of solutes, adsorbed cations, and gypsum for any given soil-moisture content from data obtained initially at a different moisture content.

For symmetrical cation exchange between Ca⁺⁺ and Mg⁺⁺ the exchange equation may be expressed as:

$$\frac{C_{\rm Ca}}{C_{\rm Mg}} = K \frac{E_{\rm Ca}}{E_{\rm Mg}} \qquad [1]$$

where $C_{\rm Ca}$ and $C_{\rm Mg}$ refer to the concentrations of solution Ca⁺⁺ and Mg⁺⁺, $E_{\rm Ca}$ and $E_{\rm Mg}$ denote the concentrations of adsorbed Ca⁺⁺ and Mg⁺⁺, and K is the Ca⁺⁺-Mg⁺⁺ equilibrium-exchange constant.

Let y be the moles of Mg^{++} per gm of soil that go into solution or are adsorbed. Let the initial concentrations of Ca^{++} and Mg^{++} be b_{Ca} and b_{Mg} moles per liter in the solution phase, and B_{Ca} and B_{Mg} be the moles per gm adsorbed on the soil-exchange complex. The change in relative composition of Ca^{++} and Mg^{++} from the interaction of solution and adsorbed phases is then:

$$E_{\rm Ca} = B_{\rm Ca} - y \qquad [2]$$

$$E_{\rm Mg} = B_{\rm Mg} + y \qquad [3]$$

$$C_{\rm Ca} = b_{\rm Ca} + \beta y \qquad [4]$$

$$C_{\rm Mg} = b_{\rm Mg} - \beta y \qquad [5]$$

where β is the ratio of gm of soil to liters of solution. Combining equations [2], [3], [4], and [5] with equation [1] results in the quadratic expression:

$$[\beta(1-K)]y^{2} + [\beta(B_{Mg} + KB_{Ca}) + b_{Ca} + Kb_{Mg}]y + [b_{Ca}B_{Mg} - Kb_{Mg}B_{Ca}] = 0$$
[6]

The nonsymmetrical cation-exchange system may be described by an equation derived from statistical thermodynamics (Krishnamoorthy, Davis, and Overstreet, 1949). The equilibrium distribution for Na⁺ and Ca⁺⁺ in the presence of Mg⁺⁺ is given by:

$$\frac{C_{\mathrm{Na}}^{2} \gamma_{\mathrm{Na}}^{2}}{C_{\mathrm{Ca}} \gamma_{\mathrm{Ca}}} = K \frac{E_{\mathrm{Na}}^{2}}{E_{\mathrm{Ca}} (E_{\mathrm{Na}} + 1.5 E_{\mathrm{Ca}} + 1.5 E_{\mathrm{Mg}})}$$
[7]

where C and E refer to the equilibrium concentrations in the solution and adsorbed phases, respectively, of the subscripted cationic species. γ is the ion activity coefficient of the subscripted cationic species and K is the Na⁺-Ca⁺⁺ equilibrium-exchange constant.

The ion activity coefficient, γ_j , of ion species j in solution can be approximated from an extension of the Debye-Hückel theory (Glasstone, 1946):

$$-\log \gamma_j = \frac{0.509Z_j^2 u^{\frac{1}{2}}}{1+u^{\frac{1}{2}}} \qquad [8]$$

where Z_j is the valence of the ion species j. The ionic strength, u, is defined by:

$$u = \frac{1}{2} \sum_{i=1}^{n} C_{i} Z_{i}^{2}$$
 [9]

where n is the number of ion species in the solution, and C_i and Z_i are the concentration and valence, respectively, of ion species *i*.

Let y be the moles of Na⁺ per gm of soil that go into solution or are adsorbed, and b_{Ca} and b_{Na} be the moles per liter of Ca⁺⁺ and Na⁺ in the solution phase. Also let B_{Ca} , B_{Mg} , and B_{Na} be the moles per gm adsorbed on the soilHILGARDIA • Vol. 38, No. 9 • June, 1967

exchange complex. Now, if β is the ratio of gm of soil to liters of solution, then the change in relative composition of Ca⁺⁺, Mg⁺⁺, and Na⁺ from the interaction of solution and adsorbed phases is:

$$E_{\rm Ca} = B_{\rm Ca} + y \qquad [10]$$

$$E_{\mathrm{Na}} = B_{\mathrm{Na}} - 2y \qquad [11]$$

$$E_{\rm Mg} = B_{\rm Mg} \qquad [12]$$

$$C_{\rm Ca} = b_{\rm Ca} - \beta y \qquad [13]$$

$$C_{\mathrm{Na}} = b_{\mathrm{Na}} + 2\beta y \qquad [14]$$

Combining equations [10], [11], [12], [13], and [14] with equation [7] results in the 4th-power equation:

$$-[2\beta^{2}] y^{4} + [(4\beta K \gamma_{Ca}/\gamma_{Na}^{2}) - 2\beta(b_{Na} + \beta B_{Ca}) + 4\beta^{2}(B_{Na} + 1.5B_{Ca} + 1.5B_{Mg}] y^{3} + [4\beta(B_{Na} + 1.5B_{Ca} + 1.5B_{Mg}] (b_{Na} + \beta B_{Ca}) - 0.5b_{Na}(b_{Na} + 4\beta B_{Ca}) - 4K \gamma_{Ca}/\gamma_{Na}^{2}(\beta B_{Na} + b_{Ca})] y^{2} + [(K \gamma_{Ca}/\gamma_{Na}^{2}\beta B_{Na}^{2}) + (4K \gamma_{Ca}/\gamma_{Na}^{2} B_{Na} + 1.5B_{Ca} + 1.5B_{Mg}) (b_{Na} + 4\beta B_{Ca}) - (0.5b_{Na}^{2} B_{Ca})] y + [b_{Na}^{2} b_{Ca} (B_{Na} + 1.5B_{Ca} + 1.5B_{Mg}) (b_{Na} + 4\beta B_{Ca}) - (0.5b_{Na}^{2} B_{Ca})] y + [b_{Na}^{2} b_{Ca} (B_{Na} + 1.5B_{Ca} + 1.5B_{Mg}) - (K\gamma_{Ca}/\gamma_{Na}^{2} B_{Na}^{2} b_{Ca})] = 0$$
 [15]

The equilibrium distribution of Ca⁺⁺, Mg⁺⁺, and Na⁺ between the exchanger phase and solution phase may be solved with equation [15]. For the case of Na⁺-Mg⁺⁺ exchange, a similar solution to equation [7] can be made by substituting Mg⁺⁺ for Ca⁺⁺.

In addition to cation exchange, precipitation and solubilization of gypsum and lime further modify the ion balance in soil solutions and the soil-exchange complex. The solubility of $CaSO_4 \cdot 2H_2O$ is adequately described by the solubility product constant concept found in textbooks (e.g., Glasstone, 1946). Carbonate salts of Ca⁺⁺ and Mg⁺⁺ have not been considered in the computer program to date. The solubility product constant for gypsum $K_{\rm CaSO4}$, is defined as:

$$K_{\text{CaSO}_{\star}} = C_{\text{Ca}}C_{\text{SO}_{\star}}\gamma^2 \qquad [16]$$

where $C_{\rm Ca}$ and $C_{\rm So4}$ are the equilibrium concentrations of subscripted ion species and γ is the mean activity coefficient. Let x be the moles per liter of Ca⁺⁺ and SO₄ = that dissolve or precipitate, and $C^o_{\rm Ca}$ and $C^o_{\rm So4}$ be the initial molar concentrations of Ca⁺⁺ and SO₄⁼. Then the change in relative composition of Ca⁺⁺ and SO₄⁼ is:

$$C_{\rm Ca} = C^o_{\rm Ca} + x \qquad [17]$$

$$C_{\mathrm{SO}_{\star}} = C^{o}_{\mathrm{SO}_{\star}} + x \qquad [18]$$

Combining equations [17] and [18] with equation [16] leads to:

$$x^{2} + (C_{Ca}^{o} + C_{SO_{*}}^{o}) x + (C_{Ca}^{o}C_{SO_{*}}^{o} [19] - K_{CaSO_{*}}/\gamma^{2}) = 0$$

In addition, the $CaSO_4-Ca^{++}$, $SO_4^{=-}$ H₂O system involves the formation of undissociated $CaSO_4$. The dissociation constant, $K_{[CaSO_4]}$, of ion pair $CaSO_4$ is defined as:

$$K_{\text{[CaSO_*]}} = \frac{C_{\text{Ca}}C_{\text{SO}_*}\gamma^2}{C_{\text{CaSO}_*}\gamma} \qquad [20]$$

where C_{CaSO4} is the molar concentration of the ion pair and γ for the ion pair is taken at unity.

Let x be the moles per liter of Ca⁺⁺ and SO₄⁼ which form undissociated CaSO₄. If the initial concentrations of Ca⁺⁺, SO₄⁼, and CaSO₄ are C°_{Ca} , C°_{SO4} , and $C^{\circ}_{CaSO_4}$, respectively, then the change in concentrations will be:

$$C_{\rm Ca} = C^o_{\rm Ca} - x \qquad [21]$$

$$C_{\rm SO_{\star}} = C^{o}_{\rm SO_{\star}} - x \qquad [22]$$

$$C_{\text{CaSO}_{\star}} = C^{o}_{\text{CaSO}_{\star}} + x \qquad [23]$$

When equations [21], [22], and [23] are combined with equation [20], rearrangement yields:

$$\gamma^{2}x^{2} - (\gamma^{2} C_{\text{Ca}}^{\circ} + \gamma^{2}C_{\text{SO}}^{\circ} + K_{[\text{CaSO}_{4}]})x$$
$$+ (\gamma^{2}C_{\text{Ca}}^{\circ}C_{\text{SO}}^{\circ} - K_{[\text{CaSO}_{4}]}C_{\text{CaSO}_{4}}^{\circ}) = 0$$
^[24]

Assuming ion activities to be adequately defined by equation [8], then the equilibrium concentrations of ion species in the solution and adsorbed phases can be calculated by utilizing equations [6], [15], [19], and [24] for the multiphase system containing soil, soil solution, and $CaSO_4 \cdot 2H_2O$.

PROCEDURE

Extensive chemical analyses on substrata materials have been reported by Doneen (see first paper in this series). The 1:1 extract method of determining soluble ions was employed. Since some of these substrata samples contained gypsum, an error in estimating solublesalt content was possible due to the dissolution of gypsum. Thus a method of converting soil-salt data obtained from 1:1 extract moisture-content samples to actual field conditions is desirable. A computer program was therefore developed for IBM 7040 Data Processing System to convert the equilibrium concentrations of solutes, adsorbed cations, and gypsum from a soil sample at a given moisture content to concentrations at another moisture content.

The source statement for this program is given on pages 312–313, and a diagram on the flow of computation is presented in figure 1.

Initial molar concentrations from a 1:1 extract are read by statement number 21. Cations Ca⁺⁺, Mg⁺⁺, and Na⁺ are represented by A, F, and S, and anions $SO_4^{=}$, Cl⁻, and HCO₃⁻ are denoted by G, H, and C, respectively. E5, C5, SA5, and XX5 refer to exchangeable Ca⁺⁺, Mg⁺⁺, Na⁺ and solid-phase CaSO₄ • 2H₂O, respectively, in moles per gm substrata material.

Exchangeable Na⁺ and Mg⁺⁺ were determined by the ammonium acetate method. It was assumed that lime present in the substrata material was in the form of CaCO₃ and that neither nesquehonite (MgCO₃) nor dolomite (Ca $Mg(CO_3)_2$) was present. From this assumption it was possible to estimate the amount of exchangeable Ca⁺⁺ from the difference between cation-exchange capacity and the sum of exchangeable Na⁺ and Mg⁺⁺. Only trace amounts of exchangeable K⁺ were present in substrata samples.

The equilibrium exchange constant for $Ca^{++} - Mg^{++}$ and $Na^+ - Ca^{++}$ are denoted by D and DA, while the exchange constant for Na⁺ and Mg⁺⁺ is computed internally from D and DA. Values of 0.7 and 7.1, determined on a Yolo soil, were assigned to D and DA, respectively, in the absence of the real constants for the substrata material. B is the gm of substrata material per liter of soil solution; PW1 is initial moisture content (100 per cent); and PW2 is final moisture content (field moisture content).

The factor PW, under statement number 202, is the ratio of initial to final moisture content. Since the present program does not take into consideration the calcite system, the initial HCO_3^- concentration is held constant rather than being increased by a factor of PW. A correction term on Ca⁺⁺ concentration is necessary, since 2 moles of HCO_3^- are required in the formation of each mole of CaCO₃.³ The correction term, $-0.5(\text{HCO}_3^{-}\cdot\text{PW}-\text{HCO}_3^{-})$, decreases the concentration of Ca⁺⁺ in accordance with the stoichiometric relationship if HCO₃⁻ is to be held constant. The procedure of keeping HCO₃⁻ con- $\overline{^{3}\operatorname{Ca^{++}}+2\operatorname{HCO}_{3}} \rightleftharpoons \operatorname{CaCO}_{3} \downarrow + \operatorname{CO}_{2} \uparrow + \operatorname{H}_{2}\operatorname{O}.$



Fig. 1. Flow diagram showing scheme of computation for predicting the equilibrium salt concentrations in soil-water systems.

centrations constant is a reasonable approximation due to the very limited solubility of $CaCO_3$.

Solutes other than HCO_3^- and Ca^{++} were increased from the initial value by a factor of PW. Exchangeable Ca^{++} , Mg^{++} , Na⁺, and $CaSO_4 \cdot 2H_2O$ are redefined to Fortran IV language as ET, CT, SAT, and XXT, respectively.

The equilibrium cycle, developed by Dutt (1962) and Dutt and Doneen (1963), consisting of statements 24 through 52 accounts for the changes in ion balance discussed previously under theoretical considerations. The changes in Ca⁺⁺, SO₄⁼, undissociated CaSO₄, and solid-phase CaSO₄ · 2H₂O are computed in statements 24 to 44 (fig. 1), including the branches. Values of 2.4×10^{-5} (Latimer, 1952) and 4.9×10^{-3} (Bell and George, 1953), were assigned to K_{CaSO4} and $K_{\text{[CaSO4]}}$, respectively, in solving equations [19] and [24]. Because of the complexity in the flow of computation it is suggested that figure 1 be consulted frequently.

The presence or absence of gypsum (XXT) at PW1 is considered at statement 24. If XXT was initially present in the system, the flow of computation proceeds to statement 26, where equation [19] is solved for x. Symbol U represents $u^{\frac{1}{2}}$ in equations [9] and [8], while EX is equivalent to $1/\gamma^2$. BB and CC are the coefficients b and c in the quadratic expression, equation [19]. CASO is the initial concentration of $CaSO_4$ ion pair, and CAS1 is the calculated concentration of additional ion pair that should be present in saturated gypsum solutions. DEL is defined as the difference between soil gypsum present at PW1 and formation of undissociated $CaSO_4$ at PW2. When DEL is equal to or greater than x of equation [19], branch statement 28 is taken where A and G are increased by xamounts and initial XXT is reduced by x as well as by CAS1. CASO in saturated gypsum solution has a value of $K_{\text{CaSO4}}/K_{\text{[CaSO4]}}$ or 4.9×10^{-3} moles per liter. The next step for this route is ion exchange, which will be considered after the different routes of gypsum solubility and undissociated CaSO₄ are discussed.

Branch statement 27 is taken when DEL is less than x. Since x calculated under statement 26 is greater than initial XXT for this route, the changes in A and G are limited to an amount equivalent to XXT, a solution unsaturated with respect to gypsum. Both

Tanji et al.: Computer Method for Predicting Salt in Soils

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XXT and CAS1 are reduced to zero, and new values of u and γ are calculated. Symbols AA, BB, and CC in statements 27 and 7 refer to coefficients a, b, and c in equation [24] which computes CaSO₄ ion pair. X1, which is xin equation [24], is calculated, and initial CASO is then changed by X1 while A and G are reduced by X1. CASO at this stage of computation has a value less than 4.9×10^{-3} moles per liter in contrast to CASO under statement 28. CASO in solutions unsaturated with respect to gypsum is defined as $a_{Ca}a_{SO4}/K_{[CaSO4]}$.

An alternative scheme of computation under statement 24, branch statement 4, is used when the soil is free of gypsum at PW1. U and AA are calculated from the first approximation on concentration of solutes-statement 202 followed by a test for XXT at PW2, equation [16]. If the activity product of Ca^{++} and SO_4^{-} exceeds $K_{\rm CaSO4}$, 2.4×10^{-5} , statement 26 is executed. When the solution is unsaturated with respect to gypsum, the computation proceeds to statement 18. A test is made successively for the presence or absence of Ca^{++} , $SO_4^{=}$, and ion pair $CaSO_4$ with statements 18, 6, and 1, respectively. If the soil solution is free of these constituents, the computation proceeds directly to ion-exchange considerations, statement 44. The flow of calculation proceeds to statement 7 if G and A or CASO is present in the system, and new values are computed for CASO, A, and G.

The exchange reactions between solution and adsorbed cations are calculated by statements 44 through 3 (fig. 1).The exchange between Na⁺ – Ca⁺⁺, equation [5], is solved by computations made through statement 46, while Na⁺– Mg⁺⁺ is computed through statement 45. The exchange between Mg⁺⁺ and Ca⁺⁺ is calculated from statements 13 to 3 by applying equation [6]. The Ca⁺⁺ and Mg⁺⁺ concentrations are compared at statement 44. If A is equal to or greater than F, branch statement 46 is taken where IJ is a directional control symbol. This route considers exchange between Na⁺ and Ca⁺⁺. If A is less than F, statement 45 is used to set up computations for Na⁺-Mg⁺⁺ exchange. Fortran symbols for Ca⁺⁺ are replaced by Mg^{++} in statement 45, and equation [15] is evaluated by statements 5 through 17. The 4th-power equation is solved for Z by Newton's approximation method. A small value, 10⁻⁶, is assigned to Z initially, and a closer approximation to the true root is computed by iteration. Fortran symbols AA, BB, CC, DD, and EE, refer to the coefficients a, b, c, d, and e, respectively, in the 4th-degree polynomial equation. EX is defined as the ratio of γ_{Ca} to γ^2_{Na} , equation [15], and AAA denotes the values enclosed in parentheses in the left-hand denominator of equation [7]. At statement 15, the first ZZ and ZZZ are defined as well as the second ZZ. An approximate solution to equation [15] is given by Z, and closer approximations to the true root are obtained by evaluating ZZ successively until it is within $\pm 10^{-3}$.

After Z is computed, the concentrations of A, S, ET, and SAT are altered by Z changes for Na⁺–Ca⁺⁺ exchange–– equations [13], [14], [10], and [11], respectively. If statement 45 (Na⁺- Mg^{++} exchange) is taken, the concentrations of F, S, CT, and SAT are altered by Z. A "conditional go to" statement is encountered next. If the flow of computation was through statement 46, the next execution is statement 13. On the other hand, if Na⁺-Mg⁺⁺ exchange was considered (statement 45), the route shifts to statement 17 where the Ca⁺⁺ symbols revert to their original form. The exchange between Ca⁺⁺ and Mg⁺⁺ is considered next. Symbols AA, BB, and CC refer to coefficients a, b, and c, respectively, in equation [6]. Y is the solution to the quadratic expression. However if (1.0–D) is zero, i.e., coefficient a is zero, the solution of Y reduces to Y = -c/b (statement 2). In statement 3, Y changes are made on the concentrations of A, F, ET, and CT equations [4], [5], [2], and [3], respectively.

A series of approximations are then made in which the computed Ca⁺⁺ concentration, A, after consideration of equations [19], [24], [15], and [6], is compared with Ca⁺⁺ concentration, A1, at the beginning of the equilibrium cycle. Computation in the equilibrium cycle proceeds from statements 3 to 24 and back to 3 until the difference between A and A1, i.e., DEL, is equal to or greater than 10^{-5} M. The flow of computation then proceeds to statement 48 where another test is made on DEL. Calculations are made in the loop formed by statements 48 to 24 and back to 48 until DEL is equal to or less than 10⁻⁵ M. The difference in calculated

The conversion of 1:1 extract data of five substrata samples to field-moisture data is presented as an illustration. The five substrata samples were selected from the Appendix tables of the first paper in this series, and differ in soluble-salt content, cation-exchange capacity, gypsum content, and fieldmoisture content.

The initial solute concentrations as found in a 1:1 extract represent the soluble salts present in the material at a moisture content of 100 per cent. Cation-exchange capacity and exchangeable cation determinations are based on dry weight of sample; however, total extractable Na⁺ and Mg⁺⁺ were corrected for soluble Na⁺ and Mg⁺⁺, obtained from the 1:1 extract. Therefore, exchangeable Na⁺ and Mg⁺⁺ values were dependent, to some degree, upon the extraction moisture content. The reported gypsum content is the amount present at a moisture content of 100 per cent and is expressed as dry weight of sample.

Ca⁺⁺ concentration, after successive approximations, is at this point within \pm 10⁻⁵ M. In a like manner A is compared with A2 and A3. A2 is the concentration of Ca⁺⁺ after consideration of equations [19] and [24], and A3 is the concentration after consideration of equations [19], [24], and [15]. Thus a series of successive approximations are made from statements 3 to 52 until the difference in Ca⁺⁺ concentrations before and after equilibrium computation is within \pm 10⁻⁵ M.

Finally, the theoretical equilibrium salt concentrations in the soil at a new moisture content are printed—statement 8. Approximately 5 to 10 iterations are made at statement 52 for each sample. The IBM 7040 computer system requires 1 minute 20 seconds to calculate 15 samples.

RESULTS

Thus when the moisture content is other than 100 per cent, changes in concentration of solutes, gypsum, and exchangeable cations are expected. Cation-exchange capacity and $HCO_3^$ concentration are the only fixed values in the computation.

The data presented at the lower moisture content (table 1) represent the predicted values based on theoretical considerations and assumptions presented earlier. On the assumption that Cl⁻ does not participate in solubility or adsorption reactions, the predicted Cl⁻ concentrations are equivalent to the initial concentration times the factor PW.

Solid-phase $CaSO_4 \cdot 2H_2O$ in samples 3–10 and 6–140 increased in concentration with change in moisture contents. Sample 8–60, which was initially nongypsiferous, had trace amounts of gypsum at field-moisture content. Samples 3–55 and 3–190 were free of gypsum but contained CaSO₄ ion pair. Solutions saturated with respect to gyp-

TABLE 1	PREDICTED CONCENTRATIONS OF SOLUTES, UNDISSOCIATED CaSO ₄ , SOLID-PHASE CaSO ₄ , 2H ₂ O, AND EXCHANGEABLE CATIONS AT FIELD-MOISTURE CONTENT FROM 1:1 EXTRACT ANALYSES
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FROM 1:1 EXTRACT ANALYSES	Exchangeable	$= [CasO_4]^* \qquad Ca^{++} \qquad Mg^{++} \qquad Na^+ \qquad Oppound \\ \\ \end{bmatrix}$	m.e. per 100 gm 100 gm 100 gm	0.0 19.8 0.6 2.1 1.5	9.8 18.7 0.9 2.9 2.9	0.0 12.3 7.8 4.6 31.9	9.8 10.7 8.3 5.7 35.8	0.0 3.7 3.7 0.9 0.0	9.8 3.1 3.7 1.5 0.7	0.0 6.2 4.7 2.3 0.0	8.7 6.6 4.3 2.3 0.0	0.0 17.4 17.8 2.5 0.0	1.9 17.4 17.7 2.6 0.0	
ICENTRATIONS OF SOLUTES, UNDISSOCIATED ABLE CATIONS AT FIELD-MOISTURE CONTEN		CI- HCC	-	22.8 1.0	87.7 1.(6.8 0.0	28.3 0.6	3.2 0.5	32.0 0.5	22.4 0.0	02.0 0.(3.2 1.1	8.4 1.4	
	Soluble	SO4-	m.e. per liter	24.0	29.4	64.0	103.0	18.0	8.76	13.0	50.4 11	8.2	19.7	-
		Na+		25.2	66.1	33.9	94.4	14.8	84.4	19.7	90.5	7.6	17.6	
		Mg ⁺⁺		4.2	3.3	9.0	18.6	2.4	30.2	3.0	30.0	1.7	7.2	
		Ca^{++}		17.5	46.6	27.8	16.9	4.7	18.2	13.0	32.0	3.2	4.9	
TED COP	Water content		per cent	100	26	100	24	100	10	100	22	100	38	-
REDICI ND EX(Site	depth	ft.	10		140		60		55		190		
P	Site	no.		3		66		8		3		3		

* Undissociated.

sum theoretically contain 9.8 m.e. per liter of undissociated $CaSO_4$. The presence of 8.7 m.e. per liter of this complex in sample 3–55 indicates that its solution was very near to gypsum saturation at field-moisture content. Under standard analytical procedures for Ca^{++} and $SO_4^{=}$ the ion pair $CaSO_4$ is not differentiated from ionic forms of Ca^{++} and $SO_4^{=}$. Hence the $CaSO_4$ ion pair is normally included in standard

The equilibrium concentrations computed by the method outlined are only as reliable as the chemical data programmed and the validity of the underlying assumptions and theoretical considerations of the computation. It is recognized that the chemical properties of a soil-soil solution system, particularly in the presence of gypsum, are not adequately described by present analytical methods and techniques.

Additional comments on the description of soil-water systems, which has been extensively treated by Babcock (1963), are in order. An assumption is made on the calculation of ionic activities in a soil-soil solution system by equations [8] and [9]. It is assumed that the liquid phase in this system can be described by an extract on the basis that a discrete solution phase and a discrete exchanger phase exist in the system. The concentrations in the extract are then considered to be the concentrations in the soil solution, and concentration gradients around charged soil colloids, described by the Guoy (1910) diffuse double-layer model, are neglected. Membrane potentials at the filtering interface and their effect on the solutes in extracts are also ignored. Thus the use of the Debye-Hückel theory in computing activity coefficients considers only the ion-ion interactions within the solution phase.

At lower moisture contents, where a large fraction of the soil water is as-

salinity determinations, with the exception of the conductance method.

The concentrations of all ion species, except HCO_3^- , are shown to have been altered due to a change in moisture content. With a reduction in water content, solute concentrations increase, but the ion balance is simultaneously modified by cation exchange, formation of undissociated CaSO₄, and precipitation of solid-phase CaSO₄ · 2H₂O.

DISCUSSION

sociated with soil colloids (Low, 1961), the computed equilibrium values probably will vary from measured concentrations. However, in the range of field moisture contents, from saturation to 15 atmosphere moisture percentages, the activity of ions was found to be of the same order of magnitude as those approximated by equation [8] (Dutt and Anderson, 1965). Moreover, calculated data have been shown by Dutt (1962) and Dutt and Doneen (1963)to be in reasonable agreement with experimental data for multiphase systems consisting of soil, soil solution, and gypsum.

Secondary reactions that may occur in a soil-soil solution system have not been fully incorporated into the equilibrium cycle. Processes that would probably be included if the program were to treat the general case are formation of other complex ions and salts, solubility of carbonate and phosphate salts, and sorption, among others. The computer method of predicting equilibrium salt concentrations is applicable only to soils with ion-exchange properties adequately described by equations [1] and [7]. Thus for any system that involves those processes and conditions, the predicted concentrations may deviate from experimental data. These reactions, with the exception of carbonate salts, are, however, of secondary magnitude, and estimates made by this computer program can be considered as first-order approximations. Strictly speaking, the utility of the program is limited to a soil-water system that is dominated by Cl^- and SO_4^- salts.

This computer program has been

SUMMARY

A computer program has been devised to calculate the theoretical equilibrium concentration of solutes, undissociated $CaSO_4$, solid-phase $CaSO_4 \cdot 2H_2O$, and exchangeable cations at any given soil-moisture content from extract data obtained initially at a different moisture content.

The calculations are based on ionic activities, solubility product constant

tested on five agricultural soil types with substantial agreement between computed and observed values. The results have been published elsewhere (Paul, Tanji, and Anderson, 1966). More recently the ion pair $MgSO_4$ has been included in the equilibrium cycle.

of $CaSO_4 \cdot 2H_2O$, dissociation constant of $CaSO_4$, and cation-exchange equations.

The computer program, although limited in scope at this stage, may be extended to include additional chemical reactions and processes occurring in soil-water systems, and may eventually be applicable for wider use.

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318

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