Modeling Unsaturated Water Flow, and CO, and Solute Transport with Major Ion Chemistry

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Abstract

In this paper we review our efforts to model the production and transport of carbon dioxide and multicomponent transport of major ions in variably saturated porous media. We present the development and demonstrate the use of the finite element codes SOILC02 for modeling CO_2 transport and UNSATCHEM for describing major ion equilibrium and kinetic non-equilibrium chemistry in soil. Since the solution chemistry in the unsaturated zone is significantly influenced by variations in water content, temperature and CO_2 concentrations in the soil gas, all these variables are calculated by the model. Transport of CO, in the unsaturated zone can occur both in the liquid and gas phases. The equation for CO, transport accounts for both microbial and root respiration of CO_2 which is dependent on water content, temperature, salinity and plant and soil characteristics. The major variables of the chemical system are Ca, Mg, Na, K, Al, SO.,, Cl, NO_3, alkalinity, silica, organic matter and CO,. The model accounts for equilibrium reactions between these components such as complexation, cation exchange and precipitation-dissolution. Either equilibrium or multicomponent kinetic expressions are used for the precipitation-dissolution of calcite and dissolution of dolomite. Dissolution-precipitation reactions are also included for gypsum, hydromagnesite, nesquehonite, and gibbsite. Both modified Debye-Huckel and Pitzer expressions were incorporated into the model to calculate single ion activities, because of the large variations in the ionic strength of soil solutions. Two examples are presented to demonstrate the applicability of SOILC02 for modeling CO_2 transport and of UNSATCHEM for simulating the reclamation of a sodic soil. The model provides quantitative predictions of the water, time and amendment requirements, as well as representation of the solute and exchanger composition with time and depth.

1. Introduction

Modeling the transport of major soluble ions in the unsaturated zone is required for prediction of ground water quality, and the proper development of irrigation and fertilization practices. Realistic modeling of root zone chemistry requires consideration of processes in the gas, liquid and solid phases. Many factors may influence the transport and reaction parameters of the chemical system. The most important factors influencing the soil chemical dynamics are water flow, heat transport, and the dynamic changes in CO, concentrations. Water is the transport medium for dissolved chemicals and also significantly affects the production and concentration of CO_2.. Soil temperature affects thermodynamic equilibrium constants and reaction rates and the production of CO_2. The CO_2 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 CO_2 concentration produce changes in soil pH (for all but acid soils), and thus alters the solubility of many solid phases such as carbonates and oxihydroxides.

Many models have been developed over the past two decades to quantify the physical and chemical processes affecting the transport of major ions. The hydrological models for water flow, solute transport and aqueous equilibrium chemistry were developed independently, and only recently has there been a significant effort to couple these models. In the past, solute transport models mostly considered only one solute and greatly simplified the different chemical processes. For example, the complex processes of adsorption and cation exchange were usually accounted for by linear [Huyakom et al., 1991] or nonlinear Freundlich isotherms *[Yeh and Huff*, 1985; *Šimůnek and van Genuchten, 1993],* where all reactions between solid and liquid phases were lumped into the distribution coefficient K_D *[Liu and Narasimhan, 1989]* and possibly into the nonlinear exponent. Other processes such as precipitation, biodegradation, volatilization or radioactive decay were simulated by simple first- or zero-order rate constants. Several models were developed which simulate several solutes involved in sequential first-order decay reactions *[Gureghian, 1981; Wagenet and Hutson, 1987; Šimůnek and van Genuchten, 1993].*

The problem of coupling hydrological models for water flow and solute transport with chemical equilibrium models has been addressed only in the last decade. Recent reviews on the development of hydrogeochemical transport models of reactive multichemical components were given by *Yeh and Tripathi [1989]* and *Mangold and Chin-Fu Tsang [1991].* Most of the modeling effort has so far been concentrated on the saturated zone, where changes in water velocity, 'temperature and pH are relatively gradual and hence less important than in the unsaturated zone. Therefore, most models were based on one-dimensional steady-state saturated water flow with fixed water velocity, temperature and pH *[Valocchi et aL, 1981; Jennings et al., 1982; Walsh et al., 1984; Cederberg et al., 1985; Kirkner et al., 1985; Bryant et al., 1986; Forster and Gerke, 1988;* among others]. Only recently several models were published which can be applied to problems that include multicomponent solute transport and variably saturated water flow *[Liu and Narasimhan, 1989; Yeh and Tripathi, 1991]. 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. Robbins' equilibrium chemistry model was also the basis for the numerical code LEACHM of *Wagenet and Hutson [1987]. These* chemical and multicomponent transport models 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 (because of the interaction of CO, gas with the solution), i.e. for the description of the chemistry of groundwater systems [Suarez, 1994]. However, in a soil environment the CO_2 concentrations fluctuate, resulting in increases in dissolved inorganic carbon and soil pH when CO, increases. Use of the open system condition which allows for transfer of carbon into or out of the system and use of alkalinity as an input variable is preferable since alkalinity is constant during changes in soil *CO,* in the absence of precipitation *[Šimůnek and Suarez, 1994]. The* second limitation is that these earlier models consider only equilibrium reactions, while published data for natural systems indicate that kinetic reactions often control solution composition. For example, studies of major ion compositions in and below the root zone of calcareous soils in arid zones show that calcite equilibrium is not a reasonable assumption for predicting water composition [Suarez, 1977; Suarez and Rhoades, 1982] and that a kinetic expression yields values closer to field measurements [Suarez, 1985].

Since the assumption of time invariant CO_2 is often not realistic, there is also a need for coupling multicomponent models not only to variably saturated water flow and solute transport models but also to a CO_2 transport model [*Šimůnek* and Suarez, 1994]. Modeling of the spatial distribution and fluxes of CO, has been limited and attempted mostly by statistical correlation with specific parameters such as air temperature, soil temperature and soil water content. Only recently, process-oriented models were developed which are suitable to predict the transport and distribution of CO_2 [Ouyang and *Boersma, 1992; Šimůnek and Suarez,* 1993a]. *Šimůnek* and **Suarez** *[1993a]* developed the SOILCO2 model, which considers variably saturated water flow, heat and CO_2 transport and biological CO_2 production. In a companion paper, Suarez and *Šimůnek [* 1993] presented a sensitivity analysis for the input parameters as well as a discussion on the selection of the parameter values.

Šimůnek and Suarez [1994] coupled the two-dimensional variably saturated water flow and solute transport model SWMS_2D of *Šimůnek et al. [1992]* with an expanded version of the speciation model CARBCHEM of Suarez [1977] and the CO_2 transport and production model of *Šimůnek and Suarez* [1993a] The modification of the speciation model consists of inclusion of the rate equations for calcite precipitation/dissolution and dolomite dissolution, addition of several solid phases, and calculation of the activity coefficients by either extended Debye-Huckel *[Truesdall and Jones,* 1974] or Pitzer's equations *[Pitzer,* 1979]. The resulting multicomponent transport model for variably saturated porous media, UNSATCHEM-2D [*Šimůnek and Suarez,* 1993b], is applicable only for nonacid environments with pH>6. This model thus couples gas, liquid and solid phase processes, while describing solid phase reactions with kinetic expressions. A new multicomponent transport model that is applicable to the full range of pH values and includes silicate weathering reactions has also been developed [Suarez and *Šimůnek, 1994].*

In this paper we review our work on multicomponent transport, major ion chemistry and CO_2 dynamics in soils. We present only the basic equations and a brief discussion of the variably saturated water flow and multicomponent solute transport sections of the model. Further details are given in the referenced papers and reports. More attention will be given in this review to the development of the CO_2 transport and production model and to the major ion speciation model. At the end of the paper, two examples are provided that demonstrate the applicability of SOlLC02 for CO_2 transport and production and of UNSATCHEM-2D for reclamation of a sodic soil.

2. Model Development

2.1. Variably Saturated Water Flow

Governing *Equation*

Two-dimensional isothermal Darcian flow of water in a variably saturated rigid porous medium is described by a modified form of the Richards equation with the assumptions that the air phase plays a negligible role in the liquid flow process and that the compressibility of both soil matrix and fluid can be ignored

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}[K(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{iz}^A)] - S \tag{1}$$

where θ is the volumetric water content [L^3L^{-3}], h is the pressure head [L], S is a sink term representing the root water uptake [T^{-1}], x_i ($i = 1,2$) are the spatial coordinates [L], t is time [T], K_{ij}^A denotes components of a dimensionless anisotropy tensor $\mathbf{K}^A$, Kis the unsaturated hydraulic conductivity function [LT^{-1}], and z represents the vertical coordinate [L].

Root Water Uptake

The sink term, S, in (1) represents the volume of water removed per unit time from a unit volume of soil due to plant water uptake. The expression proposed by *Feddes et al.* [1978] and subsequently modified to include salinity stress [van *Genuchten,* 1987] is

$$S(h) = a(h)a_\phi(h_\phi)S_p \tag{2}$$

where the dimensionless water and salinity stress response functions *a(h)* and $a_\phi(h_\phi)$ depend on the soil water pressure head, *h*, and osmotic head, h_ϕ ($0 \leq a \leq 1$), respectively, and S_p is the potential water uptake rate [T^{-1}], which is equal to the water uptake rate during periods of no water and salinity stress when $u(h) = a_\phi(h_\phi) = 1$. Values for the osmotic head are obtained using osmotic coefficients and a modified form of the van't Hoff equation [Suarez and *Šimůnek,* 1994].

2.2. Multicomponent Solute Transport

Governing Solute Transport Equation

The partial differential equation governing two-dimensional advective-dispersive chemical transport under transient water flow conditions in partially saturated porous media is taken as [*Šimůnek and Suarez, 1994*]

$$\frac{\partial(\theta c_k)}{\partial t} + \rho\frac{\partial \bar{c}_k}{\partial t} + \rho\frac{\partial \hat{c}_k}{\partial t} = \frac{\partial}{\partial x_i}(\theta D_{ij}\frac{\partial c_k}{\partial x_j} - q_i c_k) \qquad k = 1,2,\ldots,N_c \tag{3}$$

where c_k is the total dissolved concentration of aqueous component k [ML^{-3}], $\bar{c}_k$ is the total sorbed concentration of component *k [MM’]*, $\hat{c}_k$ *is the* total precipitated concentration of component *k* [MM^{-1}], ρ is the bulk density of the medium [ML^{-3}], D_{ij} is the “effective” dispersion tensor [L^2T^{-1}], q_i *is the* volumetric flux [LT^{-1}] and N_c is the number of aqueous components. Solute uptake by plant roots is not considered in (3) as plants take up a negligible fraction of the salts present in the soil water. The second and third terms on the left side of eq. (3) are zero for components that do not undergo ion exchange or precipitation/dissolution

2.3. Carbon Dioxide Transport

Governing CO, Transport Equation

A detailed development of the one-dimensional carbon dioxide transport model and justification of respective assumptions were given in ***Šimůnek and Suarez*** [1993a] We present only the major equations without discussing the boundary conditions and the specifics of the CO, production submodel.

The CO_2 transport in the unsaturated zone occurs in both the liquid and gas phases. Furthermore, we considered that 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 the two-dimensional CO, transport is described by the following mass balance equation

$$\frac{\partial(c_a\theta_a + c_w\theta)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_a D_{ij}^{a}\frac{\partial c_a}{\partial x_j}\right) + \frac{\partial}{\partial x_i}\left(\theta D_{ij}^{w}\frac{\partial c_w}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(q_i c_w) - Sc_w + P \qquad (4)$$

where c_w and c_a are the volumetric concentrations of CO, in the dissolved phase and gas phase [L^3L^{-3}], respectively, D_{ij}^a is the effective soil matrix diffusion coefficient tensor of CO_2 in the gas phase [L^2T^{-1}], D_{ij}^w is the effective soil matrix dispersion coefficient tensor of CO, in the dissolved phase [L^2T^{-1}], q_i is the soil water flux [LT^{-1}], θ_a is the volumetric air content [L^3L^{-3}] and *P* is the CO_2 production rate [$L^3L^{-3}T^{-1}$]. The term Sc, represents the dissolved CO_2 removed from the soil by root water uptake, i.e., when plants take up water the dissolved CO, is also taken up by the plant roots. The volumetric concentrations of CO_2 in the dissolved and gas phases are related by the following equation

$$c_w = K_c c_a \qquad (5)$$

where K_c is the distribution constant [-], which is strongly dependent on temperature. ***Šimůnek and Suarez*** [1993a] defined the total aqueous phase CO_2, c_w, as the sum of $CO_2(aq)$ and H_2CO_3, and related it to the CO, concentration in the gas phase with Henry’s Law. However, aqueous carbon also exists in the form of HCO,, CO_3^{2-}, and other complexed species, such as $CaCO_3^o$, and these species should be included in the expression for c,. Determination of these species cannot be made without use of a complete chemical speciation program.

Production of Carbon Dioxide

Since processes other than biological ones are generally of minor importance for CO_2 production in the soil, we did not include them into our model for CO_2 production We consider two processes for CO_2 production, production by soil microbes and production by plant root respiration. We assume that the CO_2 production by these two processes is additive and that it is possible to superpose the effects of environmental variables that alter production from the reference value [*Šimůnek and Suarez*, 1993a]. The production of CO_2 is then considered as the sum of the production rate by the soil microorganisms, γ_s $[L^3L^{-3}T^{-1}]$, and the production rate by plant roots, γ_p $[L^3L^{-3}T^{-1}]$

$$P = \gamma_s + \gamma_p = \gamma_{s0} \prod_i f_{si} + \gamma_{p0} \prod_i f_{pi} \tag{6}$$

where the subscript s refers to soil microorganisms and the subscript p refers to plant roots, $\prod f_i$ is the product of reduction coefficients dependent on depth, temperature, pressure head (the soil water content), CO_2 concentration, osmotic head and time. The parameters γ_{s0} and γ_{p0} represent, respectively, the optimal CO_2 production by the soil microorganisms or plant roots for the whole soil profile at 20°C under optimal water, solute and soil CO_2 concentration conditions $[L^3L^{-2}T^{-1}]$. The individual reduction functions are given in *Šimůnek and Suarez* [1993a] and a discussion of the selection of values for optimal production as well as coefficients for the reduction functions is given in Suarez and *Šimůnek* [1993].

2.4. Solution Chemistry

Elements of the Chemical Submodel

As mentioned in the introduction *Šimůnek and Suarez* [1994] and *Suarez and Šimůnek* [1994] presented two multicomponent chemical models. UNSATCHEM-2D is applicable only for nonacid environment with a pH > 6 [*Šimůnek and Suarez,* 1993b, 1994] and UNSATCHEM-ID can be used for acid as well as alkaline environments [*Suarez and Šimůnek,* 1994]. The chemical species which are considered in the models are given in Table 1; species that are only considered in the second model are highlighted. The chemical system for predicting major ion solute chemistry of the unsaturated zone includes either 37 or 55 chemical species (depending on the pH range). These are divided into five groups as listed in Table 1: 10 chemical components (calcium, magnesium, sodium, potassium, sulfate, chloride, nitrate, aluminum, silica, and organic matter), 25 complex aqueous species, seven possible solid species (calcite, gypsum, nesquehonite, hydromagnesite, dolomite, sepiolite, and gibbsite), six sorbed species, and seven species constituting the CO_2-H_2O system. In the following sections we present some of the equations that define this chemical system.

Mass and Charge Balance Equations

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 ten mass balance equations

Table 1. Species Considered in the Chemical Submodel

1	Aqueous components	10	Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-, NO_3^-, $H_4SiO_4^0$, Al^{3+}, Org^{3-}
2	Complexed species	25	$CaCO_3^\circ$, $CaHCO_3^+$, $CaSO_4^\circ$, $MgCO_3^\circ$, $MgHCO_3^+$, $MgSO_4^\circ$, $NaCO_3^-$, $NaHCO_3^\circ$, $NaSO_4^-$, KSO_4^-, $H_2SiO_4^{2-}$,$H_3SiO_4^-$, $AlSO_4^+$, $Al(SO_4)_2^-$, $AlHSO_4^{2+}$, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, $AlOrg^0$, $AlHOrg^+$, $HOrg^{2-}$, H_2Org^-, H_3Org^0, HSO_4^-
3	Precipitated species	7	$CaCO_3$, $CaSO_4 \cdot 2H_2O$, $MgCO_3 \cdot 3H_2O$, $CaMg(CO_3)_2$, $Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O$, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, $Al(OH)_3$
4	Sorbed species	6	$\overline{Ca}$, $\overline{Mg}$, $\overline{Na}$, $\overline{K}$,$\overline{Al}$, $\overline{H}$
5	Additional species	7	P_{CO2}, $H_2CO_3^*$, CO;-, HCO_3^-, H^+, OH, H_2O

for major components, two mass balance equations for the total analytical concentration of carbonate and bicarbonate are defined

$$\begin{aligned} CO_{3_T} &= [CO_3^{2-}] + [CaCO_3^\circ] + [MgCO_3^\circ] + [NaCO_3^-] \\ HCO_{3_T} &= [\text{HCO;}] + [CaHCO_3^+] + [MgHCO_3^+] + [NaHCO_3^\circ] \end{aligned} \tag{7}$$

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*** ($mol_c kg^{-1}$) as

$$Alk = 2CO_{3_T} + HCO_{3_T} + [OH^-] - [H^+] \tag{8}$$

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

$$\begin{aligned} &2[Ca^{2+}] + 2[Mg^{2+}] + [\text{Na'}] + [K^+] + [CaHCO_3^+] + [MgHCO_3^+] + [\text{I-I} \bullet \quad] + 3[Al^{3+}] \\ &+ 2[AlOH^{2+}] + 2[AlHSO_4^{2+}] + [AlOH_2^+] + [AlHOrg^+] + [AlSO_4^+] - 2\,[\text{CO;-}] - [HSO_4^-] \\ &- [HCO_3^-] - 2[SO_4^{2-}] - [Cl^-] - [\text{NO;}] - [OH^-] - 2[H_2SiO_4^{2-}] - [H_3SiO_4^-] - 3\,[Org^{3-}] \\ &- [NaCO_3^-] - [NaSO_4^-] - [KSO_4^-] - [Al(SO_4)_2^-] - [Al(OH)_4^-] - 2[HOrg^{2-}] - [H_2Org^-] = 0 \end{aligned} \tag{9}$$

CO, - H_2O *System*

The activities of the species present in solution at equilibrium are related by the mass-action equilibrium equations. The dissociation of water is represented by the following expression

$$K_w = \frac{(H^+)(OH^-)}{(H_2O)} \tag{10}$$

where K_W is the dissociation constant for water and parentheses denote ion activities. The **solubility** of CO,(g) in water is governed by Henry's law

$$K_{CO_2} = \frac{(H_2CO_3^*)}{P_{CO_2}(H_2O)} \tag{11}$$

where the activity of CO,,, is expressed in terms of the partial pressure P_{CO_2}, K_{CO_2} is Henry's Law constant and $H_2CO_3^*$ represents both aqueous CO_2 and H_2CO_3. The equilibrium expressions for the dissociation of carbonic acid are written as

$$K_{a_1} = \frac{(H^+)(HCO_3^-)}{(H_2CO_3^*)} \tag{12}$$

$$K_{a_2} = \frac{(CO_3^{2-})(H^+)}{(HCO_3^-)} \tag{13}$$

where K_{a1} and K_{a2} are the first and the second dissociation constants of carbonic acid.

Complexation Reactions

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

$$K_1 = \frac{(Ca^{2+})(SO_4^{2-})}{(CaSO_4^o)} \tag{14}$$

where K_1 is the equilibrium constant of the complexed species.

Cation Exchange Selectivity

Partition between the exchanger (solid phase) and the solution is described by the Gapon equation *[White and Zelazny,* 1986]

$$K_{ij} = \frac{\bar{c}_i^{y+}}{\bar{c}_j^{x+}} \frac{(c_j^{x+})^{1/x}}{(c_i^{y+})^{1/y}} \tag{15}$$

where y and x are the valences of species i and j, respectively, and K_{ij} is the Gapon selectivity coefficient. Adsorption concentrations are expressed in moles of charge per mass of dry soil ($mol_c kg^{-1}$). It is assumed that the cation exchange capacity, $\bar{c}_T$ ($mol_c kg^{-1}$), is constant and independent of the pH. The assumption of constant exchange capacity is not valid for soils containing large amounts of variable charge, such as oxisols, but is necessary in the present models to maintain conservation of mass.

Precipitation-Dissolution Reactions

We consider five solid phases that constrain the solution to equilibrium whenever the solids are specified or approached from oversaturation: 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 never included into the equilibrium system, since true ordered dolomite does not precipitate under earth surface conditions. Discussion on the selection and consideration of these solids is given in Suarez and *Šimůnek* [1994]. 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_{SP}

$$K_{SP}^{C} = (Ca^{2+})(CO_3^{2-}) \qquad \text{calcite} \tag{16}$$

$$K_{SP}^{G} = (Ca^{2+})(SO_4^{2-})(H_2O)^2 \qquad \text{gypsum} \tag{17}$$

$$K_{SP}^{N} = (Mg^{2+})(CO_3^{2-})(H_2O)^3 \qquad \text{nesquehonite} \tag{18}$$

$$K_{SP}^{H} = (Mg^{2+})^5(CO_3^{2-})^4(OH^-)^2(H_2O)^4 \qquad \text{hydromagnesite} \tag{19}$$

$$K_{SP}^{S} = \frac{(Mg^{2+})^2(H_4SiO_4)^3(OH^-)^4}{(H_2O)^{4.5}} \qquad \text{sepiolite} \tag{20}$$

$$K_{SP}^{B} = \frac{(Al^{3+})(H_2O)^3}{(Al(OH)_3)(H^+)^3} \qquad \text{gibbsite} \tag{21}$$

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

The equilibrium concentrations of Ca^{2+} and SO,” in a gypsum system are obtained by solving the quadratic algebraic equation corresponding to (17). The concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- in equilibrium with carbonate solids, as well as Al^{3+} for gibbsite, are determined by solving cubic algebraic equations, as described in ***Šimůnek and Suarez*** [1993b].

Kinetic Model of Calcite Precipitation-Dissolution

The reaction rate of calcite precipitation-dissolution, R^C, ***in*** the absence of inhibitors such as “foreign ions” and dissolved organic matter, can be calculated with the rate equation of ***Plummer et al.*** [1979]

$$R^C = k_1(H^+) + k_2(H_2CO_3^{\bullet}) + k_3(H_2O) - k_4\frac{K_{a_2}}{K_{SP}^C}(Ca^{2+})(HCO_3^-) \qquad (22)$$

where

$$k_4 = k_1 + \frac{1}{(H_S^+)}\left[k_2(H_2CO_3^{\bullet}) + k_3(H_2O)\right] \qquad (23)$$

and k_1, k_2, and k_3 ***are*** temperature dependent first order rate constants representing the forward reactions (mmol $cm^{-2}s^{-1}$) and k_4 is a function dependent on both temperature and CO_2 concentration representing the backward reactions (mmol $cm^{-2}s^{-1}$). The dissolution-precipitation rate R^C is expressed in mmol of calcite per cm^2 of surface area per second. The term (H_S^+) is the H^+ activity at the calcite surface and is assumed to be equal to the (H^+) of the solution at calcite saturation.

For the condition where pH > 8 and $P_{CO2} < 1000$ Pa, at *25” C*, the following precipitation rate expression is considered more accurate ***[Inskeep and Bloom,*** 1985],

$$R^C = -11.82[(Ca^{2+})(CO_3^{2-}) - K_{SP}^C] \qquad (24)$$

The precipitation or dissolution rate of calcite is reduced by the presence of various inhibitors. ***Šimůnek and Suarez*** [1993b] 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 ***Inskeep and Bloom*** [1986]. These surface reaction precipitation-dissolution models simulate under 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.

Kinetic Model of Dolomite Dissolution

The reaction rates of dolomite dissolution, R^D (mmol $cm^{-2}s^{-1}$), are calculated with the rate equation of ***Busenberg and Plummer [1982]***

$$R^D = k_1(\mathrm{H}^+)^{0.5} + k_2(\mathrm{H_2CO_3^*})^{0.5} + k_3(\mathrm{H_2O})^{0.5} - k_4(\mathrm{HCO_3^-}) \tag{25}$$

wdere the temperature dependent first order rate constants **k„, k_2, k_3 (mmol cm%‘),** representing the forward reactions, and k_4 (mmol **cm^{-2}s^{-1})**, representing the back reaction, are given by ***Busenberg and Plummer*** [1982] The dissolution rate R^D is again expressed in mmol of dolomite per cm^2 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 the single ion activity coefficient is specified by using either an extended version of the Debye-Huckel equation [Truesdell and Jones, 1974] or Pitzer expressions ***[Pitzer,*** 1979]. The extended version of the Debye-Hiickel equation ***[Truesdell and Jones, 1974],*** which can be used in the dilute to moderately saline concentration range, is given by

$$\ln \gamma = - \frac{Az^2\sqrt{I}}{1 + Ba\sqrt{I}} + bI \tag{26}$$

where ***A*** and ***B*** are constants that depend only on the dielectric constant, density, and temperature; z is the ionic charge, ***a*** and ***b are two*** adjustable parameters, and ***I*** is the ionic strength

$$I = 0.5 \sum_{i-1}^{M} z_i^2 m_i \tag{27}$$

where M is the number of species in the solution mixture, m_i ***is*** molality and z_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

$$\ln \gamma = a' I \tag{28}$$

where ***a'*** is an empirical parameter. The values of this parameter for neutral species are listed in ***Šimůnek and Suarez*** [1993a].

At high ionic strength, activity coefficients are no longer universal functions of ionic strength, but are also dependent on the relative concentration of the various ions present in solution ***[Felmy and Weare,*** 1986]. The activity coefficients can then be expressed in a virial-type expansion of the form [Pitzer, 1979]

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j B_{ij}(I) m_j + \sum_j \sum_k C_{ijk} m_j m_k + \dots \tag{29}$$

where γ_i^{DH} is a modified Debye-Hückel activity coefficient which is a universal function of ionic strength, and B_{ij} and C_{ijk} are specific coefficients for each ion interaction. This model is considered accurate even for solutions with very high ionic strength (up to 20 molal) and can be used down to infinite dilution.

3. Solution Strategy

The Galerkin finite element method with linear basis functions is used to obtain a solution of the water flow (1) and solute (3) and CO_2 (4) 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 *Šimůnek et al.* [1992]. The finite element method is also used to solve the heat, CO_2, and multicomponent solute transport equations. A detailed description of the numerical solution for these transport equations is given in *Šimůnek and Suarez* [1993b].

Computation of the solution species composition is accomplished in a fairly similar way as in the chemical model WATEQ *[Truesdell and Jones, 1974]*, a speciation model that does not consider solid and adsorbed phases. The inputs into the chemical submodel of UNSATCHEM-2D are the analytical concentrations of the major ions, alkalinity, adsorbed and solid phase concentrations, water content, temperature, bulk density, and CO_2 partial pressure.

The governing solute transport equation (3) contains time derivative terms for the total dissolved, sorbed and solid phase concentrations. Because of the second and third terms, the solute transport equation (3) is highly nonlinear and an iterative process must be applied to obtain its solution.

Coupling between the transport and chemical submodules was described by Walsh *et al.* [1984], *Cederberg et al.* [1985], and Bryant *et al.* [1986] (also used by Yeh and Tripathi [1990]). First, the discretized solute transport equation (3) is solved by setting the second and third terms equal to zero for the equilibrium case or by calculating the third term from equations (22) and (25) 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 kinetic reactions 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 substantially different, a new iteration is started. This iteration process is continued until the difference between the new and old concentration is less than the prescribed tolerance for all nodes.

4. Examples

In this section we present two examples. The first example demonstrates the applicability of the model SOILC02 for the prediction of CO_2 concentrations in the soil profile and CO_2 fluxes to the atmosphere [Suarez *and Šimůnek*, 1993]. The second example demonstrates the application of the model UNSATCHEM-2D to the reclamation of a sodic soil.

4.1. Missouri CO_2 transport experiment [Suarez and *Šimůnek*, 1993]

The predictive capabilities of SOILCO2 were evaluated 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 the year 1982 on CO_2 dynamics in soil under three different cropping systems; these data were discussed with regard to crop effects, microbial activity, and relevant abiotic factors including soil water content and temperature. 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. Figure 1 shows the excellent agreement between the measured CO_2 concentrations at the 0.2 m depth and the corresponding values calculated with the SOILC02 model. In all instances the calculated values are within one standard deviation of the mean of the measured values. There are no statistically significant differences between the measured and predicted CO, concentrations at the 90% confidence level. The irregular pattern of the CO, concentrations shown in Figure 1 reflects the fact that within the dry periods (first half of May, second half of July and all of October), the CO, concentrations decrease to very low values. During the wet periods the CO, concentrations are relatively high.

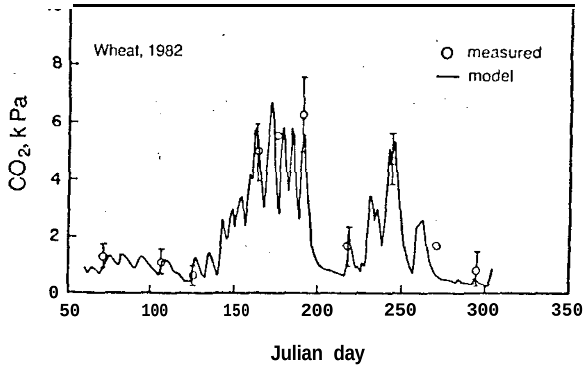

Fig. 1. Measured ***[Buyanovsky and Wagner,*** 1983] and calculated CO, concentrations at a depth of 0.20 m for the Missouri wheat experiment (after ***Suarez and Šimůnek*** [1993]).

Figure 2 shows the comparison of the calculated daily and weekly CO, 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, since these rates fluctuate significantly on a daily basis due to changes in the water content of the upper soil layer. The large fluctuations shown in Figure 2 indicate that the accurate determination of CO, flux requires an excessive number of measurements if the surface water content is rapidly changing. This change is important for rain events or whenever frequent water applications are made. As with the CO, concentration data, there is an excellent correspondence between measured and calculated fluxes.

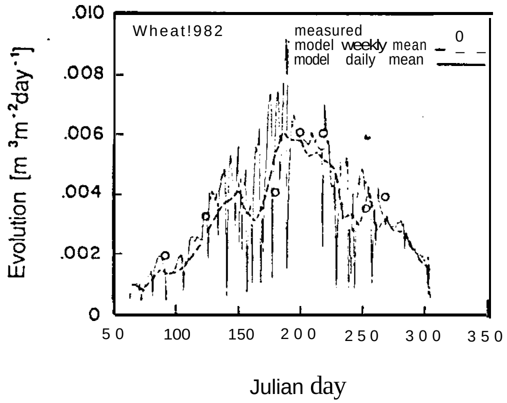

Fig. 2. Measured [Buyanovsky and *Wagner*, 1986] and calculated daily and weekly CO, fluxes to the atmosphere for the Missouri wheat experiment (after Suarez and *Šimůnek* [1993]).

4.2. Two-Dimensional Furrow Reclamation Irrigation Problem

A furrow irrigation system was used to simulate the two-dimensional infiltration of water into a sodic soil undergoing reclamation. The simulation of sodic soil reclamation demonstrates the cation exchange feature of UNSATCHEM-2D and illustrates some of the unique features. of the model. The schematic representation of the flow domain for the considered furrow irrigation together with the finite element mesh is presented in Figure 3. 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. Due to symmetry, it is only necessary to carry out the simulation for the domain between the axis of two neighboring furrows. Free drainage is used as the bottom boundary condition, while 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 [*Šimůnek and Suarez*, 1993b] were used.

The calculation was run at a constant temperature of 25 °C, with an optimal CO, production value γ_{s0} of 0.007 $m^3m^{-2}d^{-1}$. Production decreased exponentially with depth with a maximum at the surface as described in *Suarez and Šimůnek* [1993]. These production values were modified by the model according to environmental conditions (in this case pressure heads and CO, concentrations). Root water uptake and evaporation were neglected. The bulk density of the soil was taken as 1.4 g cm^{-3}, while a molecular diffusion coefficient of 2 cm^2day^{-1} was chosen. Longitudinal and transverse dispersivities values were 2 and 0.2 cm, respectively.

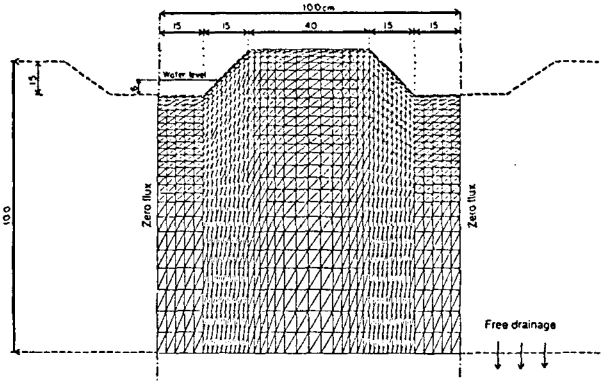

Fig. 3. Schematic representation and finite element mesh of the flow domain for the furrow irrigation system for example 2.

The solution composition of the water initially present in the soil profile is that of a highly sodic water: $Ca_T=0.2$, $Na_T=4.8$, $Cl_T=4.6$, Alkalinity=0.4 mmol$_c$L^{-1}, with other concentrations equal to zero. The cation exchange capacity is 100 mmol$_c$kg^{-1} (Ca=5.0, Na=95.0 mmol$_c$kg^{-1}). The Gapon selectivity coefficient from Wagenet and Hutson [1987] was used for calcium-magnesium exchange (K_{12} = 1.158). Two different irrigation water compositions were used. One irrigation water was almost gypsum saturated: Ca_T = 32.6, Na_T = 4.8, Cl, = 5.0, SO_{4T} = 32.0, *Alk=0.4* mmol, L^{-1} and zero for other concentrations. The second water is of the following composition: Ca_T= 1.5, Na_T=2.0, Cl_T= 1.0, SO_{4T}=2.0, *Alk=0.5* mmol$_c$L^{-1} and zero for other concentrations. Reclamation 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 is in equilibrium with calcite. Cation exchange is treated as an instantaneous process.

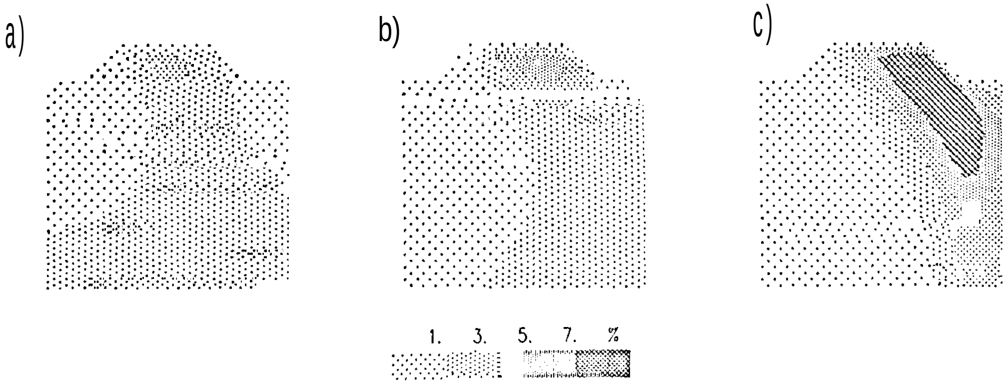

Fig. 4. CO, concentration (%) profiles at times: a) 0.5, b) 1, and c) 5 days for example 2.

Steady state water flow was reached after approximately 1.5 days. Figure 4 shows the change in CO_2 concentration in space and time. The CO_2 concentration increases with time and depth with diffusion occurring predominantly in the direction of the dry furrow. The distribution of a hypothetical tracer is shown on Figure 5. The concentration front of the tracer reached a depth of one meter approximately after one day.

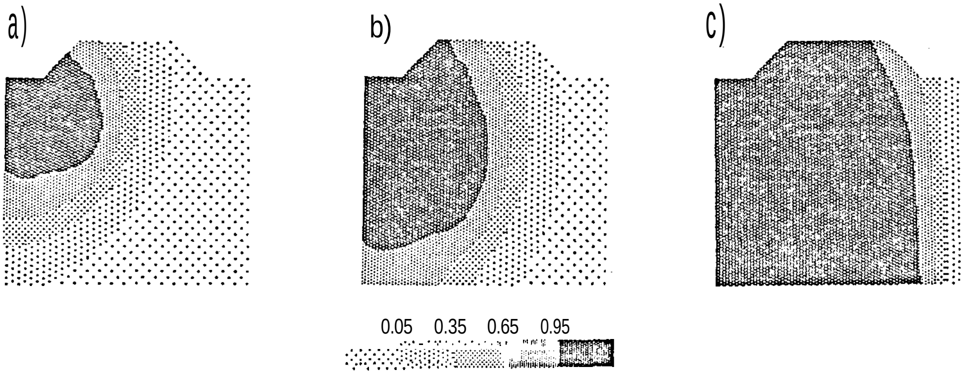

Fig. 5. Tracer concentration profiles at times: a) 0.5, b) 1, and c) 5 days for example 2.

Figure 6 presents the exchangeable concentrations of calcium for the three scenarios after five days. There is a sharp exchange front reaching to approximately 70 cm for the gypsum water (Figure 6a). In contrast to Figure 6a, Figure 6b demonstrates reclamation to a depth of less than 10 cm when irrigating with the high quality water. After 50 days the reclamation front (exchangeable Na less than 10 %) extended 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 6c). Reclamation of the region below the furrow was essentially completed down to one meter after 25 days of leaching. This figure demonstrates the importance of calcite dissolution during reclamation. Reclamation with calcite is often dismissed because of a lack of consideration of elevated CO, concentrations in the soil and the enhanced dissolution of calcite during

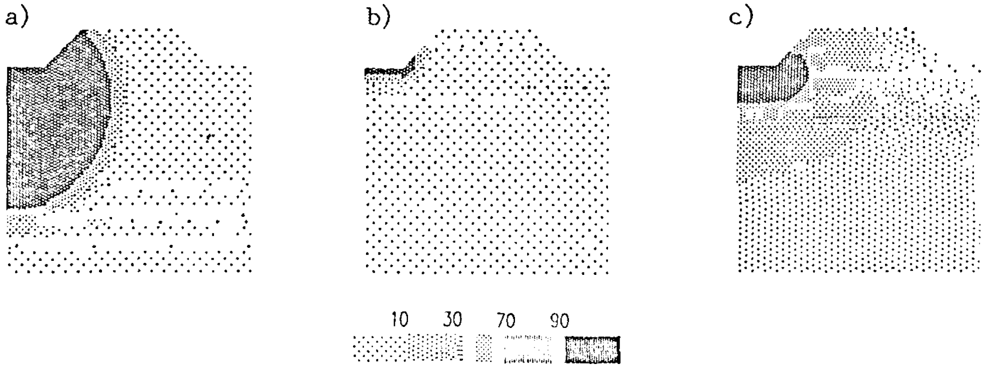

Fig. 6. Exchangeable calcium concentration ($mmol_c kg^{-1}$) profiles at 5 days for a) infiltration with gypsum saturated water, b) infiltration with high quality water, and c) infiltration with high quality water into a profile containing calcite.

the reclamation exchange. For example calcite dissolution contributed 300 eq per m^2 of soil surface area to reclamation within the first five days of leaching. Selection of a higher exchange capacity and associated hydraulic properties of a finer textured soil would enhance both the time required for infiltration, as well as quantity of water required for reclamation.

5. Summary and Conclusion

The process-based CO_2 production and transport model combined with variably saturated water flow, SOILCO2, was described. Comparison of the model to field data demonstrates its ability to predict both CO_2 concentrations in the soil and CO_2 fluxes to the atmosphere for a growing crop with changes in crop development, temperature and soil water content. The multicomponent water and solute transport model UNSATCHEM-2D was also reviewed. This model is particularly suited for simulation of major ion solute chemistry of arid zone soils. The model considers the transport of CO_2 thus allowing for calculation of soil CO, concentrations. Soil CO, concentrations are used in the chemical subroutine to calculate solute composition. The model utilizes both extended Debye-Huckel 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 CO_2 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 of oxyanions, such as B, Se, and As. The concentrations of these anions is important when considering the potential reuse of agricultural drainage waters in arid environments. A more detailed plant growth model will be incorporated to better predict plant response to environmental conditions.

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