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REACTIVE TRANSPORT IN POROUS MEDIA

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Cover: Contour plot of computed mineral volume fraction and fluid streamlines (white with arrows indicating direction) after an elapsed time of 7.500 years. Fluid undersaturated with respect to the mineral is injected at the left, causing the mineral to dissolve and thus increasing the porosity and permeability in this region. Zones of red indicate regions where the mineral has been dissolved completely while the blue zones indicate regions where the initial mineral volume fraction is still present. Due to the reactive infiltration instability. the front propagates as fingers rather than as a planar front.

(Lichtner, this volume, Figure 19. page 76).

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Chapter 5

SOLUTE TRANSPORT MODELING UNDER VARIABLY SATURATED WATER FLOW CONDITIONS

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INTRODUCTION

A proper representation of important physical and chemical processes and soil properties in the rootzone is critical to modeling the transport of major solute species in the vadose zone. A proper modeling effort is also needed for prediction of the solution chemistry of groundwater systems, since these are usually recharged via the vadose zone. Hydrological models for water flow, both saturated and variably saturated, and models describing chemical processes in earth materials have been mostly developed independently. This independent development may have been due primarily to the lack of sufficient computational capability in the past, but is also due in part to the requirements of distinct scientific disciplines. To date most approaches consist of chemical models with simple description of water flow, or water flow models with simplified descriptions of chemical processes. The solute transport models developed in the hydrological sciences have mostly considered only one solute, and assumed only simplified chemical processes, most often with linearized expressions which can be incorporated directly into the transport equation. Chemical modeling has been Predominantly based on assumptions that the system is at thermodynamic equilibrium. Realistic modeling of the vadose zone requires representation not only of physical and chemical processes but also of such biological processes as microbial respiration and Plant water uptake.

In this paper we will briefly describe variably saturated water flow, including the modeling concepts of chemical effects on hydraulic properties and root water uptake and growth. We will also briefly discuss the traditional approach& for modeling reactive transport of single solute species including the concepts of both physical and chemical nonequilibrium. Our major emphasis is on modeling of CO_2 transport and production, and in discussing multicomponent solute transport. We also include discussion of Processes required for application of multicomponent models to field systems, and describe some of the features of the UNSATCHEM model which meets at least some of these requirements. Example simulations are given to demonstrate the importance that root water uptake, CO, dynamics and kinetics of calcite precipitation have on prediction of solute concentration and distribution in the unsaturated zone.

UNSATURATED WATER FLOW

Governing equation

The Richards' equation is widely used to describe one dimensional water movement in partially saturated porous media. Application of the model to near-surface environments requires use of a source-sink term. The following relation is of general

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applicability:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left[K\left(\frac{\partial h}{\partial z}+1\right)\right] - s \qquad (1)$$

where h is the water pressure head [L], θ is the water content [L^3L^{-3}] (positive upwards), ***K*** is the hydraulic conductivity [LT^{-1}], t is time [T], z is the spatial coordinate [L] and S is the sink/source term [T^{-1}], which is used here to represent water uptake rate by plant roots. This equation assumes a rigid porous media, that the air phase does not affect the liquid flow process, and neglects the effects of thermal or solution density gradients. A discussion of the assumptions and limitations of this approach is presented in Nielsen et al. (1986).

Hydraulic **characteristics**

The hydraulic conductivity under unsaturated conditions is dependent on the water content, which is in turn related to the pressure head. A widely used representation of the unsaturated soil hydraulic properties is the set of closed-form equations formulated by van Genuchten (1980), based on the capillary model of Mualem (1976). Soil water retention and hydraulic conductivity functions are given by

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{(1 + |\alpha h|^n)^m} \qquad (2)$$

and

$$K(h) = K_s K_r = K_s S_e^{1/2}\left[1 - (1 - S_e^{1/m})^m\right]^2 \qquad (3)$$

respectively, where

$$m = l - 1/n \qquad n > 1 \qquad (4)$$

$$S_e = \frac{e - e_r}{\theta_s - \theta_r}$$

and where θ_r and θ_s denote residual and saturated water contents [L^3L^{-3}], respectively, K_s is the saturated conductivity [LT^{-1}], K_r is the relative hydraulic conductivity [-], S_e is relative saturation [-] and ***m* [-], *n* [-],** and α [L^{-1}] arc the empirical parameters of the hydraulic characteristics. The hydraulic functions are determined by a set of 5 parameters, θ_r, θ_s, α, ***n***, and ***K*,.** Use of the model requires optimizing the parameters from experimental water retention, pressure head, and saturated conductivity data. This parameter optimization can be performed using the RETC code (van Genuchten et al., 1991).

Alternative models for the prediction of the relative hydraulic conductivity of unsaturated soils include the earlier, widely used **Brooks** and Cory (1964) formulation. The relative saturation, S_e, in that case is given by

$$S_e = \begin{cases} 1 & \alpha h \leq 1 \\ (\alpha h)^{-\beta} & ah > 1 \end{cases} \tag{6}$$

and the relative hydraulic conductivity by

$$K(h) = K_s S_e^{3+2/\beta} \tag{7}$$

While it is easier to obtain the Brooks and Cory parameters, the van Genuchten model is considered to provide a better match to the experimental data (Stankovich and Lockington, 1995). Other water retention models include those described by Hutson and Cass (1987) and Russo (1988), among others. These hydraulic functions are used as input to the Richards' equation for prediction of water movement and water content.

Chemical effects on hydraulic conductivity

Among the implicit assumptions when using the above equations is that the hydraulic properties are not affected by the composition of the solution phase. That this assumption is not valid is evidenced in the numerous studies that have documented the effects of solution composition on saturated hydraulic conductivity. Elevated levels of exchangeable sodium result in swelling of smectitic clays. Dispersion of clay, migration and subsequent blocking of pores results from low electrolyte and presence of exchangeable sodium. This process is readily observed in the natural development of clay pan layers in soils. The process has also been related to the distribution of divalent cations, with Mg^{2+} being more susceptible to dispersion than Ca^{2+}. In addition, it has been determined that elevated levels of pH adversely impact saturated hydraulic conductivity (Suarez et al., 1984).

Suarez and Šimůnek (1996) considered that the equations developed above could be optimal representations and that the chemical effects on hydraulic properties could be represented by the use of a reduction function, r, given by

$$r = r_1 r_2 \tag{8}$$

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

$$r_1 = 1 - \frac{cx^n}{1 + cx^n} \tag{9}$$

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

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

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

$$\begin{array}{ll} d^* = 0 & C_0 > 300 \text{ mmol}_c \text{ L}^{-1} \\ d^* = 356.4\,(C_0)^{-0.5} + 1.2 & C_0 \leq 300 \text{ mmol}_c \text{L}^{-1} \end{array} \qquad (11)$$

and the term ESP^* is given by

$$ESP^* = ESP_{soil} - (1.24 + 11.63 \log C_0) \qquad (12)$$

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

$$\begin{array}{ll} r_2 = 1 & for\ pH < 6.83 \\ r_2 = 3.46 - 0.36\ pH & for\ pH \in \langle 6.83, 9.3 \rangle \\ r_2 = 0.1 & for\ pH > 9.3 \end{array} \qquad (13)$$

In view of the differences among soils, these specific corrections may not be generalized predictors of the soil hydraulic conductivity but they illustrate the changes in *K* that may affect infiltration and solute movement under various chemical conditions. However, it is not yet certain that these parameters need to be characterized for each soil, as do the hydraulic characteristics in Equations (2)-(5).

The relations described by Equations (9)-(13) were based on data for soils of mixed mineralogy where the processes of both dispersion and swelling were likely important. Russo and Bresler (1977) modeled the effect of electrolyte concentration and Na/Ca ratio on the unsaturated hydraulic conductivity. Their model uses the concept that clay (mostly smectites) swelling results in a decrease in pore diameter and subsequent reduction in hydraulic conductivity. The number of clay platelets of Ca saturated smectite was given as

$$N_i^{Ca} = 4 + \log_{10}[\alpha(h_i/\rho g)] \qquad (14)$$

where α is an empirical parameter (= 1.0), h_i is the pressure head (which can be calculated by the hydraulic functions given earlier), ρ is the density of water and g is the gravitational constant. The number of platelets in a mixed Na-Ca system at the same pressure head is then given by

$$\begin{array}{ll} N_i = N_i^{C} & \text{for } 0 \leq ESP < ESP' \\ N_i = N_i^{Ca} \text{ -AN,} & \text{for } ESP' \leq ESP \leq ESP'' \\ N_i = N_i^{N} & \text{for } ESP > ESP'' \end{array} \qquad (15)$$

where ESP' is the critical value above which the number of platelets in a particle decreases and ESP'' is the value at which there is only a single platelet in a particle (Russo and Bresler, 1977). Using the data of Shainberg and Otoh (1968) and assuming that $N_i = 1.0$ above ESP=35, Equation (15) can be replaced by

$$N_i = N_i^{Ca} - 0.09ESP \text{ for } \boldsymbol{ESP \leq 35} \qquad \textbf{(16)}$$

The volume of water retained by the clay in each unit of soil can be determined from

$$u_i^{Ca} = (S/2N_i^{Ca})[2b_i + b_0(N_i^{Ca} - 1)]\rho_b \qquad (17)$$

for Ca saturated soil. When ESP > ESP´´, then

$$u_i = (S/2N_i^{Ca})[2b_i + b_0(N_i - 1) - 2b_i 0.09ESP]\rho_b \qquad \textbf{(18)}$$

where S is now the specific surface area of the soil, b_0 is the thickness of the water film between two clay platelets in a particle (= 9 nm), b_i is the distance between two adjacent particles, and ρ_b is the bulk density of the soil. The value for b_i can be calculated from diffuse layer theory (Bresler, 1972), as a function of exchange composition and total salt concentration.

The pore space available for water flow, H_i, is given by

$$H_i = [\theta_i - (u_i - u_i^{Ca})]v_i \qquad (19)$$

where v_i is the volumetric water content of the Ca saturated soil. The effective porosity ϵ_i is given by

$$\epsilon_i = \epsilon_t - (H_{i-1}/V) \qquad i = 1,2.....n;\ H_0 = 0 \qquad \textbf{(20)}$$

The hydraulic conductivity at a given water content is then calculated using the equation of Marshall (1958)

$$K(\epsilon_i) = \rho\frac{g}{8\eta}\epsilon_i^2 l^{-2}\sum_{i=1}^{n}(2i-1)a_i^2, \quad a_i > a_{i+1} \qquad (21)$$

where η is the viscosity of water , $l = n - i + 1$, and a_i is the mean equivalent radius of the Pores. The term ***a,*** is given by

$$\mathbf{a,} = (\epsilon_i v_i/\pi m_i)^{0.5} \qquad \textbf{(22)}$$

Where

$$m_i = \epsilon_0 v_i/\pi a_{i0}^2 \qquad \textbf{(23)}$$

and $a_{i0} = 2\gamma/P_i$ and γ is the surface tension of the soil solution.

Both the Suarez and Šimůnek (1996) and the Russo and Bresler (1977) formulations are based on experiments in which the adverse conditions were imposed after measurements under ideal chemical conditions. It is not likely that the chemical and physical processes which cause the reduction in hydraulic conductivity are reversible; thus the models may not be suited for prediction of improvements in hydraulic properties as a result of improvement in the chemical environment (such as reclamation of soils high in exchangeable Na soil by addition of gypsum).

Chemical processes of dissolution and precipitation can also affect hydraulic properties by changes in porosity. Camahan (1990) proposed equations to account for changes in porosity resulting from dissolution and precipitation under saturated flow. It is not clear how these changes in porosity relate to changes in variably saturated water flow, which is more dependent on the changes in pore size distribution.

Within the past few years flow models have been developed to provide two (and three)-dimensional solutions to the Richards' equation, which can be represented by

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}[K(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{ij}^A)] - S \qquad (24)$$

where x_i, x_j are the spatial coordinates, K_{ij}^A are components of a dimensionless aniosotropy tensor K^A, $\boldsymbol{K}$ is the unsaturated hydraulic conductivity function [LT^{-1}], and S is again the sink/source term.

ROOT WATER UPTAKE AND ROOT GROWTH

The process of evaporation and plant transpiration exerts a major influence on the solution composition and associated water and solute distributions in the unsaturated zone, particularly in arid and semiarid environments. In these instances neither water flow, solute transport, nor solution composition can be modeled without consideration of the evapotranspiration process. As a result, where plant water uptake is important, Only agriculturally oriented models which take into account the influence of root water uptake are suitable for modeling water flow and solute transport.

Various models have been developed for description of water extraction by Plant roots. Among the models in widespread use is one initially proposed by Feddes (1978). A detailed review of different expressions used to represent root water uptake can be found in Molz (1981). In the following expression, Šimůnek and Suarez (1993a) modified the Feddes et al. (1978) relation to include the adverse effect of osmotic stress on water uptake

$$S(h, h_\phi) = \alpha_s(h)\alpha_\phi(h_\phi)S_p \qquad (25)$$

where S_p is the potential water uptake rate [$L^3L^{-3}T^{-1}$] in the root zone, $\alpha_\phi(h_\phi)$ is the osmotic stress response function [-], and h_ϕ is the osmotic head [L]. The water stress response function, $\alpha_s(h)$, is a prescribed dimensionless function of the soil water pressure head ($0 \le \alpha_s \le 1$) described by van Genuchten (1987) as

$$\alpha_s(h) = \frac{1}{1 + (\frac{h}{h_{50}})^b} \qquad (26)$$

where h_{50} [L] and b [-] are empirical constants. The parameter h_{50} represents the pressure head at which the water extraction rate is reduced by 50%. Note that this formulation of the water stress response function, $\alpha_s(h)$, in contrast to the earlier expression of Feddes et al. (1978, not shown), does not consider a reduction in transpiration at water contents near saturation. The decrease in water uptake that is sometimes observed at saturation is related to oxygen stress and is more properly treated using predictions of the gas phase composition (for models that include CO, production and transport).

The potential water uptake rate in the root zone is expressed as the product of the potential transpiration rate, T_p [LT^{-1}], and the normalized water uptake distribution function, $\beta(z)$ [L^{-1}], which describes the spatial variation of the potential water uptake rate, S_p, over the root zone, as follows

$$S_p = \beta(z) T_p \tag{27}$$

There are many ways to express the function $\beta(z)$, including equations that are constant with depth, linear (Feddes et al., 1978), or exponential with a maximum at the soil surface (Raats, 1974):

$$\beta(z) = a e^{-a(L-z)} \tag{28}$$

where L is the z-coordinate of the soil surface [L] and ***a*** is an empirical constant [L^{-1}]. Alternatively, van Genuchten (1987) suggested the following depth-dependent root distribution function $\beta(z)$:

$$\begin{aligned} \beta(z) &= \frac{5}{3L_r} && L - 0.2L_r \leq z \leq L \\ \beta(z) &= \frac{25}{12L_r}\left(1 - \frac{L-z}{L_r}\right) && L - L_r < z < L - 0.2L_r \\ \beta(z) &= 0 && z \leq L - L_r \end{aligned} \tag{29}$$

where L_r is the root depth [L]. The actual transpiration rate, T_a, is obtained by integrating the root water uptake rate over the root zone as follows

$$T_a = \int_{L-L_r}^{L} S(h, h_\phi, z)\,dz = T_p \int_{L-L_r}^{L} \alpha_s(h)\alpha_\phi(h_\phi)\beta(z)\,dz \tag{30}$$

Root growth

The root depth, ***Lr,*** can be either constant or variable during the simulation. For annual vegetation a growth model is required to simulate the change in rooting depth with time. In UNSATCHEM (Šimůnek and Suarez, 1994; Suarez and Šimůnek, 1996) the root depth is the product of the maximum rooting depth, L_m [L], and the root growth coefficient, $f_r(t)$ [-]:

$$L_r(t) = L_m f_r(t) \tag{31}$$

To calculate the root growth coefficient, $f_r(t)$, Šimůnek and Suarez (1993b) combined the Vcrhulst-Pearl logistic growth function with the growth degree day (GDD) or heat unit concept (Gilmore and Rogers, 1958). The logistic growth function is usually used to describe the biological growth at constant temperature, whereas the heat unit model is utilized for determining the time between planting and maturity of the plant. The heat unit model cannot be used directly to predict biomass during the growth stage since it would predict a linear growth with time at constant temperature. Combining the heat unit concept with the classical logistic growth function incorporates both time and temperature dependence on growth.

For the growth degree day function a suitable option is a modified version of the relation developed by Logan and Boyland (1983), who assumed that this function is fully defined by the temperature, T [K], which in turn can be expressed by a sine function to approximate the behavior of temperature during the day, and by the three temperature limits, T_1, T_2, and T_3 [K]. When the actual temperature is below the base value T_1, plants register little or no net growth. The plant growth is at a maximum level at temperature T_2, which remains unchanged for some interval up to a maximum temperature T_3, above which increased temperature has an adverse effect on growth. Based on this information, Šimůnek and Suarez (1993b) proposed the following dimensionless growth function

$$g(t) = \begin{cases} g(t) = 0 & t \leq t_p; t \geq t_h \\ \dfrac{1}{T_{Bas}} \left[\int \delta (T - T_1) dt - \int \delta (T - T_2) dt - \int \delta (T - T_3) dt \right] & t \epsilon (t_p, t_m) \\ g(t) = 1 & t \epsilon (t_m, t_h) \end{cases} \tag{32}$$

where T_{Bas} represents the heat units [KT] necessary for the plant to mature and the roots to reach the maximum rooting depth, t_p, t_m, and t_h represent time of planting, time at which the maximum rooting depth is reached and time of harvesting, respectively; and parameter δ [-] introduces into the heat unit concept the reduction in optimal growth due to the water and osmotic stress. The expression inside the parenthesis of Equation (32) reaches the value T_{Bas} at time t_m when roots reach the maximum rooting depth. The individual integrals in Equation (32) are evaluated only when the particular arguments are positive. Parameter δ [-] is defined as the ratio of the actual to potential transpiration rate:

$$\delta = \frac{T_a}{T_p} \tag{33}$$

Biomass or root development during the growth stage can also be expressed by the Verhulst-Pearl logistic growth function

$$f_r(t) = \frac{L_0}{L_0 + (L_m - L_0) e^{-rt}} \tag{34}$$

where L_0 is the initial value of the rooting depth at the beginning of the growth period [L] and r is the growth rate [T^{-1}].

Both growth functions (32) and (33) can be used directly to model root growth. However, to avoid the drawbacks of both concepts, as discussed above, Šimůnek and Suarez (1993b) combined these equations by substituting the growth function calculated from the heat unit concept (32) for the time factor in the logistic growth function (34):

$$t = t_m \, g(t) \tag{35}$$

where t_m is the time when ***GDD*** reaches the required value for the specific plant species (T_{Bas}). This value is not known a priori; only the product rt_m must be known and that can be selected, for example, so that $f_r(t)$ equals 0.99 for $g(t) = 1$.

The water uptake expressions in Equation (30) result in a decrease in water uptake by plant roots at each node where water stress exceeds a critical value. Other models, such as LEACHM (Wagenet and Hutson, 1987; and Hutson and Wagenet, 1992) and SOWATCH (Dudley and Hanks, 1991) utilize the following equation for root water extraction

$$S = [h_r + z(1 + R_c) - h - h_\Phi] \, \frac{RDF\,K(\theta)}{\Delta x \, \Delta z} \tag{36}$$

where h_r is the water head within the root, R_c is a root resistance term, h is the matric head in the soil, h_Φ is the osmotic head, RDF is the fraction of root mass at depth z, and Ax and Δz are the dimensions of the element from which water is extracted. This model assumes a stable root profile and a Darcy flux control of water movement to the plant roots. Subject to this constraint, a water deficit from a given node is compensated by water use from any other node. Cardon and Lety (1992) determined that extraction functions of the form expressed in Equation (36) are not realistic as they result in very rapid shifts between optimal and zero transpiration, in contrast to experimental data which indicates slower changes. Equation (36) also fails to predict significant decreases in transpiration under high osmotic pressure. Equations of the form described by Equation (30) provided more realistic simulations. The model described by Equation (36) assumes a mature, stable, rootzone, while Equation (30) incorporates an expression for root growth. Neither Equation (36) nor Equation (30) consider the redistribution of roots (and consequently a more realistic representation of water uptake) as a result of stress at particular depths. Such a detailed model for plant root distribution and plant water uptake may not always be essential for a chemical transport model but estimation of the evapotranspiration is essential.

HEAT TRANSPORT

Prediction of temperature in the unsaturated zone is required for prediction of water movement and water content. Plant growth, extraction of water by plant roots and evaporation of water at the soil surface are all highly dependent on temperature. In addition, soil temperature is required for calculation of the temperature dependence of the chemical, kinetic and equilibrium reactions as well as for prediction of CO_2 production and pH. Among the available heat transport models are those of Milley et al. (1980) and Nassar et al. (1992), the latter on considering heat, water and nonreactive solute transport. Simůnek and Suarez (1994) included a heat transport routine in UNSATCHEM which is used for prediction of the factors discussed above.

CONCENTRATION/PRODUCTION/TRANSPORT OF CARBON DIOXIDE

Vadose zone models typically either consider a closed system with constant inorganic carbon, as is also commonly considered for ground water systems, or assume an open system at fixed CO,. The first assumption is clearly not desirable as large amounts of

CO, are produced by plant decomposition as well as plant root respiration. Models such as LEACHM consider an open system with specification of the CO, concentration as an input variable. Specification of a fixed CO, is a marked improvement over the closed system assumption but still does not consider the spatial and temporal fluctuations. These changes are due to both changes in production of CO,, as well as changes in the transport of CO,, which is mostly related to changes in the air-filled porosity of the soil, but can also be related to the flow of water. In the shallow vadose zone, the quantity of CO, added or removed by mineral dissolution/precipitation reactions is usually relatively small compared to the production and flux values and can be neglected. Below the CO_2 production zone this process may constitute the major control on CO, gas concentration.

Carbon dioxide production

Šimůnek and Suarez (1993b) described a general model for CO, production and transport. They considered CO_2 production as the sum of the production rate by soil microorganisms, $\gamma_s\,[L^3L^{-3}T^{-1}]$, and the production rate by plant roots, $\gamma_p\,[L^3L^{-3}T^{-1}]$

$$P = \gamma_s + \gamma_p = \gamma_{s0} \prod_i f_{si} + \gamma_{p0} \prod_i f_{pi} \qquad (37)$$

where the subscript s refers to soil microorganisms and the subscript ***p*** refers to plant roots, II f_i is the product of reduction coefficients dependent on depth, temperature, pressure head (the soil water content), CO, concentration, osmotic head and time. The parameters γ_{s0} and γ_{p0} represent, respectively, the optimal CO, production by the soil microorganisms and plant roots for the whole soil profile at 20°C under optimal water, solute and soil CO, concentration conditions $[L^3L^{-2}T^{-1}]$. The individual reduction functions are given in Šimůnek and Suarez (1993a); a discussion of selection of the values for optimal production as well as coefficients for the reduction functions is given in Suarez and Šimůnek (1993).

Carbon dioxide transport

Gas transport in the unsaturated zone includes three general transport mechanisms (Massmann and Farrier, 1992): Knudsen diffusion, multicomponent molecular diffusion and viscous flow. Thorstenson and Pollock (1989) presented equations to describe these transport mechanisms in a multicomponent gas mixture. They also presented the Stefan-Maxwell approximation of these equations, where Knudsen diffusion and viscous flow are neglected. The original equations, as well as the Stefan-Maxwell approximation, are fully coupled and generally highly nonlinear. However, Massmann and Farrier (1992) showed that gas fluxes in the unsaturated zone can satisfactorily be simulated using the single-component transport equation, neglecting Knudsen diffusion, as long as the gas permeability of the medium is greater than about 10^{-10} cm^2. They also showed that overestimation of the gas fluxes using the single component advection diffusion equation becomes quite large for permeabilities of 10^{-12} to 10^{-13} cm^2. Use of the transport equation based on Fick’s law to represent diffusive fluxes seems to be justified since air permeabilities smaller than 10^{-12} cm^2 occur only for very fine grained materials or for soils close to saturation. Also, Freijer and Leffelaar (1996) showed that CO_2 concentrations and fluxes can be described by Fick’s law to within 5% accuracy.

The one-dimensional carbon dioxide transport model presented by Simdnek and Suarez (1993a) assumed that CO_2 transport in the unsaturated zone occurs in both the liquid and gas phases. Furthermore, the CO, concentration in the soil is governed by two transport mechanisms (Patwardhan et al., 1988), convective transport in the aqueous phase and diffusive transport in both gas and aqueous phases, and by CO_2 production and/or removal. Thus one-dimensional CO, transport is described by the following equation:

$$\frac{\partial c_T}{\partial t} = -\frac{\partial}{\partial z}(J_{da} + J_{dw} + J_{ca} + J_{cw}) - Sc_w + P \tag{38}$$

where J_{da} is the CO_2 flux caused by diffusion in the gas phase [LT^{-1}], J_{dw} ***the CO, flux*** caused by dispersion in the dissolved phase [LT^{-1}], J_{ca} the CO, flux caused by convection in the gas phase [LT^{-1}], and J_{cw} ***the CO, flux*** caused by convection in the dissolved phase [LT^{-1}]. The term c_T is the total volumetric concentration of CO, [L^3L^{-3}] and P is the CO, production/sink term [$L^3L^{-3}T^{-1}$]. The term Sc_w represents the dissolved CO_2 removed from the soil by root water uptake. This term represents the (reasonable) assumption that when plants take up water the dissolved CO, is also removed from the soil-water system.

The individual terms in Equation (38) can be defined as (Patwardhan et al., 1988)

$$\begin{aligned} J_{da} &= -\theta_a D_a \frac{\partial c_a}{\partial z} \\ J_{dw} &= -\theta_w D_w \frac{\partial c_w}{\partial z} \\ J_{ca} &= -q_a c_a \\ J_{cw} &= -q_w c_w \end{aligned} \tag{39}$$

where c_w and c_a are the volumetric concentrations of CO_2 in the dissolved phase and gas phase [L^3L^{-3}], respectively, D_a is the effective soil matrix diffusion coefficient of CO_2 in the gas phase [L^2T^{-1}], D_w is the effective soil matrix dispersion coefficient of CO, in the dissolved phase [L^2T^{-1}], q_a is the soil air flux [LT^{-1}], q_w is the soil water flux [LT^{-1}] and θ_a is the volumetric air content [L^3L^{-3}].

The total CO, concentration, c_T [L^3L^{-3}], is defined as the sum of CO, in the gas and dissolved phases

$$c_T = c_a\theta_a + c_w\theta_w \tag{40}$$

After substituting Equations (40) and (39) into (38) we obtain

$$\frac{\partial(c_a\theta_a + c_w\theta_w)}{\partial t} = \frac{\partial}{\partial z}\theta_a D_a \frac{\partial c_a}{\partial z} + \frac{\partial}{\partial z}\theta_w D_w \frac{\partial c_w}{\partial z} - \frac{\partial}{\partial z}q_a c_a - \frac{\partial}{\partial z}q_w c_w - Sc_w + P \tag{41}$$

The total aqueous phase CO_2, c_w, is defined as the sum of CO_2(aq) and H_2CO_3, and is related to the CO, concentration in the gas phase by (Stumm and Morgan, 1981)

$$c_w = K_H R T c_a \tag{42}$$

where K_H is the Henry's Law constant [$MT^2M^{-1}L^{-2}$], R is the universal gas constant (8.3 14 $kgm^2s^{-2}K^{-1}mol^{-1}$) [$ML^2T^{-2}K^{-1}M^{-1}$] and T is the absolute temperature [K]. The value of K_H as a function of temperature is taken from Harned and Davis (1943). Aqueous carbon also exists in the form of HCO_3^-, CO_3^{2-} and other complexed species, such as $CaCO_3^{o}$, and these species should be included in the definition of c_w. Determination of these species cannot be made without use of a complete chemical speciation program. Substituting Equation (42) into (41) gives

$$\frac{\partial R_f c_a}{\partial t} = \frac{\partial}{\partial z} D_E \frac{\partial c_a}{\partial z} - \frac{\partial}{\partial z} q_E c_a - S^* c_a + P \tag{43}$$

where R_f is the CO, retardation factor [-], D_E is the effective dispersion coefficient for CO, in the soil matrix [L^2T^{-1}], q_E is the effective velocity of CO, [LT^{-1}], S^* is the CO_2 uptake rate [T^{-1}] associated with root water uptake and θ_a is the volumetric air content [L^3L^{-3}]. These parameters are defined as

$$\begin{aligned} R_f &= \theta_a + K_H R T \theta_w \\ D_E &= \theta_a D_a + K_H R T \theta_w D_w \\ q_E &= q_a + K_H R T q_w \\ \theta_a &= p - \theta_w \\ S^* &= S K_H R T \end{aligned} \tag{44}$$

Equation (43) is a nonlinear partial differential equation in which all parameters, except for c_a and q_a, are either known or can be obtained from solutions of the water flow equation. The nonlinearity of Equation (43) is caused by the term P which is dependent on the CO, concentration, c_a. Since the model does not consider coupled water and air movement, the flux of air, q_a, is unknown and thus additional assumptions are required. One possibility is to assume that the advection of CO, in response to the total pressure gradient is not important compared to CO_2 diffusion, and therefore to assume a stagnant gas phase and consider only diffusive transport within the gas phase ($q_a=0$). Another possibility is to consider that because of the much lower viscosity of air in comparison to water, significant gas flow can be caused by a relatively small pressure gradient. Thus, only rarely will the gas phase not be at atmospheric pressure throughout the unsaturated zone. Also, under most conditions, the compressibility of the air can be neglected. Then, with the assumption that the air flux is zero at the lower soil boundary and that water volume changes in the soil profile caused by the water flow must be immediately matched by corresponding changes in the gas volume, Šimůnek and Suarez (1993) obtained

$$q_a(z) = q_w(0) - q_w(z) + \int_{L-L,}^{z} S(z)\,dz \tag{45}$$

This latter assumption seems to be reasonable, since when water leaves the soil system due to evaporation and root water uptake, air enters the soil at the surface and, vice versa, when water enters the soil during precipitation and irrigation events, soil air is escaping. Only in the case of saturation (typically at the soil surface) does the condition arise that air can not escape and is compressed under the wetting front.

Two-dimensional CO, transport (Šimůnek and Suarez, 1994) is described by the following mass balance equation

$$\frac{\partial(c_a\theta_a + c_w\theta)}{\partial t} = \frac{\partial}{\partial x_i}(\theta_a D_{ij}^a \frac{\partial c_a}{\partial x_j}) + \frac{\partial}{\partial x_i}(\theta D_{ij}^w \frac{\partial c_w}{\partial x_j}) - \frac{\partial}{\partial x_i}(q_i c_w) - Sc_w + P \tag{46}$$

where D_{ij}^a is the effective soil matrix diffusion coefficient tensor of CO, in the gas phase $[L^2T^{-1}]$, D_{ij}^w is the effective soil matrix dispersion coefficient tensor of CO_2 in the dissolved phase $[L^2T^{-1}]$, and q_i is the soil water flux $[LT^{-1}]$.

REACTIVE SINGLE COMPONENT SOLUTE TRANSPORT

Local equilibrium models

These models consider individual species and their reactions with the solid phase. The assumption is that the species of interest and the solid are unaffected by the concentration of other solutes and that the chemical processes influencing the species are instantaneous. The complex processes of adsorption and cation exchange are usually accounted for by a linear (Huyakorn et al., 1991) or nonlinear Freundlich isotherms (Yeh and Huff, 1985; Šimůnek and van Genuchten, 1994), where all reactions between solid and liquid phases are lumped into the distribution coefficient K_D (Liu and Narasimhan, 1989) and possibly into the nonlinear exponent. This approach requires experimental determination of the K_D for each material and for each set of chemical conditions, such as competing ions, pH, ionic strength, complexing ions etc. That these chemical effects are not "second-order corrections" is readily demonstrated by the findings of Means et al. (1978) who determined that the unpredicted and extensive migration of ^{60}Co from waste disposal trenches was due to the failure to consider EDTA complexation of what would otherwise be highly soibed species. Despite these severe limitations the K_D approach has the appeal of simplicity, computational efficiency and avoids the requirements of needing complete chemical descriptions. Applicability and limitations of this approach have been presented, respectively, by Vaiocchi (1984) and Reardon (1981) among others.

Nonequilibrium models

In many instances the equilibrium approach has not been successful. Nonequilibrium expressions have been developed for precipitation, biodegradation, volatilization and radioactive decay. These processes have been simulated by simple first- or zero-order rate constants. Successful modeling is often demonstrated by excellent fit between breakthrough curves from laboratory columns and model simulations using parameters generated from the same experiments. Such models have been developed for nitrogen transformations, pesticide degradation and radioactive decay. Aside from radioactive decay the above mentioned processes cannot be represented by such simple relations without the need for different parameters for each set of conditions. While suitable for the laboratory experiments used to generate the parameters, such approaches will not be generally suited for natural systems. In addition to the single solute models several models exist which simulate multiple solutes involved in sequential first-order decay reactions in one dimensional (Wagenet and Hutson, 1987) as well as in two dimensional models (Gureghian, 1981; Šimůnek and van Genuchten, 1994).

Various models are available to treat multisite sorption. For example Selim et al. (1976) and van Genuchten and Wagenet (1989) consider two-site models where one site is assumed to be at local equilibrium with the solution, while sorption on the other site is described by a kinetic expression. For a linear sorption process, the two-site transport model is given by (van Genuchten and Wagenet, 1989)

$$\frac{\partial}{\partial t}(\theta + f\rho\, k_D)c = \frac{\partial}{\partial z}\left(\theta D\frac{\partial c}{\partial z} - qc\right) - \alpha\rho[(1-f)k_D c - s_k] - \theta\mu_l c - f\rho k_D \mu_{s,e} c \tag{47}$$

$$\frac{\partial s_k}{\partial t} = \alpha[(1-f)k_D c - s_k] - \mu_{s,k} s_k \tag{48}$$

where μ_l and μ_s are first-order degradation constants for the chemical in the solution and sorbed phases, respectively; f is the fraction of adsorption sites assumed to be at equilibrium, and the subscripts e and k refer to equilibrium and kinetic sorption sites. The adsorption model has been used successfully in several laboratory column miscible displacement studies (Rao et al., 1979; Parker and Jardine, 1986).

A related model is the two-region transport model, which deals with physical nonequilibrium conditions. This approach assumes that there are two distinct solution regions, one immobile and the other mobile. Each region is in equilibrium with a specified fraction of the solid phase, and solute exchange between the regions is treated as a first-order process. The governing equations are (van Genuchten and Wagenet, 1989)

$$\frac{\partial}{\partial t}(\theta_m + f\rho k_D)c_m = \frac{\partial}{\partial z}\left(\theta_m D_m\frac{\partial c_m}{\partial z} - qc_m\right) - \alpha(c_m - c_{im}) - (\theta\,\mu_{l,m} + f\rho\, k_D\,\mu_{s,m})\,c_m \tag{49}$$

$$[\theta_{im} + (1-f)\rho k_D]\frac{\partial c_{im}}{\partial t} = \alpha(c_m - c_{im}) - [\theta_{im}\mu_{l,im} + (1-f)\rho k_D \mu_{s,im}]c_{im} \tag{50}$$

where the subscript m refers to the mobile solution region, im to the immobile solution region, l to the liquid phase and s to the sorbed phase. The term f represents the fraction of sorption sites that equilibrate with the mobile liquid phase, and α is a first-order mass transfer coefficient governing the rate of solute exchange between the mobile and immobile solution regions. The two-region physical nonequilibrium model has been successfully applied to laboratory-scale transport experiments involving tritiated water, chloride, and organic chemicals, among others (Gaudet et al., 1977; van Genuchten et al., 1977; Nkedi-Pizza et al., 1983; Gaber et al., 1995).

Since the two-site and two-region nonequilibrium models have the same mathematical structure, it is not possible to distinguish between the processes of chemical and physical nonequilibrium, based on the fit to these models. A determination as to which of the processes is applicable requires additional experimentation, such as the use of nonadsorbing tracers (van Genuchten and Šimůnek, 1996).

The two-region nonequilibrium physical model mentioned above assumes that water flow occurs only in the macropore region. While this model has been successfully used for saturated flow conditions, it clearly is less realistic for variably saturated conditions, especially for drier situations when the macropores are empty and flow only occurs through the finer pores. Among the models which describe flow in two regions are those of Wang (1991), Zimmerman et al. (1993), and Gerke and van Genuchten (1993).

The dual-porosity model developed by Gerke and van Genuchten (1993) assumes that the Richards equation for transient water flow and the convection-dispersion equation for solute transport can be applied to each of the two pore systems as follows

$$C_f \frac{\partial h_f}{\partial t} = \frac{\partial}{\partial z}\left(K_f \frac{\partial h_f}{\partial z} - K_f\right) - \frac{\Gamma_w}{w_f} \tag{51}$$

$$C_m \frac{\partial h_m}{\partial t} = \frac{\partial}{\partial z}\left(K_m \frac{\partial h_m}{\partial z} - K_m\right) + \frac{\Gamma_w}{1-w_f} \tag{52}$$

and

$$\frac{\partial}{\partial t}(\theta_f R_f c_f) = \frac{\partial}{\partial z}\left(\theta_f D_f \frac{\partial c_f}{\partial z} - q_f c_f\right) - \frac{\Gamma_s}{w_f} \tag{53}$$

$$\frac{\partial}{\partial t}(\theta_m R_m c_m) = \frac{\partial}{\partial z}\left(\theta_m D_m \frac{\partial c_m}{\partial z} - q_m c_m\right) + \frac{\Gamma_s}{1-w_f} \tag{54}$$

where the subscripts f and m refer to the macropore and matrix pore systems, respectively; Γ_w and Γ_s describe the rate of exchange of water and solute, respectively, between the two regions, w_f is the volume of the macropore region relative to that of the total soil pore system. Similarly as for the first-order mobile-immobile transport models, water and solute mass transfer between the two pore systems is described with first-order rate equations:

$$\Gamma_w = \alpha_w (h_f - h_m) \tag{55}$$

$$\Gamma_s = \alpha_s (c_f - c_m) + \begin{cases} \Gamma_w w_f \theta_f \; c_f/\theta \, , & \Gamma_w \geq 0 \\ \Gamma_w (1-w_f)\theta_m \; c_m/\theta & \Gamma_w < 0 \end{cases} \tag{56}$$

in which α_w and α_s are first-order mass transfer coefficients for water and solute, respectively. The first term on the right-hand side of Equation (56) specifies the diffusion contribution to Γ_s, while the second term gives the convective contribution. The above variably-saturated dual-porosity transport model reduces to the first-order model for conditions of steady-state flow in the macropore region and no flow in the matrix pore system (q_m ***= I’, = 0).*** The simultaneous solution of the coupled Richards equations and first-order nonlinear transfer term for approximation of fluid exchange results in **a** complex representation. Practical application of the model requires further development of accurate and efficient numerical solutions (Gerke and van Genuchten, 1993). Subsequently Tseng et al. (1995) developed a numerically stable and relatively efficient Partitioned procedure for solution of the dual-porosity problem.

COUPLED WATER FLOW AND MULTICOMPONENT MODELS

Much of the research on multicomponent solute transport is focussed on the saturated zone. Most of the developed models were based on assumptions of one-dimensional steady-state saturated water flow with a fixed water flow velocity, temperature and pH (Valocchi et al., 1981; Jennings et al., 1982; Walsh et al., 1984; Cederberg, 1985; Kirkner et al,, 1985; Förster, 1986; Bryant et al., 1986; Förster and Gerke, 1988; Kirkner and Reeves, 1988; among others). Under saturated conditions, changes in water velocity, temperature and solution composition, including pH, are relatively gradual and thus these assumptions may be acceptable for many cases. In contrast the assumptions are not reasonable for unsaturated zone modeling, particularly for simulations of conditions near the soil surface.

In the past 10 to 15 years the increasing speed of computer processing has enabled development of numerical schemes and models which couple water flow and solute transport with chemical models. Among recent reviews of hydrogeochemical transport models of reactive multichemical components are those given by Kirkner and Reeves (1988), Yeh and Tripathi (1989), Rubin (1990) and Mangold and Chin-Fu Tsang (1991). Kirkner and Reeves (1988) presented an analysis of several approximation methods for solving the governing equations for multicomponent mass transport with chemical reactions. They discuss how the choice of formulation and solution algorithm should reflect the type of chemical problem encountered. Yeh and Tripathi (1989) provided a critical review of many computational methods that have been presented in the hydrologic literature for solving multicomponent, equilibrium-controlled transport.

Equilibrium models

The majority of coupled chemistry-water flow models predict concentrations based on thermodynamic equilibrium reactions. Among these extensive chemical equilibrium models are WATEQ (Truesdell and Jones, 1974), which computes solution equilibria, and MINTEQ (Allison et al., 1990), GEOCHEM (Sposito and Mattigod, 1977) and PHREEQE (Parkhurst et al., 1980) which compute solution equilibria and have the option to predict solution-solid equilibria as well. These models have been incorporated into combined transport chemical equilibria models, such as the saturated flow models described by Narasimhan et al. (1986), Liu and Narasimhan (1989), and Griffioen (1993). These coupled models are of the type classified by Yeh and Tripathi (1989) as solving sets of linear partial differential equations and nonlinear algebraic equations using a sequential iteration approach (SIA). Yeh and Tripathi (1989) consider that only those models which employ the SIA approach and which use either “total analytical concentrations of aqueous components, or the concentrations of all species, or the concentrations of all component and precipitated species as the primary dependent variables, can encompass the full complement of geochemical processes. ” Models which simultaneously solve a set of mixed differential and algebraic equations (DAE) or directly substitute the chemical equations into the hydrological transport equation (DSA) are regarded as requiring excessive CPU memory and time to be used for other than simple chemical descriptions. A more detailed comparison of these solution methods is presented in Steefel and MacQuarrie (this issue).

Within the past few years several models were published that can be applied to problems that include multicomponent solute transport and two-dimensional variably saturated water flow (Liu and Narasimhan, 1989; Yeh and Tripathi; 1991, Šimůnek and Suarez, 1994). Narasimhan et al. (1986) and Liu and Narasimhan (1989) developed the model DYNAMIX which can be used in conjunction with an integral finite difference program for fluid flow in variably saturated porous media. Yeh and Tripathi (1991) presented the development and a demonstration of a two-dimensional finite element hydrogeochemical transport model, HYDROGEOCHEM, for simulating transport of reactive multispecies chemicals. The HYDROGEOCHEM model consists of a matrix solver in which the user adds the desired equations and components to obtain an equilibrium solution. Generalized relations are presented by Yeh and Tripathi (1991) for use in describing kinetic processes, but were not included in the model. The model is not well suited for vadose zone simulations as it considers fixed inorganic carbon and does not allow for open system CO, control where pH and CO, can vary. Except for Šimůnek and Suarez (1994), the presented examples in all of these papers are only for steady state water movement.

The governing equation for one-dimensional convective-dispersive chemical transport under transient flow conditions in partially saturated porous media is taken as (Suarez and Šimůnek, 1996)

$$\frac{\partial \theta c_{T_i}}{\partial t} + \rho \frac{\partial \bar{c}_{T_i}}{\partial t} + \rho \frac{\partial \hat{c}_{T_i}}{\partial t} = \frac{\partial}{\partial z}[\theta D \frac{\partial c_{T_i}}{\partial z} - q c_{T_i}] \qquad i=1,n_s \tag{57}$$

where c_{Ti} is the total dissolved concentration of the aqueous component i [ML^{-3}], $\bar{c}_{Ti}$ is the total adsorbed or exchangeable concentration of the aqueous component i [MM-‘], $\hat{c}_{Ti}$ is the non-adsorbed solid phase concentration of aqueous component i [MM-‘], ρ is the bulk density of the soil [ML^{-3}], D is the dispersion coefficient [L^{2}T^{-1}], q is the volumetric flux [LT^{-1}], and n_s is the number of aqueous components. The second and third terms on the left side of Equation (55) are zero for components that do not undergo ion exchange, adsorption or precipitation/dissolution. The coefficient D is the sum of the diffusion and dispersion components

$$D = \tau D_m + \lambda \frac{|q|}{\theta} \tag{58}$$

where τ is the tortuosity factor [-], D_m is the coefficient of molecular diffusion [L^{2}T^{-1}], and λ is the dispersivity [L]. This representation is a simplified treatment of the diffusion process. A more detailed description of diffusion requires calculation of the diffusion rates of individual species, with consideration of Coulombic interactions which maintain electroneutrality, requiring coupling of individual ion fluxes to the concentration gradients of all individual species (Lasaga, 1979). If ion pairs are utilized in the chemical model, this additional coupling of diffusion rates should also be made (Lasaga, 1979). However, in porous media, errors generated by uncertainty in determination of the tortuosity factor and velocity vectors are likely more significant for determination of solute transport than errors associated with a simplified treatment of diffusion.

Realistic modeling of the chemistry in the unsaturated zone requires consideration of various factors which arc usually not considered. Among these are changes in hydraulic properties of the soil as related to the solution chemistry (discussed above), water uptake by plant roots and the spatial distribution of water uptake, temperature effects on water uptake, gas phase composition, equilibrium or reaction constants, and prediction of the dynamic changes in CO, concentration with time and space, all of which affect water and solute movement as well as the chemical processes for the solutes of interest.

Generalized models

The model HYDROGEOCHEM (Yeh and Tripathi, 1991) is one of the most extensive in terms of its potential to handle a wide range of problems. The model contains generalized routines for treatment of chemical equilibrium, including aqueous complexation, adsorption reactions, ion exchange, precipitation-dissolution, redox reactions, and acid-base reactions, all considering chemical equilibria. The model calculates activity coefficients using the Davies equation. Specification of the thermodynamic constants requires that users first correct the constants for the particular temperature and pressure of the case to be run. Acid-base reactions and prediction of pH is possible by calculation of the proton balance. Oxidation-reduction processes can also be treated with this model. Oxidation-reduction reactions are treated by defining electron activity as a master variable and making this entity an aqueous component subject to transport. Such calculations allow for equilibrating redox within a closed system but will not be suitable for most environments where biological processes, such as microbial degradation of organic matter are dominant.

Adsorption equilibria in HYDROGEOCHEM are obtained from the law of mass action

$$y_i = \alpha_i^y \left[\prod_{k=1}^{N_a} c_k^{a_{ik}^y} \right] \left[\prod_{k=1}^{N_s} s_k^{b_{ik}^y} \right] \qquad \boldsymbol{i} = 1,2,\ldots,M_y \tag{59}$$

in which

$$\alpha_i^y = K_i^y \left[\prod_{k=1}^{N_a} (\gamma_k^a)^{a_{ik}^y} \right] \left[\prod_{k=1}^{N_s} (\gamma_k^s)^{b_{ik}^y} \right] (\gamma_i^y)^{-1} \qquad \boldsymbol{i} = 1,2,\ldots,M_y \tag{60}$$

where α_i^y is the stability constant of the ***i*** th adsorbed species, K_i^y is the equilibrium constant of the *i* th adsorbed species, γ_i^y is the activity coefficient of the ***i*** th adsorbed species, γ_k^s is the activity coefficient of the *k* th adsorbent component species, γ_k^{a} is the activity coefficient of the ***k*** th aqueous species, M_y is the number of adsorbed species, N_a is the number of aqueous components, N_s is the number of adsorbent components, a_{ik}^y is the stoichiometric coefficient of the ***k*** th aqueous component in the ***i th*** adsorbed species, s_k is the concentration of the ***k*** th adsorbent component species, and b_{ik}^y is the stoichiometric coefficient of the ***k*** th adsorbent component in the *i* th adsorbed species. Alternatively HYDROGEOCHEM has the capacity to treat adsorption using the triple layer model (Davis et al., 1978; Davis and Leckie, 1978, 1980).

Generalized kinetic expressions for reactions are described by Yeh and Tripathi, (1989). (although not included in the HYDROGEOCHEM code) where for formation of a complex

$$\theta \frac{\partial x_i}{at} - L(x_i) + \theta r_i^x \qquad i = 1,2,\ldots,\boldsymbol{K}_x \tag{61}$$

where K_x is the number of complexed species of kinetic reactions, and ***r,”*** can be given by

$$r_i^x = -k_i^{bx} x_i + k_i^{fx} \prod_{k=l}^{N_a} c_k^{a_{ik}^x} \quad i = 1,2,\ldots,K_x \tag{62}$$

where k_i^{bx} is the modified back reaction rate constant for the ***i th*** reaction and k_i^{fx} is the modified forward reaction constant for the ***i th*** reaction. For sorption reactions

$$\theta \frac{\partial y_i}{\partial_t} + \frac{\partial \theta}{\partial t} y_i = \theta r_i^y \qquad i = 1,3,\ldots,K_y \tag{63}$$

with the reaction rate given by

$$r_i^y = -k_i^{by} y_i + k_i^{fy} \prod_{k=l}^{N_a} c_k^{a_{ik}^y} \prod_{k=l}^{N_s} S_k^{b_{ik}^y} \qquad i = 1,2,..,K_Y \tag{64}$$

Precipitation reactions are represented by

$$\theta \frac{\partial p_i}{\partial t} + \frac{\partial \theta}{\partial t} p_i = \theta r_i^p \qquad i = 1,2,\ldots,K_p \tag{65}$$

where the reaction rate is given by

$$r_i^p = -k_i^{bp} + k_i^{fp} \prod_{k=l}^{N_a} C_k^{a_{ik}^p} \qquad i = 1,2,..,K_p \tag{66}$$

in which K_p is the number of precipitated species of kinetic reactions, k_i^{bp}, k_i^{fp} are the modified back reaction and forward reaction rate constants for the ***i*** th precipitation reaction. This generalized formulation provides great flexibility but requires a user to Provide the needed input for specific vadose zone problems. This includes deciding which reactions are pertinent, and which are to be treated vi? equilibrium expressions.

Prediction of pH in this model is made under the assumptions of either a closed system with fixed total carbon, or possibly adding an expression for the solubility of CO, in water (open system). As discussed earlier neither of these is optimal, as there is important production of CO, in the soil, as well as losses due to diffusion and transport with the water phase. In most instances biological processes are the driving force for redox changes, and the electron balance must be expanded to include these processes. Reduction processes in the subsurface generally occur as a result of oxygen consumption and microbial production of reduced species. These equilibrium models consider only the redistribution of electrons among inorganic species, or equilibration of the system to a fixed ***pE.***

Models with specified chemistry

A number of models have been developed which are limited in the number of aqueous species and solids considered, but which nonetheless include the effects of biological processes. These models simulate specific processes and provide the user with the required reaction constants. Robbins et al. (1980a,b) developed chemical precipitation-dissolution and cation exchange subroutines using equilibrium chemistry and coupled them with a one-dimensional water movement-salt transport-plant growth model. They tested their model by comparing its results with experimental data obtained from a lysimeter study.

Robbins equilibrium chemistry model was also the basis for the numerical code LEACHMS of Wagenet and Hutson (1987). The LEACHMS and SOWATCH (Dudley and Hanks, 1991) models utilize a simplified chemical routine to predict cation exchange and major ion chemistry with calcite and gypsum solid phase control. Suarez and Dudley (1996) compared the output from LEACHMS, SOWATCH and UNSATCHEM (Suarez and Šimůnek, 1996) for a simulation with application of high alkalinity, high sodium water. All models gave somewhat different results but the LEACHMS model failed to predict high alkalinity and high exchangeable sodium. This was attributed to failure to accurately converge on the proper solution to the calcite equilibrium problem, due to use of a quadratic expression with the CO_3^{2-} term rather than a third-order solution using HCO_3^-.

Russo (1986) combined the salinity model of Robbins et al. (1980a) with the transport model of Bresler (1973) to theoretically investigate the leaching of a gypsiferous-sodic soil under different soil conditions and water qualities. With the exception of the UNSATCHEM (Suarez and Simunek, 1996) and UNSATCHEM-2D (Simunek and Suarez, 1994) models, most of these models call the equilibrium chemistry routines only once at each time step without iterating between transport and chemical modules. In many cases, as was shown by Yeh and Tripathi (1991) and Simunek and Suarez (1994), this simplification produces noticeable numerical error. This error is particularly noted in the distribution with depth of the precipitated or dissolved solid phase. The UNSATCHEM model (Suarez and Šimůnek, 1994) also differs from other open system unsaturated zone models which consider plant water uptake in that it considers kinetic as well as equilibrium processes, includes chemical effects on hydraulic conductivity, predicts CO, and pH, predicts heat transport and soil temperature and corrects equilibrium or reaction expressions for temperature effects, calculates activities using the Pitzer equations at high ionic strength, and includes a larger set of possible reactions, including B adsorption, and cation exhange with organic matter as well as clay.

In comparison to the generalized coupled equilibrium-transport models, UNSATCHEM provides a limited set of potential solid phase controls. Distinction is also made between dissolution and precipitation processes, for which kinetic expressions are utilized if natural systems are not generally at equilibrium. Precipitation processes are evaluated with consideration only for phases that control solution composition under earth surface conditions, using kinetic expressions if supersaturation persists. Published data for natural systems have indicated that kinetics and poorly crystallized phases often control solution composition. For example, studies of major ion compositions in and below the rootzone of calcareous arid zone soils have indicated that calcite equilibrium is not a reasonable assumption for predicting water composition (Suarez, 1977; Suarez et al., 1992) and that a kinetic expression yields values closer to field measurements (Suarez, 1985).

As discussed earlier, most models assume either a fixed pH or a fixed CO_2, assumptions which are questionable for soils, which often exhibit rapid fluctuations in both of these variables (Suarez and Šimůnek, 1993). Although input of pH may be suitable for ex post facto simulation of data where pH has been measured, it is generally not suitable for predictive purposes. In addition there are almost no vadose zone measurements for solution pH, as this requires specialized sampling to avoid **CO,** degassing, precipitation of carbonates and oxyhydroxides and pH shifts during solution extraction, as well as during storage.

The processes of evaporation and plant transpiration serve to concentrate the salts in the remaining soil water. When these processes are combined with irrigation in arid regions, saline conditions can result, especially during transient conditions when the water content is low. These chemical conditions require that ion activities be calculated with expressions suitable for use in brines rather than the standard formulations for dilute solutions. The interaction of evapotranspiration, changing soil gas composition, ion exchange and soil-water reactions requires that we consider the potential to precipitate or dissolve various minerals. These solids and major ions (consisting mainly of Ca, Mg, Na, Cl and SO_4 and secondarily of K, alkalinity and NO,) can accumulate in certain parts of the soil profile in such amounts that water consumption, and thus further concentration increases resulting from transpiration can be seriously reduced.

Soil temperature, which can change annually from about -10 up to +50 °C, can significantly change the thermodynamic equilibrium constants and reaction rates and therefore influence even the selection of the method used for predicting soil solution chemistry, ranging from equilibrium models to models based on kinetic expressions.

UNSATCHEM CHEMICAL MODEL

The UNSATCHEM model (Suarez and Šimůnek, 1996) includes equilibrium chemistry for aqueous species and either equilibrium or kinetic expressions for the solid phase controls. All equilibrium constants are calculated from available temperature dependent expressions. Soil temperature is calculated based on a heat flow submodel. with input of air temperature. Eight major aqueous components, consisting of Ca, Mg, Na, K, SO_4, Cl, alkalinity and B are defined, along with SO,,, CO,, and HCO, complexes. Alkalinity is defined as

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + 2[CaCO_3^0] + [CaHCO_3^+] + 2[MgCO_3^0] + [MgHCO_3^+] + 2[NaCO_3^-] + [NaHCO_3^0] + [H_2BO_3^-] - [H^+] + [OH^-] \tag{67}$$

where brackets represent concentrations. The reactions in the CO_2-H_2O system and complexation reactions for major ions have been described in numerous publications; thus further discussion is not needed.

Calcite precipitation

The equilibrium condition of a solution with calcite in the presence of CO, can be described by the expression

$$(Ca^{2+})(HCO_3^-)^2 = \frac{K_{SP}^C K_{CO_2} K_{a_1}}{K_{a_2}} P_{CO_2} (H_2O) = K_{SP}^C K_T \tag{68}$$

where parenthesis denote activities, and 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, and K_{SP}^C is the solubility product for calcite. To obtain equilibrium, i.e., when the ion activity product (IAP) is equal to the solubility product K_{SP}, a quantity x of Ca^{2+} and HCO_3^- must be added or removed from the solution to satisfy the equilibrium condition. The quantity x is obtained by solving the following third-order equation

$$[Ca^{2+}+x][HCO_3^-+2x]^2 = \frac{K_{SP}^C K_T}{\gamma_{Ca^{2+}}\gamma_{HCO_3^-}^2} \tag{69}$$

Several options are available if a kinetic condition is specified. The calcite kinetic models are almost all based on the assumption that the reaction rate is dependent on the surface area of the calcite. Of all the models, the deterministic dissolution/precipitation model of Plummer et al. (1978) is the most comprehensive, as it is based on dissolution studies over a wide range in pH (2-7.0) and CO, pressure (35Pa to 100kPa). The reaction rate of calcite dissolution in the absence of DOC is thus calculated with the rate equation of Plummer et al. (1978)

$$R^C = k_1(H^+) + k_2(H_2CO_3^*) + k_3(H_2O) - k_4\frac{K_{a_2}}{K_{SP}^C}(Ca^{2+})(HCO_3^-) \tag{70}$$

where

$$k_4 = k_1' + \frac{1}{(H_S^+)}\left[k_2(H_2CO_3^*) + k_3(H_2O)\right] \tag{71}$$

and k_1, k_2, k_3, and k_1' are temperature dependent rate constants. The dissolution-precipitation rate R^C is expressed in mmol of calcite per cm^2 of surface area per s. The term (H_S^+) is the H+ activity at the calcite surface. It is assumed that (H_S^+) = (H+) of the solution at calcite saturation when P_{CO2} at the surface equals P_{CO2} in the bulk solution.

For conditions where pH> 8 and P_{CO2} < 0.01 atm, the above Equation (70) of Plummer et al. (1978) underestimates the precipitation rate (Suarez, 1983; Inskeep and Bloom, 1985). Under these conditions it seems preferable to use the rate expression of Inskeep and Bloom (1985)

$$R^C = -k_f[(Ca^{2+})(CO_3^{2-}) - K_{SP}^C] \tag{72}$$

where k_f = 118.2 $mol^{-1}m^{-2}s^{-1}$, with an apparent Arrhenius activation energy of 48.1 kJ mol^{-1} for the rate constant.

The above relationships for calcite crystal growth, and all available calcite precipitation models, are based on a clean surface in the absence of "surface poisons". The inhibiting effect of dissolved organic matter (DOC) on calcite precipitation is well established and related to surface adsorption of DOC. Inskeep and Bloom (1986) reported on the effect of water-soluble organic carbon on calcite crystal growth. From their data we developed the following relationship (Suarcz and Simůnek, 1996)

$$r = \exp(-a_1x - a_2x^2 - a_3x^{0.5}) \tag{73}$$

which represents the reduction of the precipitation or dissolution rate due to dissolved organic carbon, where r is the reduction constant [-], x is the DOC [$\mu mol\ L^{-1}$] and a_1, a_2, and a_3 are regression coefficients (0.005104,0.000426,0.069111, respectively). This relation provided an excellent fit to the data, with an R^2 value of 0.997. The reduction constant, *r*, is then multiplied by the R^C values calculated with either Equations (70) and (71), or Equation (72). to obtain the predicted rate constant in the presence of the specified DOC concentration.

These and other calcite rate models all consider reaction rates to be proportional to surface area. For simulation of calcite dissolution in natural systems, these models may be suitable, after adjustment for the poisoning of the surface, as discussed above. However, these rate models may not be suitable for predicting calcite precipitation rates, as the concentrations of DOC in near-surface natural environments are usually comparable to levels found by Inskeep and Bloom (1986) to completely inhibit calcite crystal growth. Furthermore, these precipitation rate experiments were usually done at calcite supersaturation levels where heterogeneous nucleation rather than crystal growth was dominant. As a result calcite precipitation rates in natural environments are not related to existing calcite surface areas, and these equations serve only as empirical fitting equations.

Recently Lebron and Suarez (1996) developed a precipitation rate model which considers the effects of dissolved organic carbon both on crystal growth and heterogeneous nucleation. The combined rate expression is given by

$$R_T = R_{CG} + R_{HN} \tag{74}$$

where R_T is the total precipitation rate, expressed in mmol $L^{-1}s^{-1}$, R_{CG} is the precipitation rate related to crystal growth, and R_{HN} is the precipitation rate due to heterogeneous nucleation. The R_{CG} term is given by

$$R_{CG} = s k_{CG}\left[(\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-}) - K_{SP}\right]\left[-0.14 - 0.11 \log[\mathrm{DOC}]\right] \tag{75}$$

where s is the calcite surface area, k_{CG} is the precipitation rate constant due to crystal growth, and DOC is the dissolved organic carbon in mmol L^{-1}. The R_{HN} term is given by

$$R_{HN} = k_{HN} f(SA)(\log\Omega - 2.5)(3.37 x 10^{-4}\mathrm{DOC}^{-1.14}) \tag{76}$$

where k_{HN} is the precipitation rate constant due to hethogeneous 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). The presence of calcite (varying surface area) does not affect the calcite precipitation rate when DOC is $\geq$ 0.10 mM. We consider Equations (75) and (76) to be the most realistic for precipitation in rootzone environments while Equations (70) and (72) are most suitable for dissolution. In the presence of DOC these equations should be used in combination with Equation (73), or similar expressions which can be developed to correct for the effects of DOC on dissolution.

Precipitation of gypsum

Precipitation / dissolution of gypsum can be described by

$$[Ca^{2+}][SO_4^{2-}] = \frac{IAP}{\gamma_{Ca^{2+}} \cdot \gamma_{SO_4^{2-}} \cdot (H_2O)^2} \qquad (77)$$

To obtain equilibrium, i.e., when the IAP is equal to the solubility product K_{SP}^{G}, a quantity of gypsum, x, must be added or removed from the Ca^{2+} and SO_4^{2-} concentrations in solution, obtained by solving the quadratic equation.

Magnesium precipitation

The UNSATCHEM model considers that Mg precipitation can occur as a carbonate (either nesquehonite or hydromagnesite), or as a silicate (sepiolite). 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). With this consideration magnesite can be neglected, as it apparently does not form at earth surface temperatures, is relatively rare, and its dissolution rate is exceedingly small, such that its solubility has not yet been satisfactorily determined from dissolution studies at or near 25°C. Similarly, dolomite precipitation is not considered, since true dolomite appears to very rarely form in soil environments. If dolomite is present in the soil, the model uses the kinetic formulation of Busenberg and Plummer (1982) to represent the dissolution process. The dissolution rate of dolomite is very slow, especially when the solution IAP values approach within 2 to 3 orders of magnitude of the solubility product.

If nesquehonite or hydromagnesite saturation is reached, the model will precipitate the predicted Mg carbonate. The Mg carbonate precipitated, combined with calcite precipitation, will likely represent the mixed Ca Mg precipitate called protodolomite. However, the resulting solution composition is much different than that produced by simply forcing equilibrium with respect to dolomite, as the model forms this mixed precipitate (calcite + magnesium carbonate) under conditions of approximately three orders of supersaturation with respect to dolomite. This result is consistent with the high levels of dolomite supersaturation maintained in high Mg waters (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_{SP}^{S} greater than that of well crystallized sepiolite. Formation of this mineral requires high pH, high Mg concentrations ‘and low CO, partial pressure.

Precipitation of nesquehonite and hydromagnesite

At 25°C and at CO_2 partial pressures above $10^{-3.27}$ kPa, nesquehonite $MgCO_3 \cdot 3H_2O$ is stable relative to hydromagnesite. The precipitation (if saturation is achieved) or dissolution of nesquehonite (if specified as a solid phase) in the presence of CO_2 can be described by

$$MgCO_3 \cdot 3H_2O + CO,(g) \rightleftarrows Mg^{2+} + 2HCO_3^- + 2H_2O \qquad (78)$$

with the solubility product K_{SP}^{N} defined by

$$K_{SP}^{N} = (Mg^{2+})(CO_3^{2-})(H_2O)^3 \qquad (79)$$

Substituting the equation for Henry’s law for solubility of CO_2 in water, and the equations for the dissociation of carbonic acid in water into the solubility product, we obtain:

$$(Mg^{2+})(HCO_3^-)^2 = \frac{K_{SP}^N K_{CO_2} K_{a_1} P_{CO_2}}{K_{a_2} (H_2O)^2} = \frac{K_{SP}^N K_T}{(H_2O)^3} \tag{80}$$

The equation is solved for equilibrium in a manner similar to that used for calcite, with a third order equation.

The precipitation or dissolution of hydromagnesite in the presence of CO_2 can be described by

$$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O + 6CO_2(g) \rightleftarrows 5Mg^{2+} + 10HCO_3^- \tag{81}$$

Similarly the equilibrium condition is defined by

$$(Mg^{2+})^5(HCO_3^-)^{10} = \frac{K_{SP}^H K_{CO_2}^6 K_{a_1}^{\,6} P_{CO_2}^6}{K_{a_2}^{\,4} K_w^2} = K_{SP}^H K_T \tag{82}$$

Again the equilibrium condition is solved as described for calcite and nesquehonite.

Precipitation of sepiolite

The precipitation or dissolution of sepiolite in the presence of CO, can be described by

$$Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O + 4.5H_2O + 4CO_2(g) \rightleftarrows 2Mg^{2+} + 3H_4SiO_4^0 + 4HCO_3^- \tag{83}$$

with the solubility product $K_{SP}{}^S$ defined by

$$K_{SP}^S = \frac{(Mg^{2+})^2(H_4SiO_4^0)^3(OH^-)^4}{(H_2O)^{4.5}} \tag{84}$$

In this instance we utilize the precipitated sepiolite solubility value given by Wollast et al. (1968) rather than the well crystallized equilibrium value. Freshly precipitated sepiolite has been prepared in the laboratory at IAP values of 10^{-35} comparable to the $K_{SP}{}^S$ listed by Wollast et al. (1968), thus we consider that a kinetic expression for precipitation is not essential for prediction of unsaturated zone solution composition. The equilibrium condition is expressed as

$$(Mg^{2+})^2(HCO_3^-)^4 = \frac{K_{SP}^S K_{CO_2}^4 K_{a_1}^{\,4} P_{CO_2}^4 (H_2O)^{4.5}}{K_w^4 (H_4SiO_4^0)^3} = K_{SP}^S K_T \tag{85}$$

Relatively little information exists on the controls on Si concentrations in soil waters, especially in arid zones. In soil systems Si concentrations are not fixed by quartz solubility but rather by dissolution and precipitation of aluminosilicates and Si adsorption onto oxides and aluminosilicates. As a result of these reactions Si concentrations in soil solution follow a U shaped curve with pH, similar to Al oxide solubility with a Si minimum around pH 8.5 (Suarez 1977b).

There are two options in UNSATCHEM to predict Si concentrations in solution. In arid land soils it is assumed that Si in solution is a simple function of pH, fitted to data from 8 arid land soils reacted at various pHs for two weeks by Suarez (1977b), as follows

$$\Sigma \mathrm{SiO_2} = 0.001\,(6.34 - 1.43\,\mathrm{pH} + 0.0819\,\mathrm{pH}^2) \qquad (86)$$

where SiO_2 is the sum of all silica species expressed in mol L^{-1}. This relationship likely provides only a rough estimate of Si concentrations, but we consider it acceptable because it is used only to restrain Mg concentrations at high levels of evapotranspiration, when Mg concentrations become very high at low CO, and elevated pH.

An additional option is to consider the Si concentration to be controlled by inputs from mineral weathering and concentrated only by processes of evapotranspiration. In this case UNSATCHEM utilizes kinetic expressions for the weathering of selected silicate minerals. Options are available for two kinetic models.

Silicate weathering

Several different rate expressions have been used for feldspar dissolution, the most successful of which are variations of the Furrer and Stumm (1986) model

$$R_t = R_H + R_L$$

$$R_H = k_H (C_H^s)^n \qquad (87)$$

$$R_L = k_L\, C_L^s$$

where $R_{t''}$, R_H and R_L are the proton and ligand promoted rates, k_L and **k,,** are the rate constants, C_H^S and C_L^S are, respectively, the surface concentrations of protons and ligands and *n* is the order of the reaction.

The Furrer and Stumm (1986) model developed for oxides, is not able to simulate the silicate dissolution rates in the pH range 3 to 8 (Amrhein and Suarez, 1988). Amrhein and Suarez (1988) modified this equation by adding a rate term proportional to the uncharged surface silanol groups and substituting the term Γ, which represents the sum of the proton and hydroxyl sites for the term C_H^S in Equation (87). Combining the surface proton and hydroxyl sites into one expression was justified by the essentially equal effects of the two surface groups on the dissolution rates of plagioclase feldspars. This has been determined experimentally in the work of Chou and Wollast (1985) for albite and Amrhein and Suarez (1988) for anorthite, representing the end members in the plagioclase feldspar series. However, other studies indicate that this equality cannot be generalized, thus we use the modified rate equation

$$R_t = a[\Gamma]^{4\,0} + a'\,[\Gamma']^{4.0} + b\,[\mathrm{SOH}] + c\,[\mathrm{S\text{-}L}] \qquad (88)$$

where ***a, a', b,*** and c are the rate coefficients for the proton, hydroxyl, neutral, and surface-ligand sites and I', I'', ***SOH,*** and S-L are the surface concentrations of proton, hydroxyl, neutral and surface ligand sites. Detailed rate data for use with Equation (88) are not available for all silicates, however in the pH range of 5 to 9 this equation can often be simplified to

$$R, = b\,[\mathrm{SOH}] + c\,[\mathrm{S\text{-}L}] \tag{89}$$

when $R,$ is expressed in mmol m^{-2} s^{-1}, b and c are equal to 2.09 x 10^-8 (1/s) and 4.73 x 10^{-6} (s^{-1}), respectively, for anorthite, and SOH, the total number of surface sites is taken as 0.12 mmol m^{-2} (Amrhein and Suarez, 1988).

Using the rate model expressed in Equation (89), and assuming the restricted pH range of 5 to 9, UNSATCHEM includes dissolution kinetics for anorthite, labradorite, albite, potassium feldspar, biotite and hornblende, based on specific surface areas of the minerals, and the assumption that the released Al is retained by formation of kaolinite. The selected rate constants, where available, are based on long-term weathering studies in experiments which minimized the effects of grinding and pretreatment artifacts.

An alternative approach to the Furrer and Stumm (1986) model is the rate model of Sverdrup and Warfvinge (1988)

$$R = k_{H^+} \frac{[\mathrm{H}^+]^n}{[\mathrm{M}]^x[\mathrm{Al}^{3+}]^y} + \frac{k\mathrm{H_2O}}{[\mathrm{Al}^{3+}]^u} + k_{CO_2} \cdot P_{CO_2} + k_{\mathrm{org}}[org]^{0.5} \tag{90}$$

where k is the reaction rate for the different processes, and n,x,y,u, and m are the reaction orders, all determined experimentally. Equation (90) is utilized with the reaction rates given by Sverdrup and Warfvinge (1988).

The kinetic models based on Furrer and Stumm (1986) as well as the Sverdrup and Warfvinge (1988) model do not consider a back reaction expression. This omission is acceptable only if the solution is very far from equilibrium with these phases. At earth surface temperatures all the above considered silicates are very unstable with respect to clays and oxides, and the solution phase remains very undersaturated with respect to these minerals. At elevated temperatures back reaction expressions must be added, as these mineral become the stable phases.

Cation exchange

Cation exchange is generally the dominant *chemical* process for the major cations in solution in the unsaturated zone. Cation exchange is usually treated with a Gapon-type expression of the form (White and Zelazny, 1986)

$$K_{ij} = \frac{\bar{c}_i^{y+}}{\bar{c}_j^{x+}} \frac{(c_j^{x+})^{1/x}}{(c_i^{y+})^{1/y}} \tag{91}$$

where y and x are the respective valences of species i, and j, and the overscored Concentrations are those of the exchanger phase (concentration expressed in $mol_c\,mass^{-1}$). It is assumed that the cation exchange capacity c_T is constant, and that for non-acid soils

$$\bar{c}_T = \overline{\mathrm{Ca}}^{2+} + \overline{\mathrm{Mg}}^{2+} + \overline{\mathrm{Na}}^{+} + \overline{\mathrm{K}}^{+} \tag{92}$$

Existing chemical models require either input of a soil specific selectivity value or use a generalized value for the selectivity coefficient. We note that the 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 two sets of equations for cation exchange (clay and organic matter).

Anion adsorption

Prediction of the mobility of minor element anions such as B, As and Se generally requires consideration of adsorption processes. Among the modeling approaches utilized are retardation factors (as discussed earlier), and Langmuir and Freundlich isotherms. These models generally require the input of adsorption isotherm values specific to a given pH. Such an approach is of limited value when used in transport models which need to consider a range of pH values, since anion adsorption is highly dependent on pH. Keren et a1.(1981) developed a modified Langmuir expression to account for the effect of pH on B adsorption, given as

$$Q_{BT} = T\left\{1 + \frac{PR}{F(Q_T - Q_{BT})}\left[1 + K_{OH}(OH^-)\right]\right\}^{-1} \tag{93}$$

where Q_{BT} is the total adsorbed B, Q_T is the total B (adsorbed + in solution), T is the total adsorption capacity for B, $P=K_H(OH^-)10^{14}+1$, R is the solution/clay ratio, expressed in L/g clay, $F=K_{HB}+K_B(P\text{-}1)$, and K_{HB}, K_B, K_{OH}, are constants relating to the binding energy for the ions $B(OH)_3$, $B(OH)_4^-$, and OH^-, respectively. The term K_H is the equilibrium constant of the reaction:

$$B(OH)_3 + H_2O \rightleftarrows B(OH)_4^- + H^+ \tag{94}$$

This model has been incorporated into the B transport model described by Shani et al. (1992). Anion adsorption is also treated in the one-dimensional saturated water flow model TRANQL (Cederberg et al., 1985) using the constant capacitance model, in HYDROGEOCHEM using the triple layer model, and in the variably saturated flow model UNSATCHEM using the constant capacitance model.

The constant capacitance model is also able to represent the effect of pH on adsorption affinity, and in contrast to the empirical Langmuir model, is intended to provide chemical representation of the system. The model contains the following assumptions: adsorption is a ligand exchange mechanism, all surface complexes are inner sphere, no surface complexes are formed with other salts in solution. The relation between the surface charge and the surface potential is given by

$$\sigma = \frac{CSa}{F}\Psi \tag{95}$$

where C is the capacitance density(F m^{-2}), S is the specific surface area ($m^2\,g^{-1}$), a is the suspension density (g L^{-1}), F is the Faraday constant (coulombs mol_c^{-1}), Ψ is potential (volts) and σ is expressed in mol_cL^{-1}. The intrinsic conditional equilibrium constants corresponding to B adsorption are (Goldberg and Glaubig, 1985)

$$K_+ = \frac{[SOH_2^+]}{[SOH]\,[H^+]}\exp[F\Psi/RT] \tag{96}$$

$$K_b = \frac{[SH_2BO_3]}{[SOH]\,[H_3BO_3]} \tag{97}$$

$$K_- = \frac{[SO^-][H^+]}{[SOH]}\exp[-F\Psi/RT] \tag{98}$$

The mass balance equations for the surface functional groups and B are given by

$$[SOH]_T = [SOH] + [SOH_2^*] + [SO^-] + [SH_2BO_3] \tag{100}$$

$$B_T = H_3BO_3 + SH_2BO_3 \tag{99}$$

and the charge balance equation for the surface is defined by

$$\sigma = [SOH_2^+] - [SO^-] \tag{101}$$

In the absence of soil specific data the model utilizes average soil constants of 9.3, -10.6, and 5.5, for the values of log K_+, log K_-, and log K_B, respectively (Goldberg, 1993). We utilize the value of 1.06 Fm^{-2} for the capacitance (C). Using the data of Goldberg and Glaubig (1986), the following expression relates the experimentally determined adsorption site density to soil surface area

$$[SOH]_T = 2.53 \cdot 10^{-7} + 4.61 \cdot 10^{-9} \cdot S \tag{102}$$

where S is expressed in m^2 g^{-1} and adsorption density ih mol g^{-1}. The system is defined by input of a soil surface area, specifying initial conditions, B concentration in the input water and calculating suspension density a from water content and bulk density.

EXAMPLE SIMULATIONS USING *UNSATCHEM*

In this section two sets of simulations are presented. In the first example we evaluate the impact of different CO, assumptions and different calcite models (equilibrium versus kinetic) on solution chemistry. In the second example we evaluate the impact of the chemical composition on hydraulic parameters and the resultant water flow and chemical composition in the profile.

The effect of model assumptions regarding carbonate chemistry and CO$_2$ which influence vadose zone chemistry can be demonstrated by an example involving various simulations. In this example we consider the recharge of water having the following composition (Welton-Mohawk drainage well #616; reported in Suarez, 1977), expressed in mmol$_c$L^{-1}: Ca= 5.05; Mg, 6.34; Na, 17.2; K, 0.234; Cl, 111.3; alkalinity, 7.18; SO$_4$, 15.0; and NO,, 0.8. This water is applied to a field at the rate of 15 cm/day for 0.5 days, once a week. The infiltration is into a loam soil with a K_s of ***24.4*** cm/day. The potential evapotranspiration is constant at 1.0 cm/day and the soil temperature is taken as 20°C. An exponential root distribution is used to describe root water uptake. The simulations were made for 365 days.

Figure 1 shows the Cl concentration distribution with time. The increase with depth is due to plant root extraction, concentrating the salts by a factor of 5. In arid zone regions evapotranspiration exerts a dominant influence on solution chemistry. The profiles in Figure 1 indicate that it takes approximately one year to stabilize the Cl concentration at the 100 cm depth. The concentration distribution in the shallow depths continue to undergo a cyclical change related to the infiltration events (data not shown). Figures 2a and 2b show the Ca and alkalinity concentrations with depth and time assuming atmospheric CO, throughout the profile and calcite equilibrium. This simulation corresponds to what would be predicted with a closed system model where total carbon rather than alkalinity is input. Since the well water is initially supersaturated, the simulation forces an immediate and drastic precipitation at the soil surface to achieve equilibrium (Ca decreases to below 0.8 mmol$_c$L^{-1}). Calcium concentrations also decrease with depth due to calcite precipitation (because alkalinity> Ca). The pH is 8.5 at the surface and increases to 8.8 with depth.

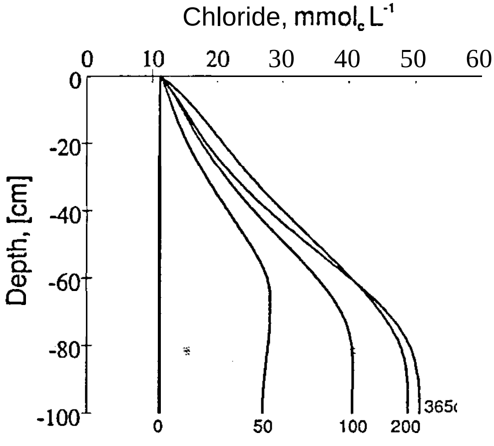
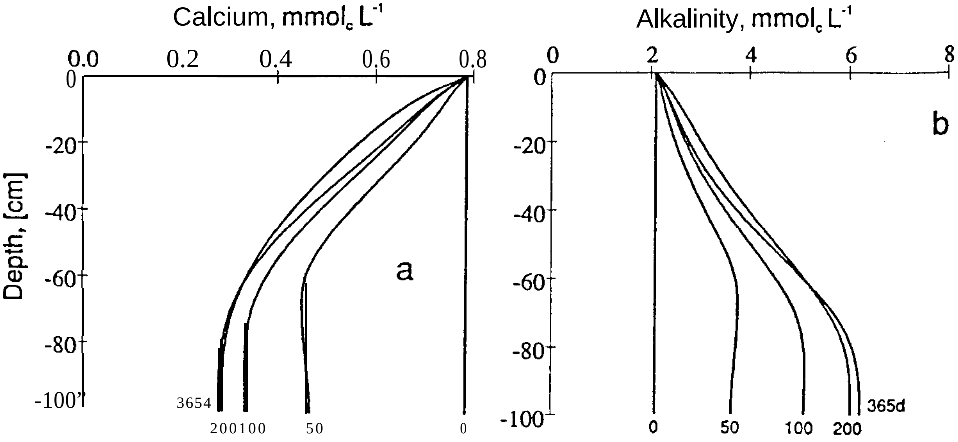


Figure 1 (right). Chloride concentration with time and depth.

Figure 2 (below). (a) Calcium and (b) alkalinity concentrations with depth and time assuming calcite equilibrium and atmospheric CO,.



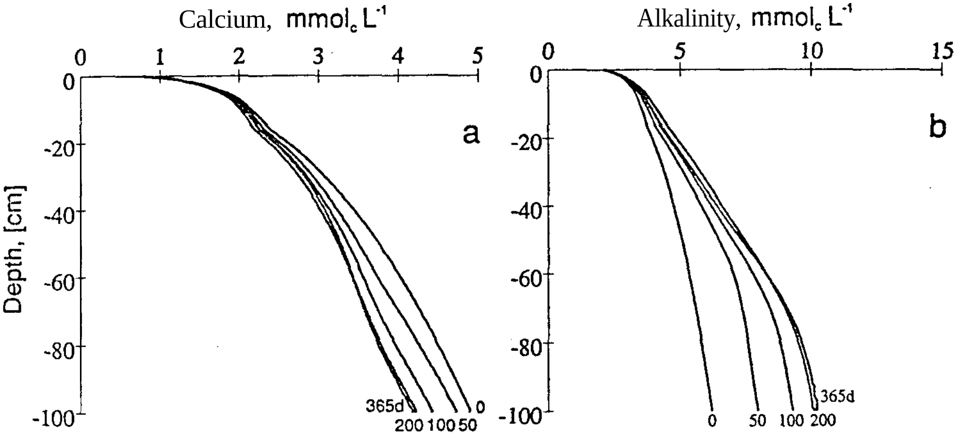


Figure 3. (a) Calcium and (b) alkalinity concentrations with depth and time assuming calcite equilibrium and CO, increasing linearly from atmospheric CO, at the surface to 0.02 atm (20 kPa) at 100 cm.

Figure *3* shows the Ca and alkalinity distributions with time and depth using the assumption of atmospheric CO, at the surface, increasing linearly with depth to a value of 0.02 atm CO_2 at 100 cm. Calcium concentrations now increase with depth, in contrast to Figure 2 where Ca concentrations decreased with depth. Calcium concentrations shown in Figure 3a are also much greater at the bottom of the profile than the concentrations shown in Figure 2a. Increasing Ca and alkalinity result from the increase in CO, with depth. The pH decreased from 8.5 at the surface to 7.35 at the bottom of the profile. Figure 4 shows the Ca, alkalinity, pH and pIAP for $(Ca^{2+})(CO_3^{2-})$ assuming a linear increase in CO_2 from atmospheric at the surface to 0.02 atm at 100 cm and a kinetic model for calcite precipitation/dissolution. Ca concentrations are greater throughout the profile as compared to the earlier simulations, especially in the shallow zones where supersaturation is greatest. As discussed earlier these represent realistic calcite saturation values. The pH was 8.9 at the surface and decreased to 7.4 at the bottom of the profile.

Figure 5 shows the Ca, alkalinity, pIAP for $(Ca^{2+})(CO_3^{2-})$, and CO_2 distribution with depth and time using the kinetic model and the CO_2 production transport model in UNSATCHEM (described in Šimůnek and Suarez, 1993b), with a CO_2 production term of 0.42 $cm^3/cm^2/day$. Calcium and alkalinity concentrations in the shallow and intermediate depths are greater than the concentrations in the earlier simulations. This increase is caused by the CO, distribution shown in Figure 5, with a CO_2 maxima near the surface. In contrast, the earlier simulations utilized a fixed CO_2 increasing linearly with depth. The cycles in the CO_2 distribution reflect the cyclic pattern of CO_2 increases associated with the infiltration events. The pIAP values show a rapid shift from supersaturation to undersaturation just below the surface, again related to the rapid increase in CO,,

The effect of soil type on CO, concentration and solution composition is demonstrated by the simulation shown in Figure 6. In this instance we again used the kinetic model for calcite and the CO, production/transport option. The only difference is that we now infiltrate the same amount of water into a silt loam with a K_s of 6 cm/day instead of into a loam soil. The Ca and alkalinity concentrations shown in Figure 6 are much greater than those shown for the other simulations. In this simulation water was

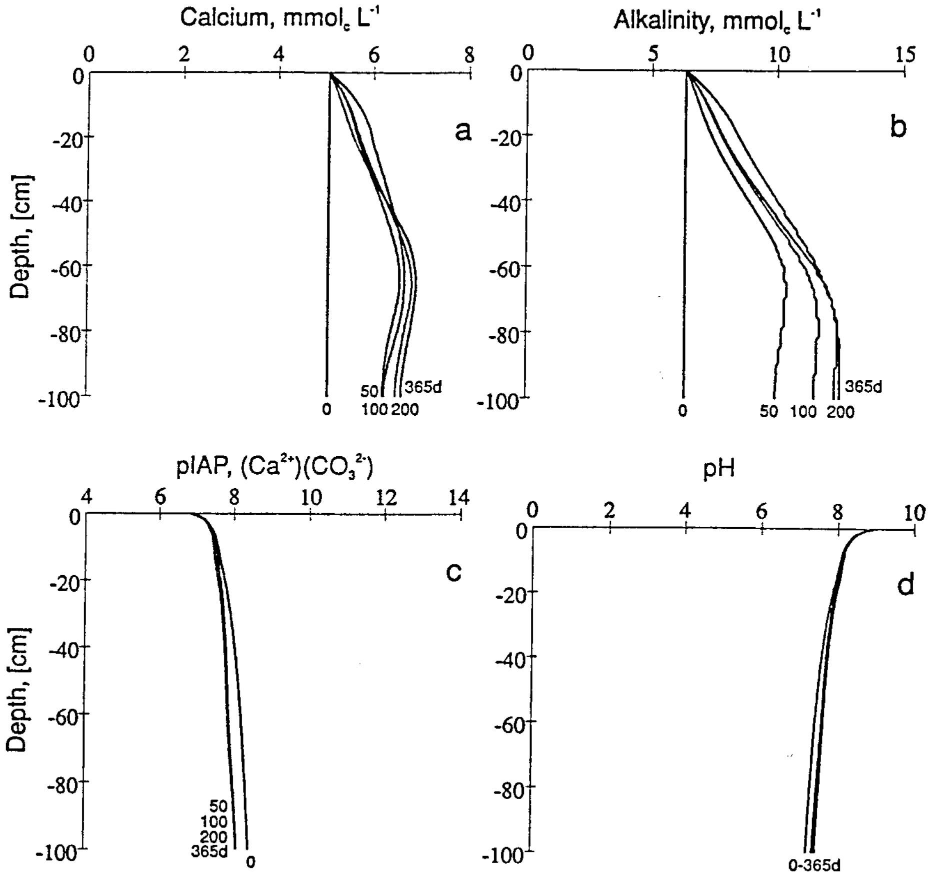
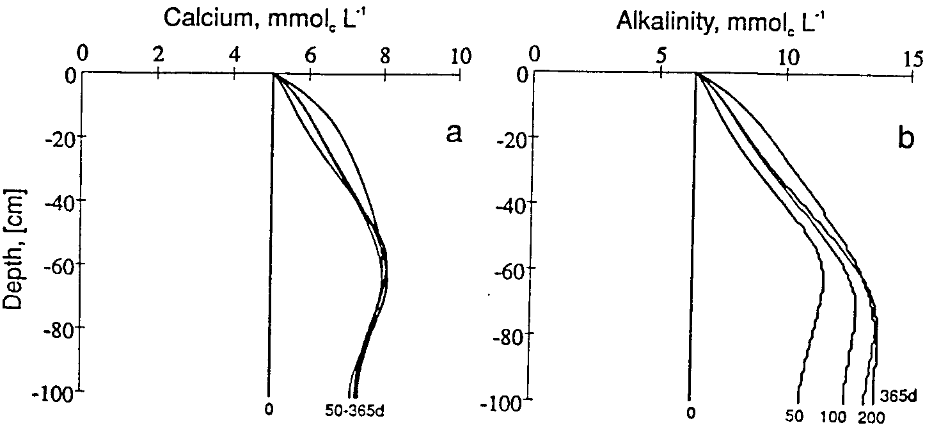


Figure 4 (above). (a) Calcium and (b) alkalinity concentrations and (c) pIAP $(Ca^{2+})(CO_3^{2-})$ and (d) pH with depth and time assuming a calcite kinetic model and CO_2 increasing linearly from atmospheric CO_2 at the surface to 0.02 atm. (20 kPa) at 100 cm.

Figure 5 (below). (a) Calcium and (b) alkalinity with depth and time assuming a calcite kinetic model and CO_2 predicted by the production/transport submodel. [Figure 5 continued next page.]



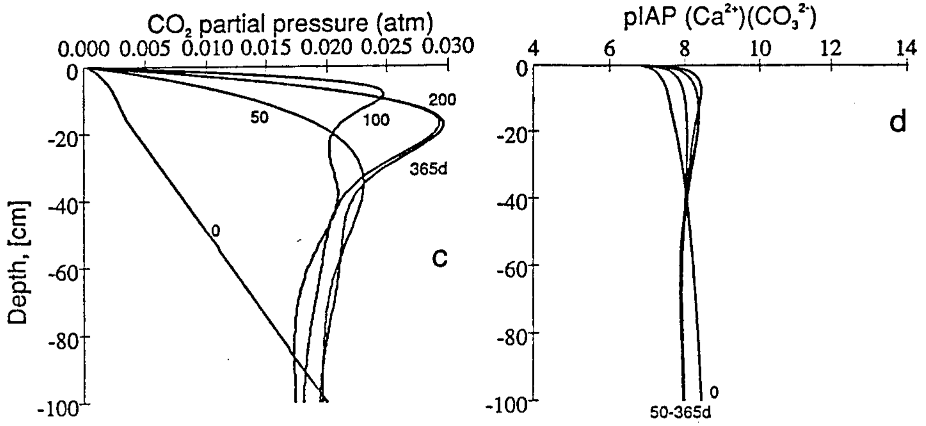
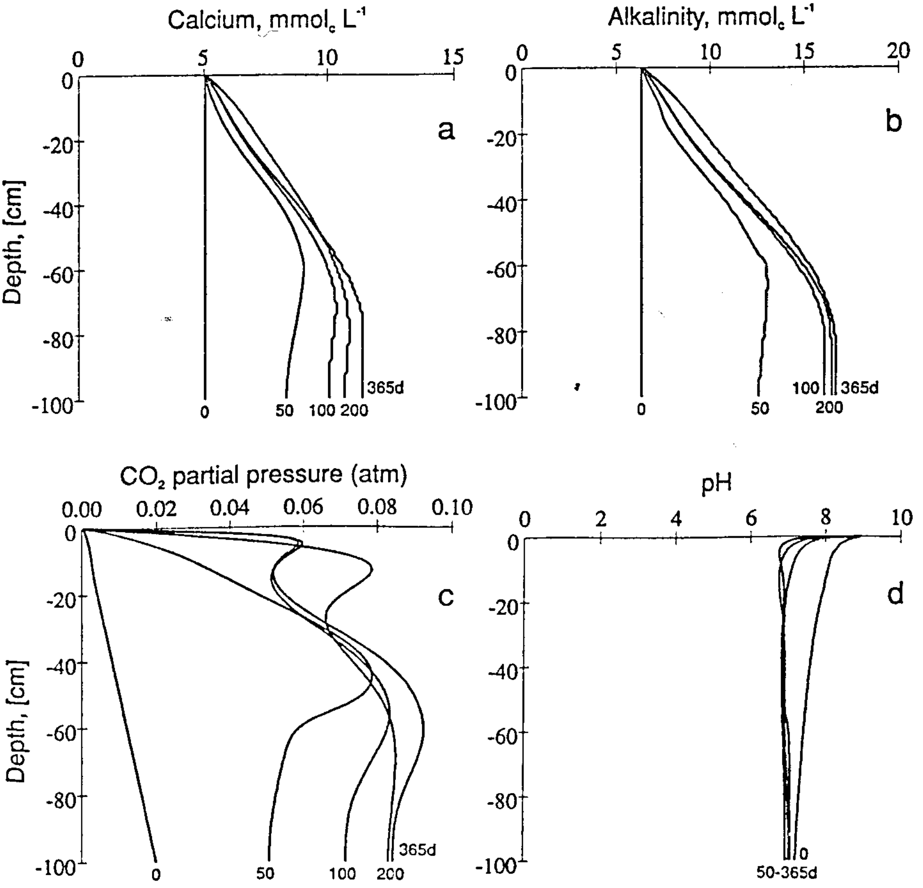


Figure 5 (above). (c) CO_2 partial pressure and (d) pIAP $(Ca^{2+})(CO_3^{2-})$ with depth and time assuming a calcite kinetic model and CO_2 predicted by the production/transport submodel.

Figure 6 (below). (a) Calcium and (b) alkalinity, (c) CO_2 partial pressure and (d) pH with depth and time assuming a calcite kinetic model and CO_2 predicted by the production/transport submodel. This simulation assumed infiltration into a silt loam soil.



ponded on the surface during the infiltration and resulted in greater water content at the surface. This in turn resulted in decreased CO, diffusion out of the soil and thus increased the soil CO_2, as shown in Figure 6. Soil pH was also much lower, as can be seen from the comparison of Figure 6 with the data given for the earlier simulations. These simulations demonstrate the interaction of biological processes and soil physical properties on the chemical composition in the vadose zone. Predictions resulting from kinetic simulation of calcite reactions and dynamic, process-based simulation of soil CO, production and transport, rather than arbitrary model input assumptions, result in vastly different solute compositions and pH.

In the second example we assume that water is ponded continuously on a sodic soil, without rootwater uptake. In the absence of adverse chemical effects the soil has a saturated hydraulic conductivity of 60.5 cm/d, $\theta_r=0.000, \theta_s=0.48, n=1.592$ and $\alpha=0.015022\ cm^{-1}$. The cation exchange capacity was 200 mmol, kg-‘. The charge fraction on the exchanger was as follows: Ca, 0.2; Mg, 0.2; Na, 0.6. The initial soil water composition (before equilibration with the exchanger phase) expressed in $mmol_cL^{-1}$ is: Ca= 0.2; Mg, 0.2; Na, 4.8; Cl, 4.6; alkalinity, 0.4; and SO,, 0.0. The composition of the infiltrating water was as follows, expressed in $mmol_cL^{-1}$: Ca= 1.5; Mg, 0.5; Na, 2.0; Cl, 1.0; alkalinity, 0.5; and SO,, 2.5.

In the first simulation of example 2 we do not consider the effect of solution chemistry on hydraulic conductivity. Figure 7a shows the infiltration of the tracer into the soil. After 0.6 d the front has moved almost to the bottom of the profile. The infiltration rate into the unsaturated soil exceeds the saturated hydraulic conductivity and then decreases to the 60.5 cm/d rate as the soil becomes saturated. As shown in Figure 7b it takes approximately 100 d for the soil solution Ca concentration to reach the concentration of the infiltrating water. The “retardation” of the Ca front is primarily due to Ca exchange with Na.

In the second simulation we utilize the functions described earlier which account for the chemical effects on hydraulic conductivity. The initial hydraulic conductivity is 2.4 X 10^{-5} cm/d, which increases to only 0.0128 cm/d as water saturation is achieved. As shown in Figure 8a after 5 years the tracer concentration in the profile has not yet stabilized to the infiltrating concentration. This delay is due to the reduced hydraulic conductivity. Note that the infiltration front of the tracer shown in Figure 8a is not as sharp as the front shown in Figure 7a, this is attributed to the increased importance of diffusion at slow infiltration rates. The Ca concentration profiles, shown in Figure 8b indicate that it takes 238 y for the Ca front to reach the 80 cm depth. Essentially all of the exchange occurred in the last 30 y. The infiltration rate increased rapidly in this time frame, as the increased Ca concentration allowed for increased infiltration which in turn allows for increased exchange.

The second set of simulations, shown in Figure 7 and Figure 8, demonstrate the importance of chemical effects on infiltration, as well as the effects of infiltration on solution chemistry. Such simulations are not only useful for describing the reclamation of a sodic agricultural soil but, are also directly applicable to waste disposal problems. Modeling contaminant transport likely represents the single largest use of chemical transport models. Sodium saturated smectites (bentonite) have been widely used in waste disposal and waste holding ponds. Such ponds have often been constructed without consideration of the effect of the waste solution on the physical properties of the restrictive clay layer. Consistent with field observations we predict that the layers can fail catastrophically due to conversion of the clay from Na-saturated to Ca saturated, causing a rapid increase in infiltration of the waste. This failure can occur after a variable

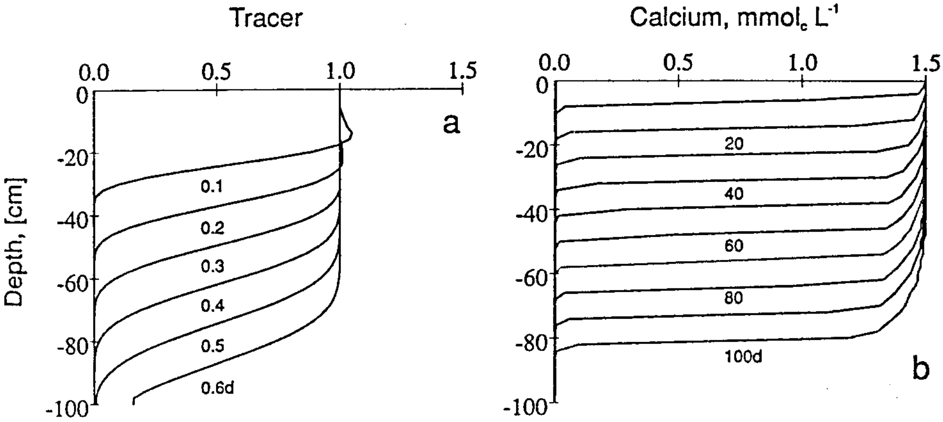


Figure 7. (a) Tracer and (b) Ca concentrations with depth and time assuming no effect of chemical composition on hydraulic properties. Simulation is infiltration of ponded water into a soil with a saturated hydraulic conductivity of 60.5 cm/d.

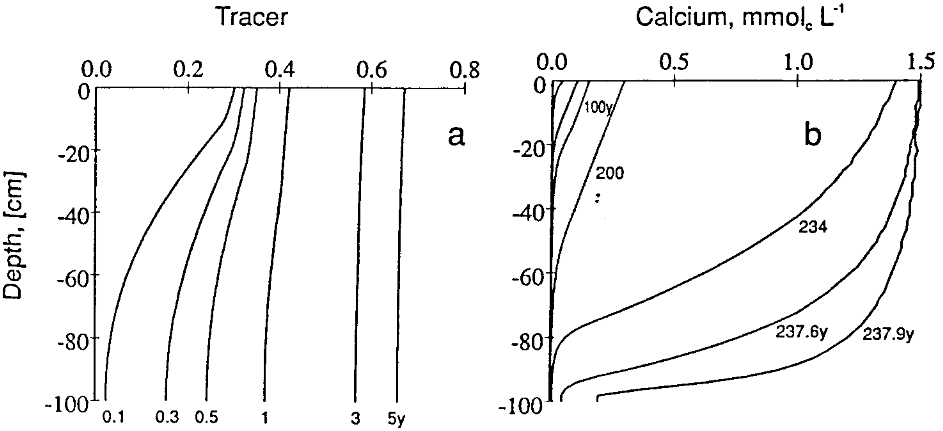


Figure 8. (a) Tracer and (b) Ca concentrations with depth and time assuming that the chemical composition of the solution affects the hydraulic properties. Simulation is infiltration of ponded water into a soil with a (optimal) saturated hydraulic conductivity of 60.5 cm/d.

number of years, depending on the initial hydraulic properties, layer thickness and solution composition. Models which attempt to simulate such processes must consider the chemical effects on soil physical properties.

FUTURE DEVELOPMENTS

Improvements in simulating solute transport in natural systems will require improved representations of the underlying chemical and physical processes. Kinetic expressions are lacking for realistic representation of most chemical processes under field conditions. At present there are no suitable representations for predicting changes in redox nor sufficient rate data for redox reactions. Representation of water flow using the Richards' equation is often not satisfactory for describing flow in natural environments. Many field scale simulations require three-dimensional representations of water flow. Computer codes which treat three-dimensional problems have not yet been coupled to solute transport and solution chemistry. Also needed are improved methods for estimating relevant flow, transport, and chemical parameters and their spatial distributions as input to the models. Finally we note that progress in model development is hindered by the severe lack of detailed field experiments which are needed to critically evaluate the existing models.

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