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Sodic soil reclamation: Modelling and field study

Donald L. Suarez

USDA, ARS, George E. Brown, Jr. Salinity Laboratory, 450 W. Big Springs Road, Riverside, CA 92507, USA; email: dsuarez@ussl.ars.usda.gov

Abstract

Reclamation of sodic soils has traditionally been undertaken using calculation of gypsum or Ca requirement assuming 100% exchange efficiency and neglect of the contribution of calcium carbonate in the profile. The UNSATCHEM model is reviewed and then evaluated for its ability to predict field reclamation of a sodic saline soil. The 40-ha field site was initially at an electrical conductivity (EC) of 50 dS/m and a sodium absorption ratio (SAR) of 144 in the top 30 cm. After installation of a drainage system, 24 Mg/ha of gypsum was applied to a depth of 15 cm in the soil. Subsequently, 114 cm of water was applied by almost continuous ponding for 3 months. Model simulations were made based on infiltration of 70–80 cm of water, correcting for the estimated evaporation of 41 cm of water. These infiltration estimates are consistent with the good fit between the measured Cl concentrations after reclamation and the model predicted values after 70–80 cm of infiltrated water. Model predictions of EC and SAR after reclamation gave a satisfactory fit to the measured values. The effectiveness of mixing gypsum to various depths was evaluated in terms of the predicted SAR profiles. Alternative management practices of green manuring in presence of calcite were simulated and appeared feasible. In this instance it appears likely that the field could have been reclaimed either with less water or without the addition of gypsum.

Additional keywords: gypsum, leaching, salinity.

Introduction

Agricultural productivity in arid regions throughout the world is being threatened by various long-term trends. Increasing urban water demands in arid regions, due in part to increasing population, makes high quality water less available for irrigation. Water extraction in many arid regions is currently much greater than sustainable rates. In order for irrigation to expand or even maintain its existing level, new water supplies, of lower quality, will have to be utilised. This includes use of urban waste waters as well as presently under-utilised brackish waters. In addition to water constraints, there is a deteriorating land resource base. Over-irrigation, inadequate drainage, and other poor management practices have resulted in rapid rates of soil salinisation. Urbanisation also occurs in prime agricultural land, forcing agriculture into newer regions. A large increase in land reclamation efforts and improved management practices will have to be undertaken in order to maintain or increase the productivity of irrigated lands.

Reclamation of saline soils requires leaching of the soluble salts. The requirements for leaching are based on the salt tolerance of the crops to be grown. General guidelines are readily available to calculate the amount of water to be applied to achieve a certain reduction in salinity. For example, the amount of water required to leach a soil can be calculated by:

$$D_{iw} = D_s(\theta_v) \qquad (1)$$

where D_{iw} is the depth of the irrigation water to be applied, D_s is the depth of the soil to be leached, and θ_v is the volumetric water content of the soil after leaching. This relationship

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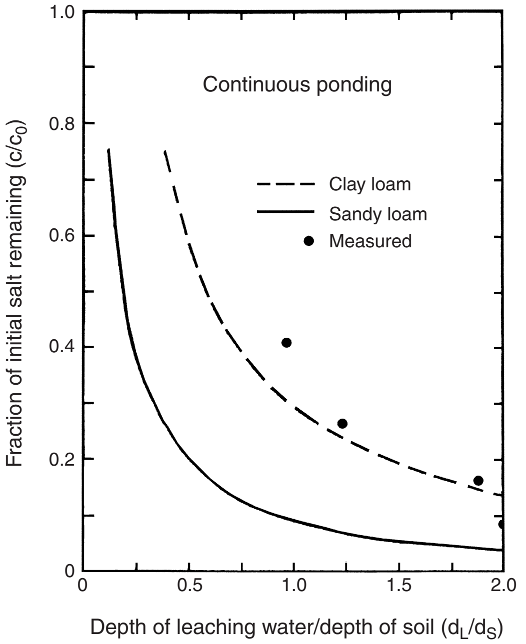

Fig. 1. Leaching recommendations of Hoffman (1980) and measured changes in salinity after leaching and reclamation.

assumes piston displacement (no macropore flow, no dispersion or convection, and no chemical interaction of the solute with the soil). Hoffman (1980) presented the empirical relationship:

$$\frac{C}{C_o} = \frac{k}{D/D_s} \tag{2}$$

where C is the salt concentration, C_o is the initial salt concentration, D is the depth of leaching water applied, D_s is the depth of the soil to be leached, and k is an empirical coefficient. This equation is based on fitting to measured leaching curves. As can be expected the k value is dependent on soil type. Hoffman (1980) observed that a value of 0.3 for clay soils and a value of 0.1 for sandy loam fitted the data examined adequately. The larger the k value, the more water is required for leaching. Clay soils may have more preferential flow due to cracks and bypass of water around aggregates, thus resulting in less efficient leaching of soils with elevated clay content. Shown in Fig. 1 are the leaching curves proposed by Hoffman (1980) for clay loam and sandy loam.

In contrast to leaching of saline soils, reclamation of saline-sodic and sodic soils requires consideration of chemical factors as well as water flow. The traditional approach has been to calculate the amendment requirement based on the amount of Ca needed to reduce the exchangeable Na percentage (ESP) in the soil to a specific level, typically to below 10 (US Salinity Laboratory Staff 1954). The general approach has been to calculate the gypsum requirement based directly on the quantity of Na to be exchanged, for example 1.23 Mg/ha for every mol_c/kg of Na to be exchanged. This calculation is based on the mass of Na to be exchanged, thus assuming quantitative replacement of the Na by Ca and that there are no other sources of Ca present in the solution; neither of these assumptions is valid. Consideration of exchange efficiency allows calculation (after Oster and Jayawardane 1998) from:

$$\mathrm{GR} = 0.00086\mathrm{F}\mathrm{D_s}\rho_\mathrm{b}(\mathrm{CEC})(\mathrm{ESP_i} - \mathrm{ESP_f}) \tag{3}$$

where GR, the gypsum requirement, is given in Mg/ha; D_s is the depth of the soil to be reclaimed (m); CEC is the cation exchange capacity in $\mathrm{mmol_c/kg}$; $\mathrm{ESP_i}$ is the initial ESP and $\mathrm{ESP_f}$ is the final desired ESP; ρ_b is the soil bulk density; and F is a Ca–Na exchange efficiency factor. Examination of cation exchange equations, such as:

$$\frac{\mathrm{Na}\,X}{\mathrm{Ca}\,X} = k_\mathrm{g}\frac{\left[\mathrm{Na}^+\right]}{\left[\mathrm{Ca}^{2+}\right]^{0.5}} \tag{4}$$

where k_g is the selectivity coefficient, demonstrates that unless Ca exchange selectivity is extremely high, significant quantities of Ca must remain in solution under saline conditions in order to exchange most of the Na. This unavoidable loss of Ca has been considered inefficiency of exchange. In general the lower the ESP and the higher the salinity the less efficient is the exchange. Oster and Frenkel (1980) calculated that this F factor (Eqn 3) varied between 1.1 at $\mathrm{ESP_f}$ of 15 and 1.3 at $\mathrm{ESP_f}$ of 5.

Offsetting exchange inefficiency during computation of amendment requirements is neglect of the role of calcium carbonate in the exchange process. Calcite dissolution has usually been dismissed as an important factor in sodic soil reclamation, the reason being that it is generally considered to be insoluble. However, this is generally not the case under soil conditions of elevated CO_2, and in the presence of a sink for Ca. The extent of calcium carbonate dissolution also depends on the irrigation water alkalinity and Ca content. The Ca content of the irrigation water can also be sufficient to cause appreciable reclamation. The net result of these processes is that the amount of amendment required is overestimated by these traditional methods, despite the inefficiency of exchange. For example, according to these guidelines, reclamation to reduce the exchangeable Na by 200 $\mathrm{mmol_c/kg}$ soil (20 meq/100 g) to a depth of 30.5 cm requires 85 Mg gypsum/ha. Such a value corresponds to reduction of the ESP from 50 to 10 for a soil with a CEC of 500 $\mathrm{mmol_c/kg}$ (50 meq/100 g). These quantities of gypsum are not economically viable; thus, these recommendations are rarely followed.

Alternative determinations of gypsum requirements can be based on the quantitative calculation of exchange efficiency, calcite dissolution, and the Ca contribution of the irrigation water using numerical models (Simunek and Suarez 1997). The objectives of this paper are to review the relevant concepts of these processes in the UNSATCHEM model and to evaluate the predictions, based on data from a field reclamation project. A comparison is made of the model predictions to field results of reclamation, as well as consideration of management alternatives.

UNSATCHEM model

The model to be applied to the reclamation problem, UNSATCHEM (Simunek and Suarez 1996; Suarez and Simunek 1997), is reviewed below. Several unique features are the prediction of CO_2 concentrations in the root-zone, consideration of the effects of soil chemistry on hydraulic properties, and inclusion of a kinetic model to describe calcite dissolution and precipitation. The model uses a modified version of the 1-dimensional Richards' equation:

$$\frac{\partial \theta_w}{\partial t} = \frac{\partial}{\partial z}\left[K\frac{(\partial h)}{\partial z} + 1\right] - S \tag{5}$$

where θ_w is the volumetric water content, K is the hydraulic conductivity function, h is the water pressure head, t is time, z is the spatial coordinate (positive up), and S is the sink term representing removal of water from the soil by plant roots. This equation neglects the effects of thermal and density gradients, and is used with the assumption that the gas phase dynamics do not affect water flow.

The unsaturated soil hydraulic properties are described by a modified version of those proposed by van Genuchten (1980). The hydraulic conductivity functions are given by:

$$K(h) = K_s \; K_r r = K_s r S_e^{\frac{1}{2}} \left[1 - (1 - S_e^{\frac{1}{m}})^m \right]^2 \tag{6}$$

where

$$m = 1 - 1/n \qquad n > 1 \tag{7}$$

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{8}$$

and where θ_r and θ_s are the residual and saturated water content [cm^3/cm^3], respectively; K_s is the saturated conductivity [cm/day]; K_r is the relative hydraulic conductivity; S_e is relative saturation; and m, n, and α [1/cm] are the empirical parameters of the hydraulic characteristics. Hydraulic characteristics are determined by the parameters, θ_r, θ_s, α, n, K_s, and r, where r represents the effect of soil chemistry on hydraulic properties. Use of the model requires optimising the first 5 parameters from the experimental water retention, pressure head, and saturated conductivity data. It is considered that for sodic soil reclamation it is sufficient to choose the default hydraulic characteristics based on soil texture (Carsel and Parrish 1988) and adjust the saturated hydraulic conductivity value to that of the soil. The major error in the default parameters, for our applications, is the saturated hydraulic conductivity and not the water retention pressure relationships.

Chemical effects on hydraulic conductivity

Equation 6 differs from previous relations in that it includes a reduction term, r, which scales the hydraulic conductivity in relation to the chemical conditions in the soil. Optimal soil chemical conditions for infiltration are represented by values where $r = 1$. Elevated levels of exchangeable sodium result in swelling of smectitic clays. Detachment of clay particles, dispersion, and subsequent clay migration and redeposition results in blocking of pores at low salinity and in the presence of exchangeable sodium (McNeal 1968; Shainberg and Levy 1992). This process is readily observed in the natural development of clay pan layers in soils and most dramatically in sodic, nonsaline soils. In addition, it has been determined that elevated levels of pH adversely affect saturated hydraulic conductivity, separate from the sodicity and salinity interactions (Suarez *et al.* 1984).

Suarez and Simunek (1997) represented the chemical effects on hydraulic properties by the use of a reduction function, r, given by:

$$r = r_1 \, r_2 \tag{9}$$

where r_1 is the reduction due to the adverse effects of low salinity and high exchangeable sodium fractions on the clay, and r_2 is the adverse effect of pH. The r_1 term is given by McNeal (1968) as:

$$r_1 = 1 - \frac{cx^n}{1 + cx^n} \tag{10}$$

where c and n are empirical factors, and x is defined by:

$$x = f_m \ 3.6 \times 10^{-4} \, \mathrm{ESP}^* d^* \tag{11}$$

where f_m is the mass fraction of smectite in the soil, d^* is an adjusted interlayer spacing, and ESP^* is an adjusted exchangeable sodium percentage (percentage of the total cation exchange charge of the soil that is neutralised by Na^+). The term d^* is defined by:

$$\begin{aligned} d^* &= 0 && C_0 > 300 \ \mathrm{mmol_c/L} \\ d^* &= 356.4\,(C_0)^{-0.5} + 1.2 && C_0 \le 300 \ \mathrm{mmol_c/L} \end{aligned} \tag{12}$$

where C_0 is the sum of the cation charge in solution expressed in $\mathrm{mmol_c/L}$ and the term ESP^* is given by:

$$\mathrm{ESP}^* = \mathrm{ESP}_{\mathrm{soil}} \ (1.24 + 11.63 \log C_0) \tag{13}$$

The reduction factor r_2, for the adverse effect of pH on hydraulic conductivity (K), was calculated from the experimental data of Suarez *et al.* (1984), after first correcting for the adverse effects of low salinity and high exchangeable sodium using the calculated r_1 values. Based on these limited data:

$$\begin{aligned} r_2 &= 1 && \text{for pH} < 6.83 \\ r_2 &= 3.46 - 0.36\,\mathrm{pH} && \text{for } 6.83 \le \mathrm{pH} \le 9.3 \\ r_2 &= 0.1 && \text{for pH} > 9.3 \end{aligned} \tag{14}$$

In view of the differences among soils, these specific values may not be generalised predictors of soil hydraulic conductivity, although they do represent conditions of 3 arid land soils examined at the US Salinity Laboratory. These equations illustrate the changes in K that affect infiltration and solute movement under various chemical conditions. This option in the model should not be considered as a quantitative prediction of what will occur at a specific site but is useful to evaluate the relative importance of the chemical effects under different soil and water conditions. Many other factors in addition to sodicity and pH affect soil aggregate stability, such as organic matter content, mode of irrigation, tillage, and extent of ground cover. It is reasonable to assume that these factors also affect the hydraulic conductivity and that there is an interaction between these factors and the chemical factors considered here.

Carbon dioxide production and transport

Unsaturated zone models typically either consider a closed system with constant inorganic carbon, as is also commonly considered for groundwater systems, or assume an open system at fixed CO_2. The first assumption is clearly not desirable for a root-zone model as large amounts of CO_2 are produced by plant decomposition as well as plant root respiration. Specification of a fixed CO_2 is a marked improvement over the closed system assumption but still does not consider spatial and temporal fluctuations. These changes are due to changes in production of CO_2, as well as changes in the transport of CO_2, which is mostly related to changes in the air-filled porosity of the soil, but can also be related to the flow of water.

Simunek and Suarez (1993) described a general soil model for CO_2 production and transport. The CO_2 production is the sum of the production rate by soil microorganisms, γ_s [cm^3/cm^3.day], and the production rate by plant roots, γ_p [cm^3/cm^3.day]:

$$P = \gamma_s + \gamma_p = \gamma_{s0} \prod_i f_{si} + \gamma_{p0} \prod_i f_{pi} \tag{15}$$

where the subscript s refers to soil microorganisms and the subscript p refers to plant roots, and Πf_i is the product of reduction coefficients dependent on depth, temperature, pressure head (the soil water content), CO_2 concentration, osmotic head, and time. The parameters γ_{s0} and γ_{p0} represent, respectively, the optimal CO_2 production by the soil microorganisms or plant roots for the whole soil profile at 20°C under optimal water, solute, and soil CO_2 concentration conditions. The individual reduction functions are given in Simunek and Suarez (1993). Discussion of selection of the values for optimal production as well as coefficients for the reduction functions is given in Suarez and Simunek (1993).

The 1-dimensional carbon dioxide transport model presented by Simunek and Suarez (1993) assumed that CO_2 transport in the unsaturated zone occurs in both the liquid and gas phases. One-dimensional CO_2 transport described by the following equation considers convective transport in the aqueous phase and diffusive transport in both gas and aqueous phases:

$$\frac{\partial c_T}{\partial t} = -\frac{\partial}{\partial z}(J_{da} + J_{dw} + J_{ca} + J_{cw}) - S c_w + P \tag{16}$$

where J_{da} is the CO_2 flux resulting from gas phase diffusion [cm/day], J_{dw} the CO_2 flux from dispersion in the dissolved phase [cm/day], J_{ca} the CO_2 flux from convection in the gas phase [cm/day], and J_{cw} the CO_2 flux from convection in the dissolved phase [cm/day]. The term c_T is the total concentration of CO_2 [cm^3/cm^3] and P is the CO_2 production/sink term [cm^3/cm^3.day]. The term Sc_w represents the dissolved CO_2 removed from the soil by root water uptake. It is assumed that when plants take up water the dissolved CO_2 is also extracted.

The total CO_2 concentration, c_T [cm^3/cm^3] is the sum of CO_2 in the gas and dissolved phases:

$$c_T = c_a \theta_a + c_w \theta_w \tag{17}$$

Combining expressions for the flux terms in the solution and gas phases with Eqns 16 and 17, then:

$$\frac{\partial(c_a \theta_a + c_w \theta_w)}{\partial t} = \frac{\partial}{\partial z}\theta_a D_a \frac{\partial c_a}{\partial z} + \frac{\partial}{\partial z}\theta_w D_w \frac{\partial c_w}{\partial z} - \frac{\partial}{\partial z} q_a c_a - \frac{\partial}{\partial z} q_w c_w - S c_w + P \tag{18}$$

where c_w and c_a are the volumetric concentrations of CO_2 in the dissolved phase and gas phase [cm^3/cm^3], respectively, D_a is the effective soil matrix diffusion coefficient of CO_2 in the gas phase [cm^2/ day], D_w is the effective soil matrix dispersion coefficient of CO_2 in the dissolved phase [cm^2/day], q_a is the soil air flux [cm/day], q_w is the soil water flux [cm/day], and θ_a is the volumetric air content [cm^3/cm^3]. The total aqueous phase CO_2, c_w, is the sum of aqueous CO_2 and H_2CO_3, and is related to the CO_2 concentration in the gas phase by (Stumm and Morgan 1981):

$$c_w = K_H R \mathrm{T} c_a \tag{19}$$

where K_H is the Henry's Law constant, R is the universal gas constant (8.314 kg m^2/s^2 k mol), and T is the absolute temperature [K]. The value of K_H as a function of temperature is taken from Harned and Davis (1943). Substituting Eqn 19 into 18 gives:

$$\frac{\partial R_f c_a}{\partial t} = \frac{\partial}{\partial z} D_E \frac{\partial c_a}{\partial z} - \frac{\partial}{\partial z} q_E c_a - S^* c_a + P \qquad (20)$$

where R_f is the CO_2 retardation factor, D_E is the effective dispersion coefficient for CO_2 in the soil [cm^2/day], q_E is the effective velocity of CO_2 [cm/day], S^* is the aqueous CO_2 uptake rate [1/day] associated with root water uptake, and θ_a is the volumetric air content [cm^3/cm^3]. The model does not consider coupled water and air movement and the flux of air, q_a, must be specified using additional assumptions. The compressibility of the air is neglected since the gas phase is at or near atmospheric pressure throughout the unsaturated zone. Assuming that the air flux is zero at the lower soil boundary and that water volume changes in the soil caused by water flow are immediately matched by corresponding changes in the gas volume, Simunek and Suarez (1993) obtained:

$$q_a(z) = q_w(0) - q_w(z) + \int_{L-L_r}^{z} S(z)dz \qquad (21)$$

This flux assumption is reasonable, since when water leaves the soil due to evaporation and root water uptake, air enters the soil at the surface and when water enters the soil during precipitation and irrigation events, soil air is escaping. However, in the case of saturated conditions (typically at the soil surface) air may be trapped and compressed under the wetting front.

Solute transport

Advective-dispersive chemical transport under transient flow conditions in partially saturated soil is expressed by (Suarez and Simunek 1996):

$$\frac{\partial \theta c_{Ti}}{\partial t} + \rho \frac{\partial \bar{c}_{Ti}}{\partial t} + \rho \frac{\partial \hat{c}_{Ti}}{\partial t} = \frac{\partial}{\partial z}\left[\theta D \frac{\partial c_{Ti}}{\partial z} - q c_{Ti}\right] \qquad i = 1, n_s \qquad (22)$$

where c_{Ti} is the total dissolved concentration of the aqueous component i [M/cm^3], $\bar{c}_{Ti}$ is the total adsorbed or exchangeable concentration of the aqueous component i [M/M], $\hat{c}_{Ti}$ is the non-adsorbed solid phase concentration of aqueous component i [M/M], ρ is the bulk density of the soil [Mg/cm^3], D is the dispersion coefficient [cm^2/day], q is the volumetric flux [cm/day], and n_s is the number of aqueous components. The coefficient D is the sum of the diffusion and dispersion components.

Chemical model

Chemical species

The chemical model currently includes consideration of 9 aqueous components: Ca, Mg, Na, K, SO_4, Cl, alkalinity, NO_3, and B. Alkalinity is defined as:

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + 2[CaCO_3^0] + [CaHCO_3^+] +$$

$$[MgCO_3^0] + [MgHCO_3^+] + 2[NaCO_3^-] + [NaHCO_3^0] + [B(OH)_4^-] - [H^+] + [OH^-] \qquad (23)$$

where brackets represent concentrations (mol/kg). From these components we obtain 11 species Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2+}, Cl, HCO_3^-, CO_3^{2-}, NO_3^-, H_3BO_3, and $B(OH)_4^-$, and the ion pair/complexes $CaHCO_3^+$, $CaCO_3^0$, $CaSO_4^0$, $MgHCO_3^+$, $MgCO_3^0$, $MgSO_4^0$, $NaHCO_3^0$, $NaCO_3^-$, $NaSO_4^-$, $KHCO_3^0$, KCO_3^-, KSO_4^-. It is assumed that all aqueous species are in equilibrium as defined by the ion association expressions and constants. Alkalinity as defined in Eqn 23 is a conservative species, affected only by dissolution or precipitation of a carbonate phase (such as calcite). After calculating the air phase CO_2 partial pressure, the $H_2CO_3^*$ (sum of aqueous CO_2 and H_2CO_3) is calculated using Eqn 19.

The equilibrium equations are solved using an iterative approach. The soil solution pH is determined as a dependent variable [H] from solution of Eqn 23 and a charge balance expression and multiplication by the activity coefficient. All equilibrium constants are calculated from available temperature-dependent expressions. Soil temperature is calculated from a heat flow submodel, with input of air temperature, as discussed above.

Osmotic pressure

The osmotic pressure is used to calculate the impact of salinity on water uptake and plant yield. The osmotic pressure is calculated using the following equation:

$$P_\varphi = R\mathrm{T}\frac{M_s v m_\varphi}{V_s m^0} \tag{24}$$

where P_φ is the osmotic pressure of the solution (Pa), v is the total number of moles of ions given by one mole of electrolyte, V_s is the partial molal volume of the water, m^0 is unit molality, m is molality of the solution, φ is the osmotic coefficient of the solution and M_s is the molar weight (Stokes 1979). The osmotic coefficient is calculated from (Pitzer 1973).

Activity coefficients

Activity coefficients are determined either using either an extended version of the Debye-Huckel equation (Truesdell and Jones 1974), or at high ionic strength, Pitzer equations (Pitzer 1973). The Pitzer approach considers ion–ion interactions for every species in solution; thus, it does not consider the individual ion pairs and complexes such as $NaSO_4$ described above as a species. The model is considered suitable for prediction of species activity in solutions up to 20 mol/kg.

Solid phases

The model considers a restricted set of solid phases; thus, it cannot be used to predict the composition of an evaporating brine. The minerals considered include calcite, gypsum, hydromagnesite, nesquehonite, and sepiolite. Since the model attempts to predict the composition of a water, predictions cannot be based only on thermodynamic considerations.

Calcite precipitation

The equilibrium condition of a solution with calcite in the presence of CO_2 is described by the expression:

$$(\mathrm{Ca}^{2+})(\mathrm{HCO}_3^-)^2 = \frac{K_{\mathrm{SP}}^{\mathrm{C}} K_{\mathrm{CO2}} K_{\mathrm{a1}}}{K_{\mathrm{a2}}} P_{\mathrm{CO2}}(\mathrm{H_2O}) \tag{25}$$

where parentheses denote activities, K_{CO_2} is the Henry's law constant for the solubility of CO_2 in water, K_{a1} and K_{a2} are the first and second dissociation constants of carbonic acid in water, K_{SP}^{C} is the solubility product for calcite, and P_{CO_2} is the partial pressure of CO_2. The equilibrium concentrations are obtained by solving the third-order equation. It has been shown that waters below irrigated regions are supersaturated with respect to calcite (Suarez 1977*a*; Suarez *et al.* 1992); thus, the equilibrium condition underestimates the Ca solubility in soil water. The cause of supersaturation has been shown to be due to poisoning of crystal surfaces by dissolved organic matter (Inskeep and Bloom 1986; Lebron and Suarez 1996).

Calcite crystal growth models are not applicable to soil systems, as the concentrations of dissolved organic carbon (DOC) in near surface natural environments are usually comparable to levels found by Inskeep and Bloom (1986) to completely inhibit calcite crystal growth. Lebron and Suarez (1996) developed a precipitation rate model which considers the effects of DOC on both crystal growth and heterogeneous nucleation. The combined rate expression is given by:

$$R_T = R_{CG} + R_{HN} \tag{26}$$

where R_T is the total precipitation rate, expressed in mmol/Ls, R_{CG} is the precipitation rate related to crystal growth, and R_{HN} is the precipitation rate due to heterogeneous nucleation. Since for soil systems the crystal growth rate can be neglected, only nucleation is an important process. The R_{HN} term is given by:

$$R_{HN} = k_{HN}\, f(SA)[\log(\Omega - 2.5)](3.37\times10^{-4}\,\mathrm{DOC}^{-1.14}) \tag{27}$$

where k_{HN} is the precipitation rate constant due to heterogeneous nucleation, $f(SA)$ is a function of the surface area of the particles (e.g. clay) upon which heterogeneous nucleation occurs (= 1.0 if no solid phase is present), Ω is the calcite saturation value, and 2.5 is the Ω value above which heterogeneous nucleation can occur. This equation leads to calcite precipitation rates which are independent of the calcite surface area, consistent with the experimental data of Lebron and Suarez (1996). For the purposes of saline and sodic soil reclamation it can be assumed that the nucleation rate is sufficiently fast such that the effective calcite solubility can be taken at the point at which there is no further nucleation. This level of supersaturation is very close to the supersaturation (3-fold) based on field measurements (Suarez 1977).

Gypsum

The model allows specification of the initial presence of gypsum, requiring input of the quantity present ($\mathrm{mmol_c}$/kg). If gypsum is present in any soil layer at the given time step, the model forces the solution to gypsum equilibrium. The program tracks changes in the amount of gypsum present. If all the gypsum initially present is dissolved in a soil layer, such as during reclamation of a sodic soil, then gypsum equilibrium is no longer forced. In all cases gypsum precipitates wherever supersaturation is indicated by solution calculations. The gypsum precipitation/dissolution expression is given by:

$$[\mathrm{Ca}^{2+}][\mathrm{SO}_4^{2-}] = \frac{K_{SP}}{\gamma_{\mathrm{Ca}^{2+}}\gamma_{\mathrm{SO}_4^{2-}}(\mathrm{H_2O})^2} \tag{28}$$

where γ represents the activity coefficient of the ion and the K_{SP} is the solubility product in solution. To obtain equilibrium, i.e. when the ion activity product (IAP) is equal to the solubility product K_{SP}^{G}, we solve a quadratic equation based on Eqn 28. For the objectives of this model it appears reasonable to assume that kinetics of gypsum dissolution/precipitation are sufficiently fast that the equilibrium condition can be used.

Magnesium precipitation

Dolomite precipitation is not considered by the present model since true dolomite has not been observed to precipitate at near earth surface conditions. It is also not reasonable to assume that a solution is dolomite-saturated merely because dolomite is present in the soil profile. If dolomite is present in the soil, the model has an option to use the kinetic expressions of Busenberg and Plummer (1982) to represent the dissolution process. The dissolution rate of dolomite is very slow, especially as the solution IAP values approach within 2–3 orders of magnitude of the solubility product. For purposes of sodic soil reclamation, dolomite dissolution kinetics may be omitted.

The model considers that Mg precipitation can occur as a carbonate or as a silicate. Since this is a predictive model, it considers only phases that either precipitate under earth surface conditions or occur frequently and are reactive under earth surface conditions. These need not necessarily be the thermodynamically most stable phases. With this consideration, magnesite is neglected, as it apparently does not form under earth surface temperatures, is relatively rare, and its dissolution rate is exceedingly small.

If nesquehonite or hydromagnesite saturation is reached, the model will precipitate the predicted Mg carbonate. These phases will occur very infrequently. The Mg carbonate precipitated, combined with calcite precipitation, will likely represent the mixed Ca–Mg precipitate, called protodolomite, that is observed in hypersaline environments. However, the resulting solution composition is much different than that produced by simply forcing equilibrium with respect to dolomite. The precipitation of calcite + magnesium carbonate results in solutions of approximately 3 orders of magnitude supersaturation with respect to dolomite. This result is consistent with the high levels of dolomite supersaturation maintained in high Mg waters (D. Suarez, unpublished data).

Precipitation (or dissolution, if present in the soil) of sepiolite is also considered by the model. Sepiolite will readily precipitate into a solid with a $K_{\mathrm{SP}}^{\mathrm{S}}$ greater than that of well-crystallised sepiolite. Formation of this mineral requires high pH, high Mg concentrations, and low CO_2 partial pressure. Details of the conditions for precipitation of magnesium containing minerals are given in Suarez and Simunk (1997).

Cation exchange

Cation exchange is generally the dominant chemical process for the major cations in solution in the unsaturated zone. The model uses a Gapon-type expression of the form (White and Zelazny 1986):

$$K_{\mathrm{ij}} = \frac{\bar{c}_{\mathrm{i}}^{y+}}{\bar{c}_{\mathrm{j}}^{x+}} \frac{(c_{\mathrm{j}}^{x+})^{1/x}}{(c_{\mathrm{i}}^{y+})^{1/y}} \tag{29}$$

where y and x are the respective valences of species i and j, and the overscored concentrations are those of the exchanger phase ($\mathrm{mol_c}$ /kg). It is assumed that the cation exchange capacity, c_{T} ($\mathrm{mol_c}$/kg), is constant, and for non-acid soils:

$$\bar{c}_{\mathrm{T}} = \overline{\mathrm{Ca}}^{2+} + \overline{\mathrm{Mg}}^{2+} + \overline{\mathrm{Na}}^{+} + \overline{\mathrm{K}}^{+} \tag{30}$$

where the overscored concentrations are those of the exchanger phase ($\mathrm{mol_c}$ /kg).

Experimentally determined selectivity values are not constant, nor is the cation exchange capacity, which varies as a function of pH, due to variable charge materials such as organic matter. It has been observed that soils have an increased preference for Ca^{2+} over Na^{+}, and Ca^{2+} over Mg^{+}, at low levels of exchanger phase Ca^{2+}. Suarez and Wood (1993) developed a mixing model which is able to approximate the nonconstant values of the soil selectivity coefficient by taking into account the organic matter content of the soil and using the published constant selectivity values for clay and organic matter. Calcium preference decreases as the organic matter exchanger sites (which have higher Ca preference than clays) become Ca saturated. UNSATCHEM uses this approach by solving 2 sets of equations for cation exchange (clay and organic matter).

Reclamation

Field experiment

The reclamation site, located in Riverside, California, consisted of a 40-ha field that was saline and sodic. The soil is classified as Indio, very fine sandy loam, Hyperthermic Typic Torrifluvent; however, substantial parts of the field consisted of silt loam. The subsoil (at 0.7–1 m) is described as silty clay loam with interstratified thin clay layers.

The initial electrical conductivity (EC_a) distribution was mapped using a Geonics EM 38, in both vertical and horizontal mode for obtaining spatial information with depth. At each sampling time 24 cores were taken at sites selected based on the EM survey. For each of the 24 cores, 4 samples were collected at 30-cm intervals to a depth of 120 cm. For each sample a saturation paste was prepared and the extract analysed for specific conductance (EC), Ca, Mg, Na, K, S (SO_4) by ICP-ES, alkalinity by titration, and nitrate by spectrometric measurements.

The EC data were used for calibration to convert the EC_a to EC_e. Exchangeable cations and cation exchange capacity were determined on selected samples using the saturation pastes and displacement of solution with 0.5 M ammonium nitrate. The exchangeable cation

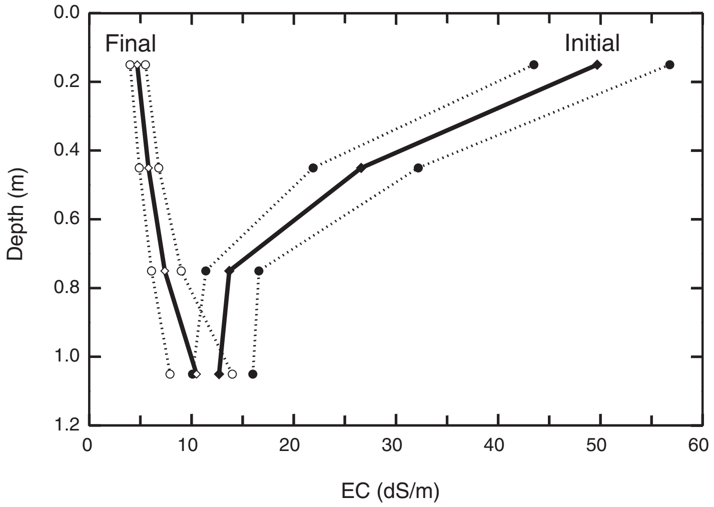

Fig. 2. Median EC values with depth for both initial and final (after leaching) conditions. Reclamation consisted of application of 24 Mg/ha of gypsum and application of 114 cm of water. The dashed lines indicate the 95% confidence limits of the median for the field.

content was corrected for carry over in the residual solution based on the saturation extract analysis and residual water content. Calcite release due to calcite dissolution during extraction was corrected using the alkalinity in the extract (Amrhein and Suarez 1990). Soil texture was determined on the collected cores.

At the time of the initial survey the median salinity levels ranged from 50 dS/m in the top 30 cm to 12.7 dS/m below 90 cm (Fig. 2). The median sodium adsorption ratio (SAR) values ranged from 144 in the top 30 cm to 94 below 90 cm (Fig. 3). The field was initially highly variable in both salinity and SAR, as shown in Fig. 4*a* and *b*, respectively. The salinity profile was 'inverted', with the highest salinity at the surface, consistent with salt accumulation by capillary rise from a shallow water table and surface evaporation.

Gypsum was applied to the soil in the field at a rate of 24 Mg/ha and disked to a depth of approximately 15 cm. A series of dikes were constructed to allow for ponding of water. A total depth of 114 cm of water was applied on the field in a series of 6 irrigation events over approximately 3 months. The water was almost continuously ponded during September, October and November; thus, evaporation was estimated from open pan evaporation. The estimated evaporation during those months was 19.3, 13.4, and 8.38 cm, for a total of 41 cm during the reclamation time (D. Ackley, pers. comm.). The calculated water infiltrated was 73 cm, after correction of the applied water for surface evaporation. The applied irrigation water was from the Colorado River, with the composition as given in Table 1.

At the completion of leaching, the field was resurveyed using the EM-38 and an additional 24 cores were taken to calibrate the EM-38 readings and to characterise the final conditions. The median salinity levels after leaching ranged from 4.7 dS/m in the top 30 cm to 10.5 dS/m below 90 cm (Fig. 2) and the median SAR values ranged from 9 in the top 30 cm to 54 below 90 cm (Fig. 3). The median SAR value of 9 in the top 30 cm of soils is just below the recommended reclamation value of SAR 10. The field data illustrate the heterogeneity of the reclamation, as after leaching only 52% of the field had an EC below 4 dS/m and 26% of the field had an EC above 8 dS/m in the top 30 cm.

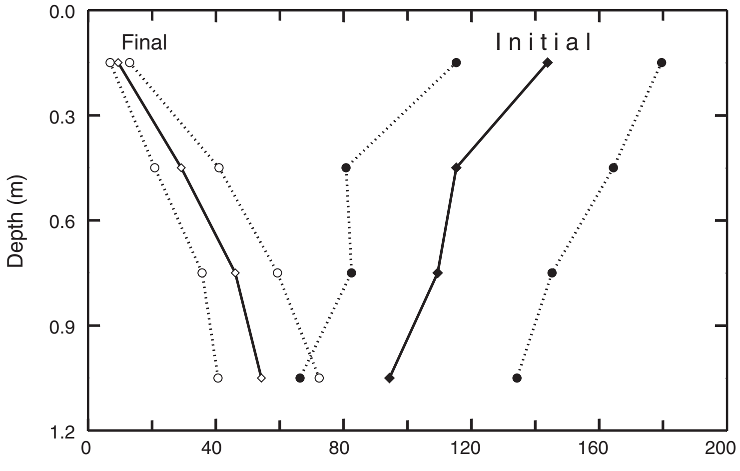

Fig. 3. Median SAR values with depth for both initial and final (after leaching) conditions. Reclamation consisted of application of 24 Mg/ha of gypsum and application of 114 cm of water. The dashed lines indicate the 95% confidence limits of the median for the field.

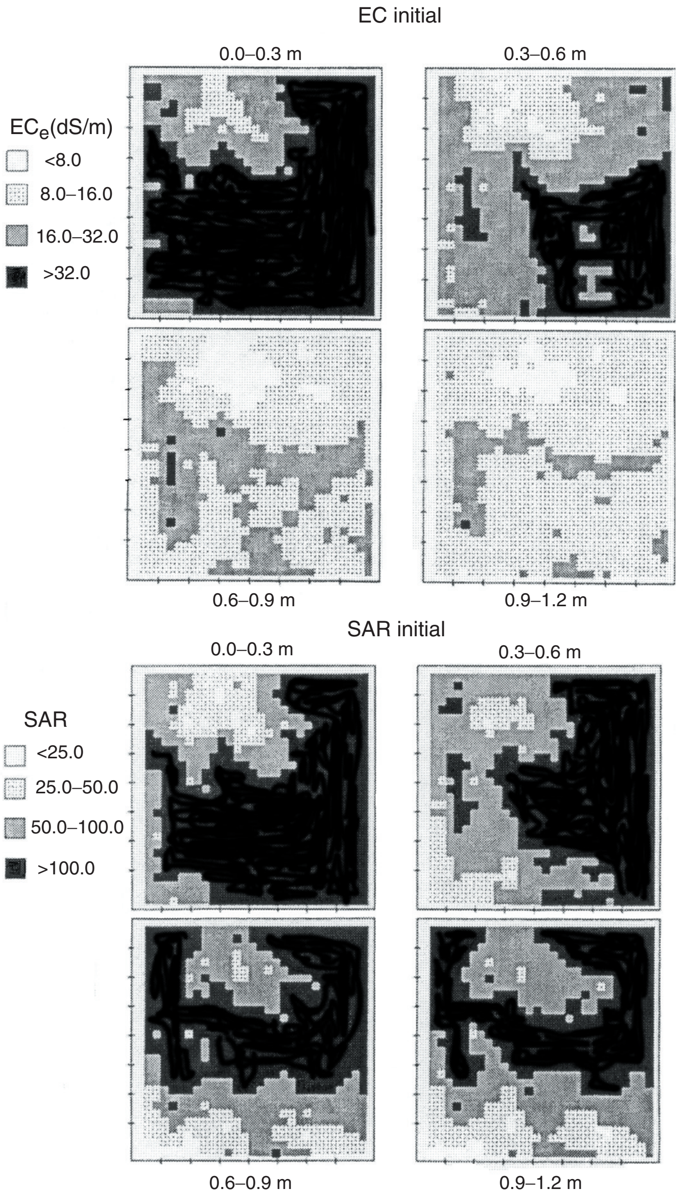

Fig. 4. (*a*) Initial EC distribution in the field, and (*b*) initial SAR distribution in the field.

It is very time consuming to determine the CEC of calcareous soils; thus, it is not feasible to measure the CEC of all samples and calculate a mean value. The mean CEC calculated for 6 soil samples taken from the 0–30 cm depth was 43.5 mmol_c/kg. The average clay of these samples was determined to be 13.2%. From these data the CEC of the clay was calculated to be 334 mmol_c/kg. The mean CEC of the field was calculated from

Table 1. Solution and exchange phase composition used in the field simulation

Depth (cm)	Ca	Mg	Na	K (mmol$_c$/L)	Alkalinity	Cl	SO_4	X_{Ca}[A]	X_{Mg}[A] (mmol$_c$/kg)	X_{Na}[A]
Irrigation water	2.00	1.00	2.00	0.10	1.50	2.00	1.60			
0–30	11.3	11.7	523	3.03	6.03	350	193	12.5	8.02	41.7
30–60	6.41	7.18	300	3.01	6.60	140	170	14.9	9.93	37.0
60–90	1.82	1.73	141	2.01	8.56	57.0	81.0	16.7	10.7	34.0
90–120	2.23	2.12	134	1.37	7.72	50.0	82.0	18.2	11.6	31.7

[A] X denotes exchangeable ion.

the large data set (96) of available saturation percentages (SP), using the empirical equation (Rhoades *et al.* 1999):

$$\%\text{clay} = (\text{SP} - 27.25)/0.76 \tag{31}$$

and the CEC of soil clay determined. The mean CEC was determined as 65.3 mmol$_c$/kg.

Predictions of the final EC$_e$ with depth, based on the Hoffman (1980) relationship, were not accurate based on the specified soil texture (Fig. 1). The sandy loam relationship overpredicted the extent of leaching, as twice as much water was required as predicted. This discrepancy is only in part due to the additional salt load generated by the dissolution of gypsum. It is considered that there was a non-uniform application of water (D. Ackley, pers. comm.). Water was ponded in a series of strips along contour. Overfilling of the strips resulted in redistribution of water into the downslope portions of the field. Differences in infiltration rates within a ponded area were also likely. The drainage system was installed immediately before application of the gypsum and leaching water. This analysis also does not account for the effects of spatial differences in measured hydraulic conductivity due to textural changes. Preferential water flow is not expected for these soils due to the lack of cracking and dominant sandy loam texture.

Evaluation of the gypsum requirement was made using the recommendations given in Handbook 60 as well as those using Eqn 3. The mean CEC was taken as 65.3 mmol$_c$/kg. The initial median ESP of 67 was calculated based on the SAR of the saturation extracts (using the relationship given in Handbook 60) Using the recommendation to reduce the ESP to <10 along with the values in Table 6 (Handbook 60) results in a median gypsum requirement of 16.1 Mg/ha to reclaim the top 30 cm of soil. The median gypsum requirement is 19.2 based on Eqn 3 and using a bulk density of 1.4 and an efficiency factor of 1.2.

The median gypsum requirement is not entirely satisfactory as there were portions of the field at very high SAR and gypsum requirement. It was calculated that 40% of the field was at an SAR of >200, corresponding to an ESP of >75, and the CEC ranged from 20 to 96 mmol$_c$/kg. Based on the CEC and SAR distribution it is estimated that 25% of the field had a gypsum requirement of 28.5 Mg/ha.

Model simulation

Validation of the processes represented in a model requires a controlled set of experiments. Field experiments serve a useful purpose in that they represent actual conditions that may include additional factors and processes not considered in controlled experiments. The ability of UNSATCHEM to predict changes in soil water content and thus water flow at the field scale, as well as CO_2 concentration in the root-zone, has been demonstrated earlier

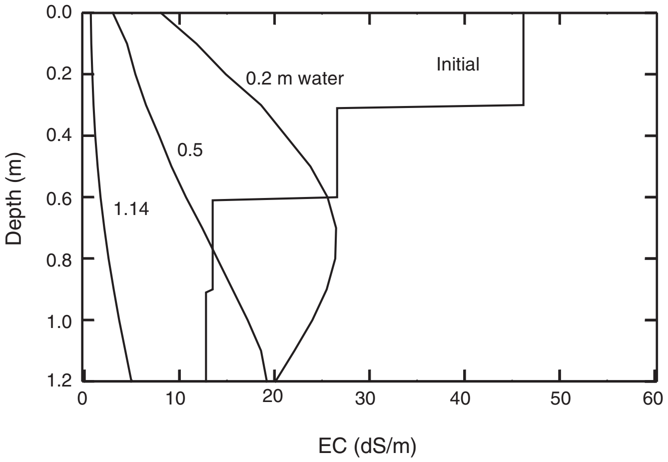

Fig. 5. Model predicted changes in salinity with depth after mixing 24 Mg/ha of gypsum into the top 15 cm and leaching with 20, 50, and 114 cm of water.

(Suarez and Simunek 1993). The capability of various models to predict reclamation is less certain. Suarez and Dudley (1998) examined the predictions of 3 models to simulate the chemistry of a soil irrigated with sodic water. There were large differences in the model predictions of EC and exchange ion composition.

Dudley *et al.* (1981) observed a poor relation between predicted and observed concentrations of Ca and Cl in irrigated field plots using the SALTFLO model. Even under controlled experimental conditions, variations in soil properties and infiltration may be sufficiently large to discourage use of such simulations using average properties and a single 1-dimensional simulation.

Simulation of the reclamation of the field using UNSATCHEM was done using the field values of CEC, ESP initial solution, and applied and infiltrated water. The initial soil solution and exchange phase conditions used for the simulation are presented in Table 1. The simulations used a CO_2 partial pressure of 0.5 kPa, and soil temperature of 25°C. The Ca/Na selectivity coefficient of 4.0 was used to establish SAR–ESP relationships compatible with those in USDA Handbook 60 (US Salinity Laboratory Staff 1954).

As shown by a comparison of the field data (Final) in Fig. 2 with the model predictions in Fig. 5, there was an overprediction of the extent of leaching if we consider only applied water, uncorrected for surface evaporation. The predicted EC after leaching was 0.8 and 1.31 dS/m in the top 30 and 60 cm of soil, respectively. Similarly, the predicted SAR after application of 114 cm of leaching water (Fig. 6) was lower than the observed SAR (Fig. 3). The calculated infiltration values of 70–80 cm of water were used in all subsequent simulations.

The effective reclamation can be evaluated by first examining the Cl distribution after leaching with the Cl distribution simulated by the model. In these soils Cl can be utilised as a non-reactive tracer for water flow. As shown in Fig. 7, the predicted Cl distribution is highly dependent on the amount of water infiltrated. The mean Cl distribution measured after reclamation was well predicted by the model simulation after infiltration of 80 cm of water. This value is consistent with the 73 cm of water calculated as water infiltrated.

Based on the data and simulation of EC presented in Fig. 8, it is considered that the model provided a good prediction of EC for all but the uppermost depth, where the

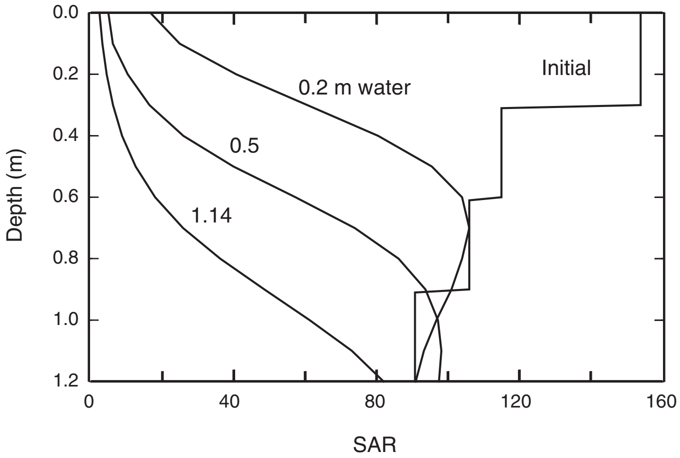

Fig. 6. Model predicted changes in SAR with depth after mixing 24 Mg/ha gypsum into the top 15 cm and leaching with 20, 50, and 114 cm of water.

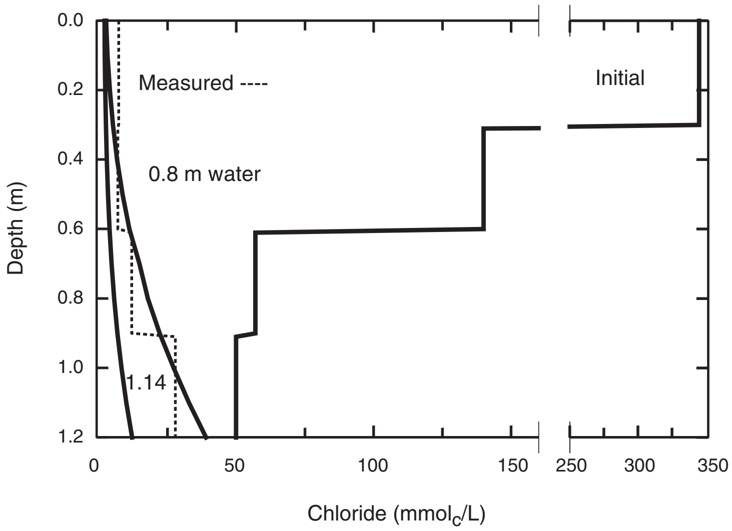

Fig. 7. Distribution of measured Cl concentration with depth before and after reclamation, and model predicted distributions after infiltration of 70 and 114 cm of water.

measured value of 4.7 dS/m is contrasted with the 1.61 predicted value, and outside the 95% confidence limits. Since the EC–leaching relationship is not linear (see Fig. 1), this difference may be due to the construction of mean values from a spatially variable population.

The prediction of SAR, shown in Fig. 9, was a reasonable fit to the observed data, and is considered satisfactory for its purpose of evaluating various management decisions. The top 30 cm had a predicted SAR of 5.6 in contrast to the measured value of 9.4, but this value is just outside the 95% confidence limits of the measured mean. Predictions at the other 3 depths are also within or close to the confidence limits of the field measurements. These

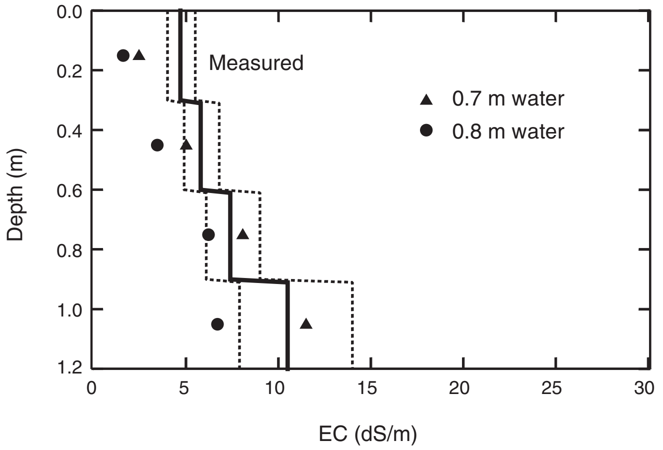

Fig. 8. Comparison of measured and model predicted changes in EC with depth after mixing 24 Mg/ha of gypsum into the top 15 cm and then infiltration of 70 and 80 cm of water.

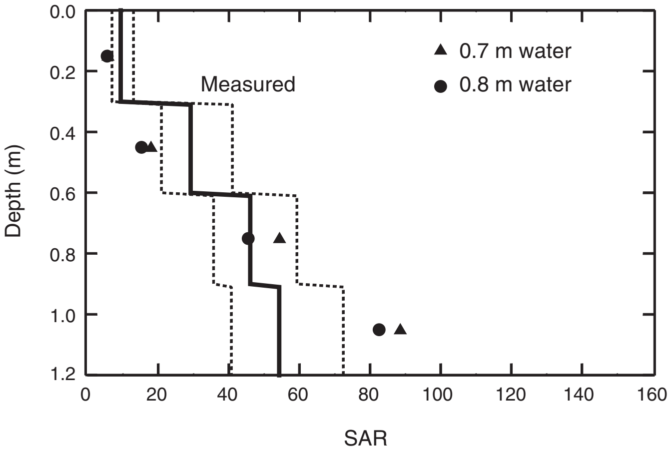

Fig. 9. Comparison of measured and model predicted changes in SAR with depth after mixing 24 Mg/ha of gypsum into the top 15 cm and then infiltration of 70 or 80 cm of water.

simulations have been performed using generalised cation selectivity coefficients and without consideration of the effects of soil levelling after leaching.

This analysis indicates that the reclamation based on averaged field conditions can be predicted from a single simulation of average soil properties and water composition. The model is also able to predict the extent of leaching and reclamation in soil cores (D. Suarez, unpublished data); thus, it can be utilised to evaluate reclamation and management practices for salinity and sodicity control.

Evaluation of alternative management practices is made using additional simulations. The predicted EC values with depth and time were only slightly affected by altering the depth of incorporation of gypsum to the depths of 2, 8,15, and 30 cm (simulation not shown). In contrast, as shown in Fig. 10, these differences had an important impact on the

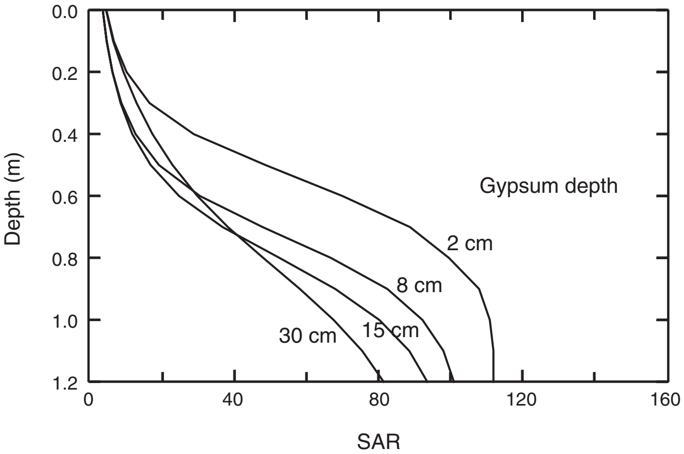

Fig. 10. Comparison of model predicted changes in SAR with depth after mixing 24 Mg/ha gypsum into the top 2, 8, 15, and 30 cm of soil and leaching with 80 cm of water.

SAR values. The sodic reclamation of the middle and lower portion of the profile is more rapid when the gypsum is mixed deeper. The upper part of the profile was reclaimed slower by the extremes in gypsum placement. Placing gypsum on the surface caused slower reclamation as more water was required to dissolve the gypsum. Alternatively, mixing the same amount of gypsum down to 30 cm resulted in insufficient gypsum available near the surface to completely reclaim the upper part of the profile. In this instance mixing gypsum to 8 cm may have been more cost-effective and produced comparable results in terms of reclamation of the upper 50 cm of the soil. A shallower or deeper placement of gypsum would require more water for leaching. The cost of mixing the gypsum into the soil can be evaluated against the cost of water and costs associated with time of reclamation.

The extent to which reclamation can be achieved without the use of gypsum, by dissolution of calcium carbonate in the profile, was evaluated in additional simulations. This corresponds to the alternative reclamation option called green manuring. The ideal practice would be to incorporate fresh organic matter into the soil when the soil is warm, thereby having high carbon dioxide production as a result of decomposition. If the soil is kept at or near saturation, CO_2 diffusion out of the soil is greatly restricted, CO_2 concentrations are elevated and substantial calcite can be dissolved (assuming calcite is present in the profile), and pH maintained within desirable levels.

Elevation of the CO_2 partial pressure to 5 kPa in the soil can be readily achieved; thus, this relatively conservative value was used for the simulations considering only calcite for reclamation. There was a slightly faster decrease in the EC with calcite alone compared with calcite and gypsum since the calcite is less soluble than the gypsum (simulation not shown). As expected the SAR was considerably greater when only calcite was used. Based on the simulations shown, reclamation with calcite alone was feasible (Fig. 11) but did require the use of more water than when gypsum was applied (compare Fig. 11 with Fig. 8). However, comparison of Fig. 11 with the field results shown in Fig. 3 indicates that calcite alone could have reduced the SAR in the upper 80 cm of the profile to values lower than observed in the field with application of gypsum and infiltration of 75 cm of water.

The upper 30 cm of the soil was predicted to be reclaimed to a mean SAR below 10 after application of 115 cm of water in the presence of calcite and a P_{CO_2} of 5 kPa. In contrast

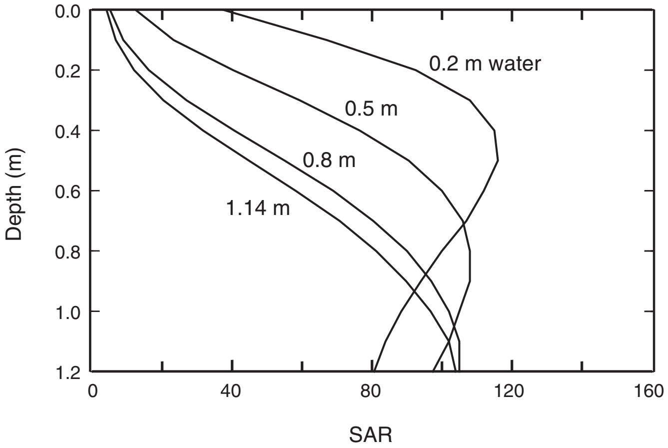

Fig. 11. Model predicted changes in SAR with depth after elevating the CO_2 to 5 kPa in the presence of calcite, then leaching with 20,50, 80, and 114 cm of water.

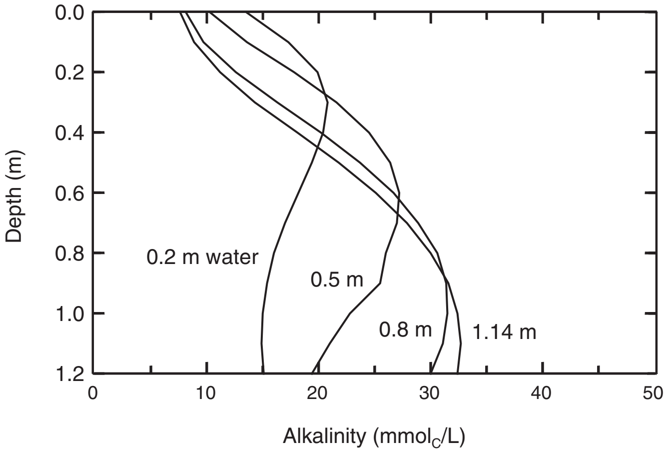

Fig. 12. Model predicted alkalinity concentrations (mmol$_c$/L) with depth after elevating the CO_2 to 5 kPa in the presence of calcite, and then leaching with 20, 50, 80, and 114 cm of water.

the reclamation of the upper 30 cm of soil to below SAR 10 was predicted after only 48 cm of water when 24 Mg/ha of gypsum was applied to the top 15 cm of soil. Reclamation with calcium carbonate alone is feasible but requires about twice as much water. This estimate is comparable to that observed in field studies comparing reclamation using green manuring and gypsum reclamation of a sodic soil (Manzoor Qadir, pers. comm., 2001). If the CO_2 partial pressure is only 0.5 kPa, then based on the simulations, it is predicted that reclamation will require application of 150 cm of water.

Earlier Oster and Frenkel (1980) calculated that in the presence of gypsum, an increase in CO_2 partial pressure from 1 to 4 kPa only increased by 5% the depth reclaimed. This small effect is due to the common ion effect that suppresses calcite dissolution in the presence of gypsum. However in the absence of gypsum we determined that there is a large P_{CO_2} effect on Na replacement.

The extent to which calcite acts as a Ca source can be evaluated by examination of the alkalinity in the profiles. As shown in Fig. 12 concentrations of alkalinity as high as 32 $\mathrm{mmol_c/L}$ are predicted. This corresponds to release of 32 $\mathrm{mmol_c/L}$ of Ca from calcite in addition to the Ca present in the irrigation water that is not associated with alkalinity. Elevated alkalinity occurs as a result of Ca adsorption on the exchange sites, reducing Ca in solution and allowing for further calcite dissolution. Once exchange is complete, the alkalinity concentrations decrease to around 5 $\mathrm{mmol_c/L}$.

This analysis suggests that in terms of Na replacement, gypsum use could have been avoided, and furthermore that the reclamation effort should have more thoroughly considered water application uniformity and time of year for leaching. Uniform application of 48 cm of water during a period of low evaporation would have enabled the top 30 cm of the soil to be sufficiently reclaimed in terms of salinity and SAR. The only hazard associated with this management practice is that the EC must be sufficiently high and pH sufficiently low during reclamation to maintain soil structural stability until the SAR decreases to a safe level.

An important consideration when using calcite as the Ca source for reclamation is that the EC–SAR combination remain suitable to maintain good soil structure and aggregate stability. In these simulations UNSATCHEM predicted that the hydraulic conductivity of the soil was reduced to as low as 30% of the optimal value during reclamation in the absence of gypsum and at $P_{\mathrm{CO_2}}$ of 5 kPa. This reduction was due to the initial decrease in EC while the SAR was still relatively high. The reduction in hydraulic conductivity remained until about 150 cm of water had passed through the profile. In addition to the extra time required for leaching, it is not clear that the adverse chemical effects on hydraulic conductivity would be reversible under field conditions.

The importance of maintaining high CO_2 concentrations during sodic soil reclamation in the absence of gypsum is further illustrated by results of hydraulic conductivity predictions at $P_{\mathrm{CO_2}}$ of 0.5 kPa. In this instance the hydraulic conductivity of the most affected layers (below 120 cm), and thus the infiltration, was reduced to <4% of the optimal value. Clearly reclamation would not be successful under these conditions. The required infiltration of 150 cm of water would require up to 5 years. The additional adverse effect of reduced CO_2 was due to the relatively greater pH as well as the elevated SAR. The larger $P_{\mathrm{CO_2}}$ (5 kPa) served to keep the pH below 7.8 at all times, while at 0.5 kPa the pH rose to above 8.4.

These simulations illustrate how the model can be used as a management tool at the field level both to evaluate an existing practice and to predict the results of alternative practices. In this instance water use could have been reduced by almost 50% with improved uniformity in application and avoiding reclamation during periods of high evapotranspiration. In this instance it may also have been possible to avoid the expense of gypsum application.

Representation of the spatial variation in EC and SAR after reclamation is important but clearly not possible if we use average field values as was done in this analysis. However, if we were to consider the spatial distribution of the water inputs and hydraulic properties and initial soil conditions it would be possible to run the UNSATCHEM model at numerous locations and then create a spatial map of the predicted distributions. Such maps could be used to develop precision reclamation and management practices for a field.

Acknowledgments

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