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CALCIUM CARBONATE EQUILIBRIA IN SOILS

Technical Completion Report

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TECHNICAL COMPLETION REPORT
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Abstract

A thorough understanding of calcium carbonate equilibria is essential to the development of computer models capable of predicting the effect of irrigation management on water quality degradation in irrigated areas.

The objectives of this research were: 1) to develop a model capable of describing calcium carbonate equilibria in soil solutions, and 2) to test the model against data for calcareous soils equilibrated with waters of various compositions.

A chemical model developed previously and capable of describing calcium carbonate equilibria in aqueous systems open to the atmosphere was applied to soil systems. Published data for large lysimeters irrigated repeatedly with waters characteristic of Western United States rivers were used to verify the model.

The model is chemically sound and compares favorably with a more empirical computer model developed by the U.S. Salinity Laboratory which adequately predicts water quality changes as a function of irrigation management. Lacking further refinement of the models to include additional soil solid phases, the Salinity Laboratory model is preferable to the model based on pure calcite as the dominant CaCO_3 form in soils.

Keywords: Calcium carbonate equilibria, Computer models, Irrigation return flow, Water quality degradation.

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Calcium Carbonate Equilibria in Soils

An inescapable result of irrigated agriculture is the concentration of the soil solution (irrigation water) due to evapotranspiration. As the soil solution is concentrated, various salt species may precipitate beginning usually with the alkaline-earth carbonates, e.g. CaCO_3 , $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, or $\text{CaMg}(\text{CO}_3)_2$. The concentrations of dissolved salt in equilibrium with precipitated carbonates are very low and normally are not a significant fraction of the dissolved salts in soils. However, the quantities of salt precipitated as carbonates are often a major fraction of the total salt initially present in the system, and thus carbonate precipitation and dissolution become important factors in irrigation management design (McNeal, 1974).

The solubility of salts such as the carbonates can be described in terms of the basic chemical principles of solubility products, ionic strength, and ion-pairing. For example, O'Connor and Cadena (1975) developed a model incorporating these chemical principles which adequately described CaCO_3 equilibria in aqueous solutions open to the atmosphere. Unfortunately, the use of pure solution chemistry models to describe salt precipitation from soil solutions is not straightforward. Soil solutions contain complex mixtures of salts, so the chemical species being precipitated can vary with salt concentration, as well as with changes in temperature (Kramer, 1964). One serious limitation to the solubility product principle as applied to soils is the uncertainty regarding the exact form of solid

phase that precipitates. One solid phase for which this uncertainty is reportedly most serious is calcium carbonate. Calcium carbonate may exist as calcite, vaterite, aragonate, or as hydrated calcium carbonate (McNeal, 1974). Each polymorphic form has a different solubility and although calcite is the most stable form, transformations from other forms to calcite are apparently very slow. Thus, the solubility product of calcite rarely describes the solubility of calcium carbonate in soils (McNeal, 1974).

Some authors, although cognizant of the possibility of more soluble form of CaCO_3 in soils, have suggested that the apparent greater solubility of CaCO_3 was really an expression of other factors affecting CaCO_3 solubility (O'Connor and Cadena, 1975; J. D. Oster, personal communication). Such factors as partial pressure of CO_2 (P_{CO_2}) ionic strength, and ion-pair formation may greatly increase CaCO_3 solubility and give the impression of a controlling solid phase with greater solubility than pure calcite. O'Connor and Cadena (1975) developed a model that accounted for P_{CO_2} , ionic strength, and ion-pairing in aqueous (pure) solutions controlled by pure calcite. The purpose of this research was to apply the model to soil systems. Predictions of the soil solution compositions were then compared with drainage water data from large lysimeters equilibrated with waters characteristic of various rivers in the Western United States.

PROCEDURES

Chemical Model

Several attempts have been made to model the precipitation of CaCO_3 in soils. Considerable success has been made in predicting variations in salt concentrations with depth in soil profiles; despite the uncertainties described above (Dutt and Tangi, 1962; Oster and McNeal, 1971; Oster and Rhoades, 1975).

Chemical theory used in this study has been previously detailed (O'Connor and Cadena, 1975). The computer program utilized was graciously supplied by workers at the U.S. Salinity Laboratory in Riverside, California, and has been described by Oster and Rhoades (1975).

The model as originally developed by O'Connor and Cadena (1975) assumed CaCO_3 (calcite) as the controlling solid phase. Input included the solution concentrations of all ions present in the soil system and P_{CO_2} . Equations were included to calculate ionic strength, activity coefficients for each ion, and all ion-pairs thought to be present. When the model was applied to soil systems, additional solid phases were included ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and MgCO_3). All solid phases were allowed to dissolve or precipitate as dictated by their respective solubility products. Calculations proceeded in a cyclic manner until ionic activities differed by less than 0.1% between iterations, and until electrical neutrality (sum of cations = sum of anions) was attained.

Drainage Water Data

Data used to test the predictive model were taken from Rhoades, et al (1973). The data represent the compositions of percolated drainage waters

resulting from the use of synthesized river waters of the western USA in lysimeters cropped to alfalfa. The lysimeters contained calcareous Pachappa sandy loam soil equilibrated with the various irrigation waters at leaching fractions of 0.1, 0.2, and 0.3 over a period of two years. These data were selected because of the care with which they were obtained and the detailed soil CO_2 data available for each lysimeter. Much of the similar data available in the literature does not include P_{CO_2} information which is critical to the success of the chemical model. Two of the synthesized river waters (Gila and Pecos) are similar to river waters common to New Mexico, the Rio Grande, and Pecos Rivers, respectively. Chemical characteristics of the irrigation waters are given in Table 1.

RESULTS AND DISCUSSION

Predicted and observed compositions of drainage waters from the calcareous lysimeters are given in Table 2. Two sets of predicted values are presented: data calculated by Method A represent values predicted by the model of Oster and Rhoades (1975), whereas Method B represents values predicted by the author's model. The main difference in the two models is the assumption of the solubility product describing CaCO_3 in soils. Oster and Rhoades (1975) assume a solubility product (Ksp) indicative of aragonite ($K_{\text{sp}} = 6.46 \times 10^{-9}$), whereas Method B assumes a value of Ksp indicative of pure calcite ($K_{\text{sp}} = 3.29 \times 10^{-9}$) (O'Connor and Cadena, 1975). Conceptually, Method A assumes a form (or combination of forms) of CaCO_3 more soluble than pure calcite to precipitate in soil solutions with an apparent solubility indicative of aragonite. Method B assumes that the solubility product found in pure calcite solutions can be applied to soil systems if

Table 1. Composition of river waters used in lysimeter study.

River	EC*	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	SAR**
	mmhos/cm	-----			-----			-----	-----
					meq/l				
Gila	3.14	7.22	5.88	18.55	0.09	3.17	20.17	8.48	7.3
Pecos	3.26	16.98	9.07	11.38	0.08	3.11	12.13	22.39	3.2

* EC = electrical conductivity

** SAR = $Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$ where all concentrations are expressed in meq/l.

Table 2. Predicted and observed drainage water compositions (meq/l) of a calcareous soil with P_{CO2} = 0.13 atm. (See text for explanation of abbreviations).

River	LF	Method	TCA	TMG	TNA	SAR	EC	TSO ₄	TALK	LIME	GYP	MGCO ₃
Gila	0.30	A	28.2	19.6	61.8	12.6	10.2	28.3	13.0	-4.2	0	0
		B	24.9	19.6	61.8	13.1	9.9	28.3	9.6	-0.8	0	0
		Observed	31.4	19.1	70.4	14.0	10.6	31.3	17.3	-	-	-
Gila	0.20	A	36.5	29.4	92.8	16.2	14.6	42.4	13.1	-0.4	0	0
		B	33.0	29.4	92.8	16.6	14.4	42.4	9.6	3.1	0	0
		Observed	34.8	20.9	84.6	16.0	12.2	37.0	20.6	-	-	-
Gila	0.10	A	48.3	58.8	185.5	25.4	25.9	69.2	14.2	8.3	15.6	0
		B	46.3	58.8	185.5	25.6	25.8	71.2	10.1	12.3	13.6	0
		Observed	59.6	36.5	151.9	21.9	20.6	65.4	20.6	-	-	-
Pecos	0.30	A	36.6	30.2	37.9	6.6	8.5	51.1	12.2	-3.5	23.5	0
		B	34.9	30.2	37.9	6.7	8.4	52.8	8.8	-0.1	21.8	0
		Observed	42.5	30.5	36.4	6.0	8.3	59.5	12.4	-	-	-
Pecos	0.20	A	36.3	45.4	56.9	8.9	11.3	62.3	13.4	-1.0	49.6	0
		B	34.6	45.4	56.9	9.0	11.1	64.4	9.6	2.7	47.6	0
		Observed	39.4	37.5	47.3	7.6	9.6	62.0	13.2	-	-	-
Pecos	0.10	A	37.2	76.8	113.8	15.1	19.0	84.5	15.4	-6.8	139.4	14.0
		B	34.0	90.7	113.8	14.4	19.6	97.8	11.7	9.8	126.1	0
		Observed	53.8	75.9	106.8	13.3	17.7	94.9	22.3	-	-	-

other factors, e.g., ionic strength, ion-pairs, etc. are adequately considered. Values of dissociation constants for some ion-pairs also differ slightly in Methods A and B yielding more ion-pairing in Method B than in Method A. However, data not presented indicate that differences in ion-pair consideration are of very minor concern when comparing solution compositions calculated by the two methods.

There were only small differences in soil solution compositions calculated by either Method A or B (Table 2). Values of total magnesium (TMG), total sodium (TNA), total potassium (TK), and total sulfate (TSO_4) calculated by either method were very similar. Additionally, calculated values (by either method) and observed data for the above ions agreed reasonably well. This agreement was especially good for the important water quality criteria of SAR and EC. Apparently, although the calculated ionic compositions did not always agree with observed values, the combination of various ionic constituents resulted in reasonable SAR and EC values. In terms of SAR and EC of irrigation drainage water then, a chemical model assuming calcite as the form of CaCO_3 in soils may be used when other factors such as ionic strength and ion-pairing are adequately considered (Method B).

The largest discrepancies between predicted and observed results, and between methods of calculations are in values for total calcium (TCA) and total bicarbonate plus carbonate (TAlk). Method B resulted in consistently lower TCA and TAlk values than Method A. These lower values would be expected on the basis of a smaller assumed solubility product for CaCO_3 in Method B (3.29×10^{-9} vs. 6.46×10^{-9}). Method A also resulted in better predictions of the observed data than Method B which would seem to justify

using the larger (apparent) solubility product for CaCO_3 . Oster and Rhoades (1975) however, also reported using a K_{sp} for CaCO_3 even greater than that utilized in Method A ($K_{sp} = 15.4 \times 10^{-9}$ vs. 6.46×10^{-9}) and found no significant improvement in agreement between predicted and observed results. Thus, although some of the discrepancy between predicted and observed results can be eliminated by assuming an apparent solubility of CaCO_3 indicative of aragonite (Method A) rather than calcite (Method B), other factors not considered in either model must be operative. Rhoades and Oster (1975) have suggested, for example, that at $P_{\text{CO}_2} > 9 \times 10^{-4}$ atm. some soil silicates are more soluble than soil CaCO_3 and may thus increase TCA and TALK upon dissolution. Further refinement of the model will have to await development of equations for these, and possibly other soil solid phases. McNeal (1974) has also reasoned that the effects of variation in CaCO_3 solubility should not be of major importance in predicting salt concentrations with depth in soil profiles since the level of dissolved ions in equilibrium with carbonate minerals would normally make up only a small proportion of the total ions in a saline soil.

The value of K_{sp} assumed for CaCO_3 is, of course, of major importance in calculating the amount of CaCO_3 that will dissolve or precipitate as irrigation water passes through a soil. The effect of K_{sp} on CaCO_3 precipitation is shown in Table 2 under the heading LIME. Negative values indicate CaCO_3 dissolution; positive values, CaCO_3 precipitation. Method A (greater K_{sp}) consistently indicates more CaCO_3 dissolution or less precipitation than Method B. Precipitation or dissolution considerations are critical to the salt load of water leaving the soil profile. An excellent measure of the

salt load, however, is the EC of the drainage water which previously was shown to agree reasonably well between calculation methods and with observed data. Thus although Method A precipitates less (dissolves more) CaCO_3 than Method B, the method also precipitates more gypsum (GYP) than Method B resulting in similar total salt loads of the drainage water which are commensurate with observed values.

SUMMARY AND CONCLUSIONS

A chemical model developed previously and capable of describing CaCO_3 equilibria in aqueous solutions open to the atmosphere was modified to be applicable to soil systems. The model includes considerations of ionic strength and ion-pairing characteristic of soil systems and assumes calcite with $K_{sp} = 3.29 \times 10^{-9}$ as the form of CaCO_3 in calcareous soils.

The model was compared with a similar computer model developed by workers at the U.S. Salinity Laboratory which assumes an apparent K_{sp} of CaCO_3 indicative of aragonite ($K_{sp} = 6.46 \times 10^{-9}$). Predicted values from both models were compared with data collected in a lysimeter study using irrigation water similar to two New Mexico rivers.

Values predicted by the models were very similar and, in most cases, agreed reasonably well with observed data. The important water quality criteria, SAR and EC, predicted by either model agreed especially well with observed data.

The discrepancies between predicted and observed data are probably a result of a failure to include in either models additional soil solid phases active in controlling the composition of the soil solution. Further

refinement of the model is, therefore, necessary if exact prediction of each ionic constituent in the soil solution is desired. In the absence of such refinement, the Salinity Laboratory model with an assumed K_{sp} for CaCO_3 indicative of aragonite is preferable to a model based on pure calcite as the dominant CaCO_3 form.

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