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MODELING EQUILIBRIUM AND KINETIC MAJOR ION CHEMISTRY WITH CO₂ PRODUCTION/TRANSPORT COUPLED TO UNSATURATED WATER FLOW

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ABSTRACT

Modeling the aqueous phase composition in the unsaturated zone requires prediction of the gas-phase composition as well as water flow and chemical reactions. We discuss and demonstrate the use of two finite-element codes developed for variably saturated media at near earth-surface temperature. The SOILCO₂ code was designed for predicting the CO₂ concentration in the unsaturated zone, while the UNSATCHEM-2D code was designed for predicting major ion composition in the unsaturated zone. The SOILCO₂ code couples CO₂ production and transport with a variably saturated water flow model. The UNSATCHEM-2D code couples a variably saturated water flow model to CO₂ production and transport, solute transport, and major ion chemistry submodels. Since the solution chemistry in the unsaturated zone is significantly influenced by variations in water content, and in temperature and CO₂ concentrations in the soil gas, all these variables are calculated by the models. The CO₂ transport submodel includes both liquid and gas-phase transport. The production sub-model accounts for microbial and root respiration of CO₂, both of which are dependent on water content, temperature, salinity, and plant and soil characteristics. The chemistry sub-model accounts for equilibrium reactions such as precipitation, cation exchange, and precipitation-dissolution among the major chemical species. In addition, the user can select either equilibrium or multicomponent kinetic expressions for precipitation-dissolution of calcite and dolomite. Precipitation-dissolution reactions are also included for gypsum, and for various carbonate and silicate phases.

Modified Detye-Hückel as well as Pitzer expressions were incorporated into the sub-model to calculate single-ion activities for the range of dilute to hypersaline waters. Examples are presented to demonstrate the applicability of the codes for predicting CO₂ concentrations and transport, and for simulating soil chemical processes and changes in dissolved major ion composition with time and depth.
INTRODUCTION

Prediction of groundwater quality requires consideration of the chemical composition of recharge water. This, in turn, requires modeling of water flow and solute transport, as well as pertinent chemical processes in the unsaturated zone. This modeling is especially important for environmental concerns related to human activities, where steady-state assumptions are not likely to be valid. Realistic modeling of chemical processes in the unsaturated zone requires consideration of processes in the gas, liquid, and solid phases. Among the important factors influencing chemical dynamics in the unsaturated zone are water flow, heat transport, and dynamic changes in CO₂ concentrations. Water is not only the transport medium for inorganic dissolved chemicals but also significantly affects the production and concentration of CO₂. Soil temperature affects thermodynamic constants and reaction rates and, more importantly, the production of CO₂. The CO₂ concentration exerts a major control on the biological and chemical processes in the soil, and has a direct effect on the solution chemistry of the entire subsurface. Variations in soil CO₂ concentration produce changes in soil pH (for all but acid soils), and thus alter the solubility of many solid phases (e.g., carbonates and oxyhydroxides), and the transport of species whose absorption is pH-dependent.

Over the past two decades a large number of models have been developed to quantify the physical and chemical processes affecting major ion transport. Hydrological models for water flow, solute transport, and aqueous equilibrium chemistry were developed independently of one another, and only recently has there been a significant effort to couple these models. Solute transport models typically considered only one solute and greatly simplified the different chemical processes (Yeh and Huff, 1985; Huyakorn et al., 1991). For example, the complex processes of adsorption and cation exchange were usually accounted for by linear or Freundlich isotherms, where all reactions between solid and liquid phases were lumped into a distribution coefficient, \( K_d \), and possibly into the nonlinear exponent, so that the adsorption processes were modeled independently of the behavior of other solution species. Other processes, such as precipitation, biodegradation, volatilization or radioactive decay, were simulated by simple first- or zero-order rate constants. Several models were developed that simulate several solutes involved in sequential first-order decay reactions (Guregian, 1981; Wagener and Hutson, 1987; Šimůnek and van Genuchten, 1994).
Researchers have also addressed the problem of coupling hydrological models for water flow and solute transport with chemical equilibrium models. Recent reviews of hydrogeochemical transport models that consider multiple reactive chemical components were presented by Yeh and Tripathi (1988) and Mangold and Tsang (1991). Until now, most of the models were developed for saturated water flow where changes in water velocity, temperature, and pH are relatively gradual and hence less important than in the unsaturated zone. Therefore, most models are based on one-dimensional, steady-state, saturated water flow with fixed water velocity, temperature, and pH (e.g., Valocchi et al., 1981; Jennings et al., 1982; Walsh et al., 1984; Cedergreen et al., 1985; Kirkner et al., 1985; Bryant et al., 1990; Förster and Gerke, 1989). Only recently were several models published that can be applied to problems that include multicomponent reactive solute transport and variably saturated water flow (Liu and Narasimhan, 1989; Yeh and Tripathi, 1991). In addition, 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, solute transport, and plant growth model. Robbins’ equilibrium chemistry model was also the basis for the numerical code LEACHM of Wagenet and Hutson (1987).

The chemical reaction and multicomponent transport models described above use either the total inorganic carbon as a conservative property and/or fixed pH as an input variable. This approach can be used only for closed systems, which makes it applicable to the chemistry of only some groundwater systems (Suarez, in press); nonetheless, it has also been applied to open systems such as soil environments. The alternative assumption of an open system with fixed CO$_2$ is preferable to an assumption of fixed pH, but it suffers from not accounting for the dynamics of the gas phase. In the unsaturated zone, the CO$_2$ concentration varies in space and time, resulting in increases in dissolved inorganic carbon and decreases in soil pH when CO$_2$ increases. Use of the open system, variable CO$_2$ concentration (that allows for transfer of carbon into or out of the system), and the use of alkalinity as an input variable is preferable, because alkalinity is conserved during changes in soil CO$_2$ (and is transferred to the solid phase during precipitation).

Since the assumption of time-invariant CO$_2$ is often not realistic, there is a need to couple multicomponent models not only to variably saturated water flow and solute transport models, but also to CO$_2$.
transport-production models. Modeling of the spatial distribution and fluxes of CO₂ has been limited and was undertaken mostly through statistical correlation with specific parameters such as air or soil temperature, latitude, and soil water content. Recently, process-oriented models were developed that are suitable to predict the transport and distribution of CO₂ (Ouyang and Boersma, 1992; Simůnek and Suárez, 1993a). Simůnek and Suárez (1993a) developed the SOLCO₂ model, which considers variably saturated water flow, heat and CO₂ transport, and biological CO₂ production. In a companion paper, Suárez and Simůnek (1993) evaluated the sensitivity of the model to the input parameters and recommended values to be used for the parameters.

Another consideration is that most earlier models treat only equilibrium reactions, while published data for natural systems indicate that reaction rates often control solution composition. For example, studies of major ion compositions in the unsaturated and shallow groundwater zones beneath calcareous soils in arid zones show that calcite equilibrium is not a reasonable assumption for predicting water composition (Suárez, 1977; Suárez and Rhoades, 1982) and that a kinetic expression yields values closer to field measurements (Suárez, 1985).

The UNSATCHEM-2D code developed by Simůnek and Suárez (1984) couples the two-dimensional, variably saturated water flow and solute transport model SWMS-2D (Simůnek et al., 1992) with a much expanded version of the speciation model CARCHEM (Suárez, 1977) and the two-dimensional version of the CO₂ transport and production model SOLCO₂ (Simůnek and Suárez, 1993a). The chemical speciation model was modified and expanded into a predictive model. The model differs fundamentally from a pure equilibrium model in that only processes that have been demonstrated to be represented by the equilibrium condition are treated as equilibrate processes. The model is limited only to the species, solids, and processes or reactions that have been evaluated for field conditions. The model now includes options for forcing equilibrium with various solid phases (e.g., gypsum, calcite, dolomite, nequeuhonite, and hydromagnesite), allowing the solution to precipitate various solid phases if saturation is reached, or utilizing rate equations for calcite precipitation/dissolution and dolomite dissolution. We consider that gypsum, nequeuhonite or hydromagnesite, if present, are likely to equilibrate with the solution phase. Calcite, and particularly dolomite, cannot be assumed to be in equilibrium with the solution phase. The UNSATCHEM-2D model Simůnek
and S turnaround; 1993b) is only applicable to nonacid environments with pH > 6. The 1-D version under development (Saround; 4, 9, 99; in preparation) is applicable to the full range of pH values and includes silicate weathering reactions, aluminium species, gibbsite, as well as functions that describe changes in hydraulic properties due to chemical conditions.

In the following sections we present the basic equations and a brief discussion of the variable saturated water flow, CO₂ production and transport, and multicomponent solute transport of the UNSATCHEM-2D and SOILCO₂ codes. Detailed descriptions of the codes and numerous test cases are given in the referenced papers and user manuals. Emphasis here is given to the CO₂ transport and production and to the chemical submodel. We also present examples that demonstrate the applicability of SOILCO₂ for predicting CO₂ transport and production, and of UNSATCHEM-2D for simulating the precipitation of calcite and movement of an exchange front in the soil as a function of depth and time.

MODEL DEVELOPMENT

Varially Saturated Water Flow

Two-dimensional isothermal Darcy flow of water in a variably saturated rigid porous medium is described by a modified form of the Richards equation, with the assumption that the air phase plays a negligible role in the liquid flow process and that the soil matrix and fluid are incompressible:

\[
\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x_i} \left[ K_i \left( \frac{\partial h}{\partial x_i} \right) \right] = -S,
\]

where \( \theta \) is the volumetric water content (LT⁻¹), \( h \) is the pressure head (L), \( S \) is a sink term representing root water uptake (LT⁻¹), \( x_i \) (\( i = 1, 2 \)) are the spatial coordinates (L), \( t \) is time (T), \( K_i \) denotes components of a dimensionless anisotropy tensor \( K^* \), \( K \) is the unsaturated hydraulic conductivity function (LT⁻¹), and \( i \) represents the vertical coordinate (L).

The sink term, \( S \), in equation (1) represents the volume of water removed per unit time from a unit volume of soil due to plant water uptake. The expression for \( S \) proposed by Feddes et al. (1978) and subsequently modified to include salinity stress (van Genuchten, 1987) is
\[ S(h, \lambda_1, x, z) = a_0(h) a_1(h) \delta(x, z), \]  

(2)

where the dimensionless water and salinity stress response functions \( a_0(h) \) and \( a_1(h) \) depend on the soil water pressure head, \( h \) (0 ≤ \( h \) ≤ 1), and osmotic head, \( \lambda_1 \) (0 ≤ \( \lambda_1 \) ≤ 1) [see van Genuchten (1987) for a detailed description], respectively, and \( \delta(x, z) \) is the potential water uptake rate at coordinates \( x, z \) (T'). The actual water uptake, \( S(x, z) \), is equal to the potential uptake rate, \( \delta(x, z) \), during periods of no water and salinity stress (e.g., when \( a_0(h) = a_1(h_1) = 1 \)). Values for the osmotic head are obtained using osmotic coefficients and a modified form of the van 't Hoff equation (Suarez and Siminek, in preparation).

The potential water uptake rate in the root zone, \( S(x, z) \), depends on the root density at the particular depth. \( S(x, z) \) can be expressed as the product of the potential transpiration rate, \( T \), \((LT')\), and the normalized water uptake distribution function, \( \delta(x, z) \) \((LT')\), which describes the spatial variation of the potential water uptake rate, \( S_0 \), over the root zone:

\[ S_0(x, z) = \beta(x, z) I_1 \mu_1, \]  

(3)

where \( L_1 \) is the length of the soil surface associated with transpiration.

There are many ways to express the function \( \delta(x, z) \); e.g., van Genuchten (1987) suggested the following one-dimensional depth-dependent root distribution function \( \beta(z) \):

\[ \beta(z) = \begin{cases} \frac{S}{3L_1} & z = 0, z_i \\ \frac{25}{12L_1} (1 - \frac{z}{L_1}) & 0.2L_1 < z < L_1 \\ 0 & z > L_1 \end{cases}, \]  

(4)

where \( L_1 \) is the root depth (L). Note that integrating both sides of equation (3) with respect to space, using equation (4) for \( \beta(x, z) \) \((=\beta(z)L_1)\), shows that the potential transpiration for the entire soil profile is given by the integral of \( S(x, z) \) over space (the function \( \beta(z) \) integrates to unity over the rooting volume). The actual transpiration rate, \( T \), \((LT')\), is similarly obtained by integrating the root water uptake rate over the root zone as follows:
\[
T_r = \frac{1}{4} \mathcal{L}_x \int \mathcal{S}(h, s, z) \, dh = T_r \mathcal{S}_x(h) \, \mathcal{S}_y(h) \, \beta(h, s, z) \, dh,
\]

where \( \Omega_x \) is the region occupied by the root zone.

The root depth, \( L_r [L] \), can be either constant or variable during the simulation. For annual vegetation, a growth model is required to simulate the change in root depth with time. In this model we consider the root depth to be the product of the maximum root depth, \( L_{\text{max}} [L] \), and the dimensionless root growth coefficient, \( f(t) \):

\[
L_r(t) = L_{\text{max}} f_r(t).
\]

To calculate the root growth coefficient, \( f(t) \), we combined the Verhulst-Pearl logistic growth function with the growth degree day (GDD) (Gilmore and Rogers, 1958). The logistic growth function describes biological growth at constant temperature, whereas the GDD model is typically utilized for determining the time interval between planting and maturity of the plant. Thus, to model the root growth for changing temperature we scale the time in the logistic growth function by the GDD function.

For the GDD function we used 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 can be expressed by a sine function to approximate the behavior of temperature during the day), and by three temperature limits, \( T_L, T_T \), and \( T_H \). When the actual temperature is below the base value \( T_B \), plants register no effective growth. Between temperatures \( T_L \) and \( T_T \), plant growth increases from zero to the maximum value. Plant growth is at a maximum level at temperature \( T_T \) and remains unchanged within the interval up to a maximum temperature, \( T_H \). Above \( T_H \), increased temperature has a negative effect on growth. Based on this reasoning we developed the following dimensionless growth function:

\[
\text{GDD}(t) = \begin{cases} 
0 & 0 \leq t \leq t_L \\
\frac{1}{t_H - t_L} \left[ \delta(T - T_L) \, dt - \delta(T - T_T) \, dt - \delta(T - T_H) \, dt \right] & t_L < t < t_T \\
1 & t_T \leq t \leq t_H 
\end{cases}
\]
where \( T_{ma} \) are the heat units (KT) necessary for the plant to mature and the roots to reach the maximum rooting depth; \( L_0, L_m, \) and \( t_1 \) represent time of planting, time at which the maximum rooting depth is reached, and time of harvesting, respectively. The parameter \( \delta \) introduces into the GDD the reduction of the instantaneous heat unit contributions due to water and cosmic stress. The individual integrals in equation (8) are evaluated only when particular arguments are positive. Parameter \( \delta \) is defined as the ratio of the actual to potential transpiration rates:

\[
\delta = \frac{T_1}{T_0}
\]  

(8)

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

\[
f_r(t) = \frac{L_0}{L_0 + (L_m - L_0)e^{-rt}}
\]  

(9)

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 constant (T⁻¹).

Growth functions, equations (7) and (9), can both be used directly to model the root growth. However, as discussed above, to avoid limitations in both concepts, we combine equations (7) and (9) by substituting the growth function calculated from the heat unit concept (7) for the time parameter in the logistic growth function (equation (9)) as follows:

\[
t = \tau_{GDD}(t),
\]  

(10)

where \( t_1 \) is the time when GDD reaches the required value for the specific plant species \( T_{ma} \). This value is not known a priori, however; only the product \( \tau_{ma} \) must be known, and then can be selected, for example, so that \( f_r(t) = 0.99 \) for GDD(t) = 1.

Multicomponent Solute Transport

The partial differential equation governing two-dimensional advective-dispersive chemical transport under transient water flow condi-
tions in partially saturated porous media is taken as (Šimněk and Suárez, 1994)

\[
\frac{\partial (\theta_k)}{\partial t} + \frac{\partial}{\partial x_i} \left( \theta_k \rho \frac{\partial u}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left( \theta_k \rho \overline{u} \right) = \frac{\partial}{\partial x_i} \left[ \theta_k \rho \frac{\partial u}{\partial x_i} \right] - \rho \frac{\partial \theta_k}{\partial x_i} \frac{\partial \theta_k}{\partial x_i} \quad k = 1, 2, \ldots, N \tag{11}
\]

where \( \theta_k \) is the total dissolved concentration of aqueous component \( k \) (ML\(^{-1}\)), \( \theta_s \) is the total sorbed concentration of component \( k \) (MM\(^{-1}\)), \( \rho \) is the bulk density of the medium (ML\(^{-1}\)), \( D_0 \) is the "effective" dispersion tensor (LT\(^2\)), \( q \) is the volumetric soil water flux (LT\(^{-1}\)), and \( N \) is the number of aqueous components. Solute uptake by plant roots is not considered in equation (11), as plants take up a negligible fraction of the salts present in the soil water. Equation (11) also assumes that the aqueous component does not undergo any decay or production reactions. The second and third terms on the left side of equation (11) are zero for components that do not undergo ion exchange (which is the only sorption-type interaction for these species) or precipitation/dissolution.

Carbon Dioxide Transport

Modeling CO\(_2\) transport in the unsaturated zone requires consideration of both liquid- and gas-phase transport. Furthermore, we consider that the CO\(_2\) is transported via two mechanisms (Patwardhan et al., 1988), convective transport in the aqueous phase and diffusive transport in both gas and aqueous phases, and that the concentration is affected by both CO\(_2\) production and removal. Thus, the two-dimensional CO\(_2\) transport is described by the following mass balance equation:

\[
\frac{\partial (\theta_c c + \theta_s c_0)}{\partial t} + \frac{\partial}{\partial x_i} \left( \theta_c c \frac{\partial u}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left[ \theta_c c \frac{\partial u}{\partial x_i} \right] - \theta_c c_0 \frac{\partial (\theta_c c_0)}{\partial x_i} - P \tag{12}
\]

where \( c \) and \( c_0 \) are the volumetric concentrations of CO\(_2\) in the solution phase and gas phase (L\(^{-1}\)T\(^{-2}\)), respectively; \( D_r^* \) is the effective soil matrix diffusion coefficient tensor of CO\(_2\) in the gas phase (L\(^2\)T\(^{-1}\)); \( D_r^* \) is the effective soil matrix dispersion coefficient tensor of CO\(_2\) in the solution phase (L\(^2\)T\(^{-1}\)); \( q \) is the volumetric soil water flux (L\(^2\)T\(^{-1}\)); \( \theta \) is the volumetric air content (L\(^3\)L\(^{-3}\)); and \( P \) is the CO\(_2\) production rate (L\(^3\)T\(^{-1}\)). The term \( Sc \) represents the dissolved CO\(_2\) removed from the soil by root water uptake. This term is necessary because, when plants take up water, the dissolved CO\(_2\) is also taken up by the plant roots. The
Volumetric concentrations of CO$_2$ in the solution and gas phases are related by the equation

$$c_s = K_c c_g,$$

where $K_c$ is the distribution constant, which is strongly dependent on temperature. Šiminek and Suárez (1993a) defined the total aqueous-phase concentration of CO$_2$, $c_s$, as the sum of CO$_2$(aq) and HCO$_3^-$, and related it to the CO$_2$ concentration in the gas phase, $c_g$, with a modified Henry's Law. However, aqueous carbon also exists in the form of dissociated carbonic acid, HCO$_3^-$, CO$_3^{2-}$, as well as other species, such as CaCO$_3^{2-}$, and these species should be included in the expression for $c_s$. Partitioning of total carbon or alkalinity into these species requires a fairly detailed chemical speciation program and thus cannot be considered in a strictly gas-water transport model (such as SOILCO2) but requires a model that includes chemical reactions and speciation (such as UNSATCHEM-2D). It is therefore suggested that UNSATCHEM-2D be used rather than SOILCO2 whenever solution species composition is available.

### Carbon Dioxide Production

We treat CO$_2$ production as the sum of microbial and plant root respiration. It is assumed that it is possible to superpose the effects of environmental variables that alter the biological production from the reference value under optimal conditions (Šiminek and Suárez, 1993a). The production of CO$_2$ is then taken as the sum of the production rate by the soil microorganisms, $\gamma_s$ (L/L$^2$-T$^{-1}$), and the production rate by plant roots, $\gamma_r$ (L/L$^2$-T$^{-1}$).

$$P = \gamma_s \cdot \gamma_r \cdot \prod f_{a_i} \cdot \prod f_{b_j} \cdot \prod f_{c_k} \text{ and}$$

$$\prod f_{a_i} = f_{a_1} \cdot f_{a_2} \cdot f_{a_3} \quad \prod f_{b_j} = f_{b_1} \cdot f_{b_2} \cdot f_{b_3} \quad \prod f_{c_k} = f_{c_1} \cdot f_{c_2} \cdot f_{c_3}$$

where the subscript $a$ refers to soil microorganisms, and the subscript $p$ refers to plant roots, $f$ is the product of reduction coefficients that depends on depth ($L^2$), pressure head (or the soil water content) ($L$),

$$f = p, s.$$
temperature (-), CO₂ concentration (-), osmotic head (-) and time (-), and \( L_0 \) is the width (L) of the soil surface associated with the CO₂ production processes. The parameters \( \gamma_a \) and \( \gamma_w \) represent the CO₂ production by the soil microorganisms or plant roots, respectively, for the entire soil profile at 20°C under optimal water, solute, and CO₂ concentration conditions (L²L⁻¹M⁻¹). Detailed discussion of the optimal production value, as well as coefficients for the reduction functions are given in Suarez and Šimůnek (1993).

The CO₂ production by microorganisms decreases sharply with depth as a result of a decrease in root mass and readily decomposable organic matter. There are many available one-dimensional expressions which can be utilized to relate the dependence of the CO₂ production term \( f(x,z) \) on soil depth, including the exponential distribution with depth:

\[
f_x(x,z) = \frac{dx}{e^{ax}},
\]

where \( a \) is an empirical constant (L⁻¹). The exponential function is multiplied by the constant \( a \) in order to ensure that the integral of the function \( f(x,z) \) from the soil surface to infinite depth is equal to unity. However, because the depth of the soil profile or the root depth is finite, the distribution function \( f(x,z) \) must always be normalized. We assume that the dependence of the CO₂ production by plant roots corresponds to the root growth function \( L(t) \) and the distribution function \( b(x,z) \) used for the water uptake by plant roots.

In view of the experimental data of Williams et al. (1972) and Rixon (1968), the CO₂ reduction coefficient \( f(h) \) as a function of the soil water pressure head for soil microorganisms is expressed as

\[
\begin{align*}
\frac{f_x(h)}{h_c} &= 1 & h \in (h_1, \infty) \\
\frac{f_x(h)}{h_c} &= \log |h| - \log |h_1| & h \in (h_1, h_2) \\
\frac{f_x(h)}{h_c} &= 0 & h \in (-\infty, h_1),
\end{align*}
\]

where \( h \) is the pressure head when CO₂ production is optimal (L) and \( h_c \) is the pressure head when production ceases (L). The dependence of
the reduction terms \( f(h) \) and \( f(h_a) \) on soil water pressure head and osmotic head, respectively, are represented by expressions similar to the reduction functions described for water uptake (namely, \( \alpha(h) \) and \( \alpha_a(h) \)).

The influence of temperature on chemical processes is described by the Arrhenius equation (Stumm and Morgan, 1981):

\[
\ln q = -\frac{E}{RT} + s,
\]

(18)

where \( T \) is absolute temperature (K), \( E \) is the activation energy of the reaction (\( ML^{-2}P^{-1}M^2 \)), and \( q \) is the reaction rate constant. In our model, \( q \) represents the CO\(_2\) production rate. This equation, together with the Van't Hoff equation, has been used by many authors to represent the influence of temperature on soil and root CO\(_2\) production. Assuming that \( f(T) = 1 \) for \( T_m = 293.15 \) K, then the temperature reduction coefficient can be expressed as

\[
f(T) = \exp \left( \frac{E(T - T_0)}{RT_0} \right)
\]

(19)

The use of the term "reduction" coefficient with \( f(T) \) may seem inappropriate, since this coefficient is higher than 1 for temperatures greater than 20°C. We use the term to characterize the change in production with temperature, with values greater than 1 above 20°C and less than 1 below 20°C.

The dependence of CO\(_2\) production on its own concentration (actually, O\(_2\) deficiency) can be obtained from an expression for the rate at which oxygen utilized by respiration is consumed as a function of oxygen concentration in the soil gas phase. The combined volumetric content of O\(_2\) and CO\(_2\) in the soil gas phase is assumed to be constant at 21%. The rate of oxygen uptake for respiration can be expressed with the Michaelis-Menton equation (Giiniski and Stepniewski, 1985):

\[
a = \frac{q_{\text{max}}}{1 - (q_{\text{max}}/C_{Q})},
\]

(20)

where \( K_m \) is the Michaelis' constant (L/L\(^2\)), i.e., the oxygen concentration, \( c_{Q} \), at which the oxygen uptake is equal to \( 1/2 \) \( q_{\text{max}} \) and where \( q \) is oxygen uptake rate, and \( q_{\text{max}} \) is the maximum oxygen uptake rate (L/L\(^2\)). Assuming that the respiratory quotient (i.e., the amount of
CO₂ produced per amount of O₂ consumed) is equal to unity, the Michaelis’ constant for the CO₂ concentration, \( K_a \), is then equal to 0.21 - \( x_a \), and \( x_a = 0.21 \cdot c_a \). The reduction coefficient is then given by

\[
f_j(x_a) = \frac{c_j}{c_j + K_a} = \frac{0.21 - c_j}{0.42 - c_j}
\]

The disadvantage of this expression is that if \( c_j = 0 \), the value for \( f_j(x_a) \) is not equal to one. Therefore, the values of the optimal production \( \gamma_a \) and \( \gamma_o \) must be adjusted accordingly.

The coefficient \( f(x) \) introduces a time dependence into the production term. This coefficient should describe the diurnal and seasonal dynamics of soil and plant respiration. We assume that the diurnal dynamics for both soil and plant respiration are reflected by the temperature dependence coefficient \( f(T) \) and that the seasonal dynamics of soil microorganism production of CO₂ is sufficiently described by the reduction coefficients. Therefore, we use this coefficient only for the description of the changes in CO₂ production caused by the different growth stage of plants. For example, we use the same approach for annual vegetation as we used for root growth (equations (7) through (9)). The coefficient \( f(t) \) can either be described in the same way as coefficient GDD(t) when the GDD concept is used (equation (7)), possibly with different constants, or in combination with the classical Verhulst-Pearl logistic function (equation (8)). In this case, the maximum and initial values of the root depth should be replaced by the corresponding values of CO₂ production by plant roots.

The calculated actual CO₂ production rate, \( P_a \), is obtained by integrating the CO₂ production throughout the whole soil profile as follows:

\[
P_a = \int_0^{P_{DM} + \gamma_a f_j(x_a) f_j(x_a') f_j(x_a'' f_j(x_a''') f_j(x_a''') f_j(x_a'''' f_j(x_a''''') d\alpha}
\]

Solution Chemistry

As mentioned in the introduction, UNSATCHM-2D is only applicable to nonacid environments with a pH > 6 (Simunek and Sayre, 1993b, 1994); and UNSATCHM-1D can be used for acid as well as alkaline
environments (Suarez and Simznik, in preparation). The chemical species that are considered in the codes are given in Table 1; species that are only considered in the 1-D code are highlighted. The chemical system for predicting major ion solute chemistry of the un saturated zone includes either 57 or 59 chemical species (depending on the pH range) as listed in Table 1: 10 aqueous chemical components (calcium, magnesium, sodium, potassium, sulfate, chloride, nitrate, aluminum, silica, and organic matter), 28 complex aqueous species, seven possible solid species (calcite, gypsum, nesquehonite, hydromagnesite, dolomite, sepiolite, and gibbsite), six sorbed species, and seven species constituting the COO-H_2O system.

Mass balance equations for the major components in the first group of Table 1 are defined as the sum of the corresponding constituent species. In addition to 10 mass balance equations for major components, two mass balance equations for the total analytical concentration of carbonate and bicarbonate are defined:

\[
\begin{align*}
\text{CO}_{3}^- &= [\text{HCO}_3^-] + [\text{CaCO}_3^+] + [\text{MgCO}_3^+] + [\text{NaCO}_3^+] \\
\text{HCO}_3^- &= [\text{CO}_2^+] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] + [\text{NaHCO}_3^+] \quad (23)
\end{align*}
\]

Table 1. Species considered in the chemical model.

<table>
<thead>
<tr>
<th>1 Aqueous components</th>
<th>10 Ca^2+, Mg^2+, Na^+ , K^+, SO_4^2-, Cl^-, NO_3^-, H_2SO_4^-, AP^+, Org^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Complexed species</td>
<td>25 CaCO_3, CaHCO_3, CaSO_4, MgCO_3, MgHCO_3, MgSO_4, NaHCO_3, NaNO_3, Mg(NO_3)_2, H_2SO_4, AHO, AHSO_4, AHSO_4, AIDH_4, AIDH_4, AIDH_4, AIDH_4, AIDH_4, AIDH_4, AIDH_4, AIDH_4, H_2SO_4, HSO_4,</td>
</tr>
<tr>
<td>3 Precipitated species</td>
<td>7 CaCO_3, CaSO_4, 2H_2O, MgCO_3, 3H_2O, CASO_4(CO_3)_2, MgSO_4(2H_2O), 4H_2O, CaSO_4(2H_2O), 4H_2O, CaSO_4(2H_2O), 4H_2O,</td>
</tr>
<tr>
<td>4 Sorbed species</td>
<td>6 Ca, Mg, Na, R, Ti, Fe</td>
</tr>
<tr>
<td>5 Additional species</td>
<td>7 PNH, HCO_3^-, CO_3^-, HCO_3^-, H^+, CH_3COOH, H_2O</td>
</tr>
</tbody>
</table>
where variables with subscript T represent the total solution concentration of that particular variable, and brackets refer to molalities (mol/kg). The expressions given above are used to calculate carbonate alkalinity, Alk (mol/kg), as

$$\text{ALK} = 2\text{CO}_2\text{T} + \text{HCO}_3\text{~T} + [\text{H}^+] - [\text{OH}^-].$$  \hspace{1cm} (24)

In addition to the mass balance equations, the charge balance equation for the solution is

$$2[\text{Ca}^{2+}] + 2[\text{Ba}^{2+}] = [\text{Na}^+] + [\text{K}^+] + ([\text{Ca(HCO}_3\text{)}\text{~}]) + ([\text{Ba(HCO}_3\text{)}\text{~}]) + ([\text{H}^+] - 2[\text{Al}^{3+}])$$

$$-2[\text{Al(OH)}_3\text{~}^{-}] - 2[\text{Al(OH)}_2\text{~}^{+}] - [\text{Al(OH)}_4\text{~}^{-}] - 2[\text{Na}_2\text{SO}_4\text{~}^{-}] - 2[\text{Ca}^{2+}] - [\text{H}_2\text{SO}_4\text{~}^{-}]$$

$$-2[\text{Na}_2\text{CO}_3\text{~}^{-}] - 2[\text{CaCO}_3\text{~}^{-}] - [\text{Na}^+] - [\text{K}^+] - [\text{H}_2\text{SO}_4\text{~}^{-}] - 2[\text{CaSO}_4\text{~}^{-}] - 3[\text{H}_2\text{O}] - 2[\text{Na}_2\text{CO}_3\text{~}^{-}] - 2[\text{Ca}^{2+}] - 2[\text{Al(OH)}_3\text{~}^{-}] + 2[\text{H}_2\text{O}] = 0.$$  \hspace{1cm} (25)

The activities of the species present in solution at equilibrium are related by the equilibrium mass-action expressions. These include the expressions for the dissociation of water, and the first and second dissociation constants for carbonate acid. The solubility of CO$_2$(g) in water is governed by a modified Henry's law,

$$K_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{[\text{H}_2\text{CO}_3\text{~}^{-}]}.$$  \hspace{1cm} (26)

where the activity of CO$_2$ is expressed as partial pressure $P_{\text{CO}_2}$, $K_{\text{CO}_2}$ is a modified Henry's Law constant, and parentheses denote ion activities. The term $H_2CO_3$ represents both aqueous CO$_2$ and HCO$_3$ CO$_2$. The value for $P_{\text{CO}_2}$ is calculated at each node and time step by the production-transport submodel.

Each complexation reaction for species in the second group of Table 1 is represented by equilibrium mass-action expression. For example, for the calcium sulfate complex:

$$K_i = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{[\text{CaSO}_4]}.$$  \hspace{1cm} (27)
Partitioning between the exchanger phase and the solution is described by a generalized Gapon equation for cation exchange (White and Zelazny, 1986):

\[ K_{ij} = \frac{z_i^+ (\epsilon_i^+) \gamma_i}{z_j^- (\epsilon_j^-) \gamma_j} \]  

(28)

where \( y \) and \( x \) are the valences of species \( i \) and \( j \), respectively, and \( K_\gamma \) is the Gapon selectivity coefficient. This equation is modified from the original Gapon expression by the substitution of ion activities for the concentration terms. Adsorbed concentrations are expressed in moles of charge per mass of dry soil (mol kg\(^{-1}\)). It is assumed that the cation exchange capacity (mol kg\(^{-1}\)), is constant and independent of pH. The assumption of constant exchange capacity is not valid for soils containing large amounts of variable charge, such as oxides, but is necessary in the present models to maintain conservation of mass.

The following solid phases constrain the aqueous-phase solution to equilibrium whenever the solids are specified or approached from over-saturation: gypsum, nesquehonite, hydromagnesite, sepiolite, and gibbsite. Precipitation-dissolution of calcite is optionally treated with either equilibrium or kinetic expressions. In the latter case, the equation corresponding to calcite equilibrium is omitted from the equilibrium system and the rate of calcite precipitation-dissolution is calculated from a rate equation, as described later. Dissolution of dolomite, also discussed later, is always considered to be a kinetic process and is not included in the system of equilibrium equations (because ordered dolomite does not precipitate under earth surface conditions). Dissosiation of the selection and consideration of these solids is given in Suarez and Šimanek (in preparation). The precipitation or dissolution of gypsum, calcite (if considered in the equilibrium system), nesquehonite, hydromagnesite, sepiolite, and gibbsite in the presence of CO\(_2\) is described in terms of the corresponding solubility products \( K_\gamma \):

\[ K_\gamma^c = (Ca^{+1}) (CO_3^{2-}) \]  

(29)

\[ K_\gamma^g = (Ca^{+1}) (SO_4^{2-}) (Na^+) (H^+) \]  

(30)
\[ K_n^G = \left( \text{Mg}^{2+} \right) \left( \text{CO}_3^{2-} \right)^2 \left( \text{H}_2\text{O} \right)^3 \text{ nesquehonite} \]  \( (31) \)

\[ K_p^G = \left( \text{Mg}^{2+} \right)^2 \left( \text{CO}_3^{2-} \right)^4 \left( \text{OH}^{-} \right)^{-4} \left( \text{H}_2\text{O} \right)^4 \text{ hydromagnesite} \]  \( (32) \)

\[ K_s^G = \left( \text{Mg}^{2+} \right)^2 \left( \text{H}_2\text{SiO}_4 \right)^2 \left( \text{OH}^{-} \right)^4 \left( \text{H}_2\text{O} \right)^{-4.5} \text{ sepiolite} \]  \( (33) \)

\[ K_g^G = \left( \text{Al}^{3+} \right) \left( \text{H}_2\text{O} \right)^3 \left( \text{H}^{+} \right)^2 \text{ gibbsite,} \]  \( (34) \)

where indexes C, G, N, H, S, and P refer to calcite, gypsum, nesquehonite, hydromagnesite, sepiolite, and gibbsite, respectively.

The equilibrium concentrations of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} in a gypsum system are obtained by solving the quadratic algebraic equation corresponding to equation (30). The concentrations of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and HCO\textsubscript{3}\textsuperscript{-} in equilibrium with carbonate solids, as well as Al\textsuperscript{3+} for gibbsite, are determined by solving cubic algebraic equations, as described in Šimunek and Suárez (1995b).

**Kinetic Model of Calcite Precipitation-Dissolution**

The reaction rate of calcite precipitation-dissolution, \( R \), in the absence of inhibitors such as "foreign ions" and dissolved organic matter, can be calculated with the rate equation of Plummer et al. (1978),

\[ \frac{d}{dt} \cdot \text{calcite} = k_1 \left( \text{H}^{+} \right)^{-1} \cdot k_2 \left( \text{Ca}^{2+} \right)^{-1} \cdot k_3 \left( \text{CO}_3^{2-} \right) \cdot k_4 \left( \text{H}_2\text{O} \right)^{-1} \cdot k_5 \left( \text{H}_2\text{O} \right)^{-1} \left( \text{CO}_3^{2-} \right)^{-1}, \]  \( (35) \)

where

\[ k = k_1 \cdot k_2 \cdot \frac{1}{k_3} \cdot \frac{1}{k_4} \cdot \frac{1}{k_5} \left[ k_1 \left( \text{H}_2\text{O} \right)^{1} \cdot k_2 \left( \text{H}_2\text{O} \right)^{-1} \right]. \]  \( (36) \)

and where \( K \) is the second dissociation constant of carbonic acid, and \( k_1, k_2, \) and \( k_3 \) are temperature-dependent, first-order rate constants representing the forward reactions (mmol cm\textsuperscript{-2} s\textsuperscript{-1}); and \( k_4 \) is a function dependent on temperature, surface hydrogen ion activity; and \( \text{CO}_3^{2-} \) concentration representing the backward reactions (mmol cm\textsuperscript{-2} s\textsuperscript{-1}). The dissolution-precipitation rate \( R \) is expressed in mmol of calcite per cm\textsuperscript{2} of
surface area per second. The term (H₂⁺) is the H⁺ activity at the calcite surface and is assumed to be equal to the (H⁺) of the solution at calcite saturation. Whenever pH > 8 and Pco₂ < 1.0 kPa, at 25°C, the following precipitation rate expression is considered more accurate (Inskipp and Bloom, 1985):

$$\dot{R} = 11.82 \{(Ca^{2+})(CO_3^{2-}) - k_p^r\}.$$  

(37)

The precipitation or dissolution rate of calcite is reduced by the presence of various inhibitors. Šiminek and Suarez (1995b) developed a function for the reduction of the precipitation-dissolution rates due to surface poisoning by dissolved organic carbon, based on the experimental data of Inskipp and Bloom (1986). These surface reaction precipitation-dissolution models simulate undersaturated and supersaturated conditions, such as those existing in field environments, but are questionable from a mechanistic point of view for precipitation. Pedogenic calcite forms as a microcrystalline cement, often with occlusions of clay and organic matter, which suggests a heterogeneous nucleation mechanism either by microbial activity or by surface reactions on clay.

**Kinetic Model of Dolomite Dissolution**

The reaction rates of dolomite dissolution, R² (mmol cm⁻² s⁻¹), are calculated with the rate equation of Bussenberg and Plummer (1982):

$$R^2 = k_t^r (H^+)^{1.5} \cdot k_h (HCO_3^-)^{1.5} \cdot k_b (H_2O)^{1.5} - k_b^r (HCO_3^-),$$  

(38)

where the temperature-dependent, first-order rate constants k_r, k_h, k_b (mmol cm⁻² s⁻¹), representing the forward reactions, and k_b (mmol cm⁻² s⁻¹), representing the back reaction, are given by Bussenberg and Plummer (1982). The dissolution rate R² is again expressed in mmol of dolomite per cm² of surface area per second. As mentioned earlier, we do not consider the precipitation of dolomite. Formation of protodolomite, which has been observed in hypersaline environments, can be treated as a mixture of magnesium carbonate and calcium carbonate, both of which are considered in our chemical model.

**Activity Coefficients**

Calculation of single-ion activity coefficients is specified by using either an extended version of the Debye-Hückel equation (Tressell and Jones, 1974) or Pitzer expressions (Pitzer, 1979). The extended version
of the Debye-Hückel equation (Truesdell and Jones, 1974), used in the
dilute to moderately saline concentration range, is given by
\begin{equation}
\ln \gamma = \frac{A \sqrt{I}}{1 + B \sqrt{I}} + bI,
\end{equation}
where A and B are constants that depend only on the dielectric con-
stant, density, and temperature; \( z \) is the ionic charge; \( a \) and \( b \) are two
adjustable parameters; and \( I \) is the ionic strength.
\begin{equation}
I = 0.5 \sum_{i=1}^{N} a_i^2 \eta_i,
\end{equation}
where \( M \) is the number of species in the solution mixture, \( m \) is mobi-
licity, and \( \eta_i \) is valence. The adjustable parameters \( a \) and \( b \) for individual
species are given by Truesdell and Jones (1974). Activities of neutral
species are calculated as
\begin{equation}
\ln \gamma = a' I,
\end{equation}
where \( a' \) is an empirical parameter. The values of this parameter for
neutral species are listed in Šimunek and Suarez (1993b).
At high ionic strength activity coefficients can no longer be considered
universal functions of ionic strength but are also dependent on the con-
centration of the various ions present in solution (Felmy and Weare,
1986). The activity coefficients can then be calculated with a virial-type
expansion of the form (Pitzer, 1979):
\begin{equation}
\ln \gamma_i = \ln \gamma_i^0 + \sum_j B_{ij} (1) \eta_j + \sum_k C_{ik} \eta_k \eta_j + \cdots,
\end{equation}
where \( \gamma_i^0 \) is a modified Debye-Hückel activity coefficient (which is a
universal function of ionic strength), and \( B_i \) and \( C_{ik} \) are specific coeffi-
cients for each ion interaction. This model is considered accurate even
for solutions with very high ionic strength (up to 20 molar) and can be
used down to infinite dilution.

Solution Strategy

The Galerkin finite-element method with linear basis functions is used
to obtain a solution of the water flow and solute and CO₂ transport
equations subject to the imposed initial and boundary conditions. The
"mass-conservative" iterative method proposed by Celia et al. (1990) is used for evaluating the water content term in equation (1). This method has been shown to provide excellent results in terms of minimizing the mass balance error. A detailed description of the solution of Richards' equation was given in Šimněk et al. (1992). The finite-element method is also used to solve the heat (see Šimněk and Suarez, 1993b); CO₂, and multicomponent solute transport equations. A detailed description of the numerical solution for these transport equations is given in Šimněk and Suarez (1993b).

Computation of the solution speciation is done in a way that is fairly similar to that in WATEQ (Truesdell and Jones, 1974), a speciation model that does not consider solid and adsorbed phases. The inputs to the chemical submodel of UNSAHEYEM-2D are the analytical concentrations of the major ions, alkalinity, adsorbed and solid-phase concentrations, water content, temperature, bulk density, and CO₂ partial pressure (calculated in the gas subroutine).

The governing solute transport equation (1) contains time-derivative terms for the total dissolved, sorbed, and solid-phase concentrations. Because of the second and third terms, the solute transport equation is highly nonlinear, and its solution requires an iterative process. Coupling between the transport and chemical submodules was performed by the so-called "2-step" method as described by Walsh et al. (1984), Cederberg et al. (1985), and Bryant et al. (1986) (and also used by Yeh and Trigubovski (1991)). First, the discretized solute transport equation is solved by setting the second and third terms equal to zero for the equilibrium case, or by calculating the third term from equations (33) and (34) for the kinetic case. The newly calculated dissolved concentrations are then compared with the initial concentrations for this iteration, and the chemical module is called for those nodes where changes in concentrations were higher than a prescribed concentration tolerance. When the rate equations for calcite or dolomite are used, the chemical module is called for all nodes at the first iteration. The chemical module provides us with updated values of aqueous, solid-phase, and adsorbed concentrations. The new aqueous concentrations are checked against those calculated before the chemical module was called and, if outside the specified tolerance, a new iteration is performed. This iteration process is continued until the difference between the new and old concentration is less than the prescribed tolerance for all nodes.
APPLICATIONS OF THE SOILCO2 AND UNSATCHM-2D MODELS

In this section we present two simulations. The first case compares water content and CO$_2$ predictions using the SOILCO2 model, with a published data set where the temperature and rainfall data were given, along with soil water content and gas composition (Suarez and Šimůnek, 1993). The second case demonstrates an application of the UNSATCHM-2D model to a chemical problem with calcite precipitation and movement of an exchange front into the soil.

Prediction of CO$_2$ Concentrations—Field Experiment

The predictive capabilities of SOILCO2 were examined by comparing simulations to the field data published by Buyanovsky and Wagner (1983) and Buyanovsky et al. (1986) for wheat grown in Missouri. Buyanovsky and Wagner (1983) presented data for water and CO$_2$ dynamics in soil under three different cropping systems for the year 1982. In a subsequent paper, Buyanovsky et al. (1986) investigated annual cycles of CO$_2$ evolution into the atmosphere from a soil cultivated to wheat and related the CO$_2$ flux to plant development, considering the effects of temperature and water content. Since they did not provide the hydraulic characteristics of the soil, we used the soil texture description and the measured air porosity at field capacity, along with the regression equations developed by Rawls et al. (1982), to obtain a water content-pressure head relation for this soil.

The following example is taken from Suarez and Šimůnek (1993). Figure 1 shows the water content at the 0.2-m depth as reported by Buyanovsky and Wagner (1983), and the model prediction of water content with time at the same depth. Overall, the model provides a good fit to the experimental data, especially in view of the need to use Thornthwaite’s equation (de Marsily, 1986) for the calculation of potential evapotranspiration and the method used to calculate the hydraulic parameters.

Figure 2 shows the excellent agreement between the measured CO$_2$ concentrations at the 0.2-m depth and the corresponding values calculated with the SOILCO2 code. There are no statistically significant differences between the measured and predicted CO$_2$ concentrations at the 90% confidence level. The irregular pattern in the CO$_2$ concentrations shown in Figure 2 can be understood if we consider both the soil temperature and the water content data shown in Figure 1. The CO$_2$
concentration is low during cold periods when production is low, as well as within relatively dry periods when the gas transport is high. During wet periods of moderate to warm temperatures, the CO₂ concentrations are relatively high (because of reduced transport and substantial production). The model was further tested against three other similar data sets from Missouri, and the fit was excellent in all cases.

Figure 1. Measured (Buyanovsky and Wagner, 1986) and calculated water content at a depth of 0.4 m for Missouri wheat experiment (after Suarez and Simunek, 1993).

Figure 3 shows the comparison of the calculated daily and weekly CO₂ fluxes to the atmosphere with the flux measurements reported by Buyanovsky et al. (1986). We present the weekly values in addition to the daily values, because changes in the water content of the upper soil layer cause these rates to fluctuate significantly on a daily basis. The large fluctuations shown in Figure 3 indicate that accurate determination of CO₂ flux requires an excessive number of measurements if the surface water content is rapidly changing. This change in CO₂ flux is significant over time periods corresponding to rain events or water applications. As with the CO₂ concentration data, there is an excellent correspondence between measured and calculated fluxes.
Figure 2. Measured (Buyanovsky and Wagner, 1983) and calculated CO$_2$ concentrations at a depth of 0.2 m for Missouri wheat experiment (after Suarez and Simunek, 1993).

Figure 3. Measured (Buyanovsky and Wagner, 1983) and calculated daily and weekly CO$_2$ fluxes to the atmosphere for Missouri wheat experiment (after Suarez and Simunek, 1993).
Two-Dimensional Furrow Reclamation Irrigation Problem

A furrow irrigation system was used as a conceptual model of two-dimensional infiltration of water into a soil with high exchangeable sodium. The simulation demonstrates the cation exchange feature of UNSATCHM-2D. The schematic representation of the flow domain for the furrow irrigation, together with the finite-element mesh, are presented in Figure 4. Because of symmetry, we need only simulate the domain between the axes of two neighboring furrows.

![Figure 4. Schematic representation and finite-element mesh of the flow domain for furrow irrigation system for example 2.](image)

It is assumed that every other furrow is flooded with water and that the water level in the irrigated furrow is kept at a constant level of 6 cm. A fixed head boundary condition is used for the portion of the boundary in contact with the flooding water in the furrow. Free drainage is used as the bottom boundary condition; a zero flux condition is used for the rest of the boundary. The initial pressure head is 200 cm, and the soil hydraulic properties for a hypothetical loam soil (Simunek and Suarez, 1993b) were used.
Root water uptake and evaporation were neglected (which also means that $\gamma_1 = 0$). The calculation was run at a constant temperature of 25°C, with an optimal CO$_2$ production value $\gamma_2$ of 0.007 m$^3$ m$^{-3}$ d$^{-1}$. Production decreased exponentially with depth, as described in Suarez and Siminak (1993). This production value was also modified by reduction coefficients calculated by the code according to environmental conditions (in this case, coefficients depending on pressure head and CO$_2$ concentration). The bulk density of the soil was taken as 1.4 g cm$^{-3}$, while a molecular diffusion coefficient in water for solute transport of 2 cm$^2$ h$^{-1}$ was chosen. Longitudinal and transverse dispersivity values were 2 and 0.2 cm, respectively.

The solution composition of the water initially present in the soil profile is that of a highly sodic water: Ca$_2$ = 0.2, Na$_2$ = 4.8, Cl$_2$ = 4.6, alkalinity = 0.4 mmol L$^{-1}$, with other concentrations equal to zero. The cation exchange capacity is 100 mmol kg$^{-1}$: Ca$_e$ = 5.0, Na$e$ = 55.9 mmol kg$^{-1}$. The Ca-Mg gapon selectivity coefficient (K$_{Ca}$ = 1.158) was taken from Wagenaar and Hutson (1987). Two different irrigation water compositions were used. One water was almost gypsum-saturated: Ca$_2$ = 32.6, Na$_2$ = 4.8, Cl$_2$ = 5.0, SO$_4$ = 32.0, alk = 0.4 mmol L$^{-1}$, and zero for other concentrations. The second water is of the following composition: Ca$_2$ = 1.5, Na$_2$ = 2.0, Cl$_2$ = 1.0, SO$_4$ = 2.0, alk = 0.6 mmol L$^{-1}$, and zero for other concentrations. Infiltration was attempted in three different ways. In the first case, gypsum-saturated water was applied to a soil without consideration of calcite dissolution. In the second case, high-quality water was applied to a soil, again, without consideration of calcite dissolution. In the third case, high-quality water was applied to a soil where the soil solution was in equilibrium with calcite. Cation exchange is treated as an instantaneous process.

Steady-state water flow was reached after approximately 1.5 days. Figure 5 shows the change in CO$_2$ concentration in space and time. The CO$_2$ concentration increases with time, with diffusion occurring predominantly in the direction of the dry furrow. The distribution of a hypothetical tracer is shown in Figure 6. The concentration front of the tracer reached a depth of approximately 1 meter after 1 day.

Figure 7 presents the exchangeable concentrations of calcium for the three scenarios after 5 days. There is a sharp exchange front (exchangeable sodium less than 10 %) reaching to approximately 70 cm for the gypsum water (Figure 7A). In contrast to Figure 7A, Figure 7B demonstrates penetration of the calcium front to a depth of less than 10 cm.
when irrigating with the high-quality water. In this case, after 50 days the exchange front extended only to a depth of 40 cm (data not shown). Irrigation with the high-quality water, allowing for calcite equilibrium, showed a diffusive exchange front extending to a depth of 50 cm, with complete reclamation down to 15 cm (Figure 7C). Reclamation of the region below the furrow was essentially completed down to 1 meter after 26 days of leaching (data not shown).

Figure 5: CO₂ concentration (%) profiles at different times for example 2: (A) 0.5, (B) 1, and (C) 5 days.

Figure 6: Tracer concentration profiles at different times for example 2: (A) 0.5, (B) 1, and (C) 5 days.
Figure 7. Exchangeable calcium concentration (mmol/kg) profiles after 5 days of infiltration: (A) infiltration with gypsum-saturated water, (B) infiltration with high-quality water, and (C) infiltration with high-quality water into profiles containing calcite.

This figure demonstrates the importance of calcite dissolution during reclamation. Reclamation with calcite is often dismissed because of a lack of consideration of elevated CO₂ concentrations in the soil and the enhanced dissolution of calcite during the reclamation exchange. For example, calcite dissolution contributed 300 eq per m² of soil surface area to reclamation within the first 5 days of leaching. Selection of a higher exchange capacity and associated hydraulic properties of a finer-textured soil would increase both the time required for infiltration, and the quantity of water required for reclamation.

SUMMARY AND CONCLUSION

The SOILCO₂ code, a process-based CO₂ production and transport model, combined with a variably saturated water flow model, was described. Comparison of the model to field data demonstrates its ability to predict both CO₂ concentrations in the soil and CO₂ fluxes to the atmosphere for a growing crop with changes in crop development, temperature, and soil water content. The multicomponent water and solute transport code UNSATCHEM-3D was also reviewed. This code is particularly suited for simulation of major ion solute chemistry of arid zone soils. The model considers the transport of CO₂, thus allowing for calculation of soil CO₂ concentrations. Soil CO₂ concentrations are used in the chemical subroutine to calculate solute composition. The model utilizes both extended Debye-Hückel and Pitzer activity coefficients; thus, it is suitable for use in extremely saline environments. The
chemistry subroutine includes both equilibrium and kinetic expressions for various solid phases. The reclamation example demonstrates the importance of elevated CO₂ concentrations combined with ion exchange in enhancing the solubility of calcite. Use of the model for reclamation and soil water management should enable more efficient use of amendments and water resources.

Future research will incorporate the chemistry and transport of oxygen ions (such as boron, selenium, and arsenic) that are important when considering impacts of agricultural drainage waters in arid environments. In addition, a more detailed plant growth model will be incorporated to better predict plant response to environmental conditions.

REFERENCES


