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UNSATCHEM 3.1: Computer Model for Prediction of Water and Multicomponent Solute Transport

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1 INTRODUCTION

The previously developed computer model UNSATCHEM has been upgraded with several new capabilities. The model contains capability to predict B adsorption and transport based with prediction of the constant capacitance constants from generally available soil properties, a calcite kinetic model that considers the effect of dissolved organic carbon, as well as a clay organic matter mixing model to predict cation selectivity constants. Several existing features are still unique, such as prediction of CO_2 concentrations in the root zone, consideration of the effects of soil chemistry on hydraulic properties and inclusion of a kinetic model to describe calcite dissolution and precipitation

2 WATER FLOW

2.1 *Chemical effects on hydraulic conductivity*

The water flow routines in UNSATCHEM (Suarez and Simunek, 1996, Suarez and Simunek, 1997) use a modified version of the one-dimensional Richards= equation

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

where θ_w is the volumetric water content, K is the hydraulic conductivity function, h is the water pressure head, t is time, z is the spatial coordinate, and S is the sink term representing removal of water from the soil by plant roots. The unsaturated soil hydraulic properties are described by a new modified version of those proposed by van Genuchten (1980). The hydraulic conductivity functions are now given by

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

where

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \qquad (3)$$

and where θ_r and θ_s are the residual and saturated water content [cm^3/cm^3], respectively, K_s is the saturated conductivity [cm/ d], K_r is the relative hydraulic conductivity, S_e is relative saturation and m, n, and α [1/cm] are the empirical parameters. The r term is a scaled parameter that represents the effect of soil chemistry on hydraulic properties. It is considered for most irrigation reclamation problems that it is sufficient to chose default hydraulic characteristics based on soil texture and adjust the saturated hydraulic conductivity value to that of the soil.

2.2 *Chemical effects on hydraulic properties*

Equation 2 differs from previous relations in that it includes a reduction term, r, which scales the hydraulic conductivity in relation to the chemical conditions in the soil. Optimal soil chemical conditions for infiltration are represented by values where $r=1$. Elevated levels of exchangeable sodium result in swelling of smectitic clays. Detachment of clay particles, dispersion, and subsequent clay migration and redeposition results in blocking of pores at low salinity and in the presence of exchangeable sodium (McNeal, 1968, Shainberg and Levy, 1992). This process is readily observed in the natural development of clay pan layers in soils and most dramatically in sodic, nonsaline soils. In addition, it has been determined that elevated levels of pH adversely impact saturated hydraulic conductivity, separate from the sodicity and salinity interactions (Suarez et al., 1984).

The chemical effects on hydraulic properties are calculated from the interaction of two factors given by

$$r = r_1 \, r_2 \qquad \textbf{(4)}$$

where r_1 is the reduction due to the adverse effects of low salinity and high exchangeable sodium fractions on the clay and r_2 is the adverse effect of pH. The r_1 term is given by McNeal (1968). The reduction factor r_2, for the adverse effect of pH on hydraulic conductivity, was calculated from the experimental data of Suarez et al. (1984), after first correcting for the adverse effects of low salinity and high exchangeable sodium using the calculated r_1 values. In view of the differences among soils, these specific values may not be generalized predictors of soil hydraulic conductivity, although they do represent conditions of arid land soils examined at the U.S. Salinity Laboratory.

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

3 PREDICTION OF CARBON DIOXIDE PRODUCTION AND TRANSPORT

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

$$P = \gamma_s + \gamma_p = \gamma_{s0} \prod_i f_{si} + \gamma_{p0} \prod_i f_{pi} \qquad \textbf{(5)}$$

where the subscript s refers to soil microorganisms and the subscript p refers to plant roots, 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. The model incorporated the individual reduction functions given in Simunek and Suarez (1993) and values for optimal production as well as coefficients for the reduction functions (Suarez and Simunek, 1993). The one-dimensional carbon dioxide transport model assumes that CO_2 transport in the unsaturated zone occurs in both the liquid and gas phases. The total aqueous phase CO_2, c_w, is the sum of aqueous CO_2 and H_2CO_3, and is related to the CO_2 concentration in the gas phase by the Henry's Law constant.

4 CHEMICAL MODEL AND TRANSPORT

4.1 *Components*

The model considers advective-dispersive chemical transport under transient flow conditions in partially saturated soil.

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

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + 2[CaCO_3^0] + [CaHCO_3^+] + 2[MgCO_3^0] + [MgHCO_3^+] + 2[NaCO_3^-] + [NaHCO_3^0] + [B(OH)_4^-] - [H^+] + [OH^-] \tag{6}$$

where brackets represent concentrations (mol/kg). From these components there are 11 species Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2+}, Cl, HCO_3^-, CO_3^{2-}, NO_3^-, H_3BO_3, and $B(OH)_4^-$, and the ion pair/complexes $CaHCO_3^+$, $CaCO_3^0$, $CaSO_4^0$, $MgHCO_3^+$, $MgCO_3^0$,$MgSO_4^0$, $NaHCO_3^0$, $NaCO_3^-$, $NaSO_4^-$, $KHCO_3^0$, KCO_3^-, KSO_4^-. It is assumed that all aqueous species are in equilibrium as defined by the ion association expressions and constants. Alkalinity as defined in equation (6) is a conservative species, affected only by dissolution or precipitation of a carbonate phase (such as calcite). After calculating the air phase CO_2 partial pressure, the $H_2CO_3^*$ (sum of aqueous CO_2 and H_2CO_3) is then calculated

The soil solution pH is determined as a dependent variable [H] calculated from solution of Eqn. 6 and a charge balance expression and multiplication by the activity coefficient. All equilibrium constants are calculated from available temperature dependent expressions. Soil temperature is calculated from a heat flow submodel, with input of air temperature, as discussed above.

4.2 *Osmotic pressure and activity coefficients*

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

$$P_\varphi = RT\frac{M_s v m_\varphi}{V_s m^0} \tag{7}$$

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

Activity coefficients are determined either using either an extended version of the Debye-Huckel equation or at high ionic strength, Pitzer equations. The Pitzer approach considers ion- ion interactions for every species in solution and is considered suitable for prediction of species activity in solutions up to 20 mol/kg.

4.3 *Solid phases*

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

Calcite Precipitation. It has been shown that waters below irrigated regions are supersaturated with respect to calcite (Suarez et al., 1992) thus the equilibrium condition underestimates the Ca solubility in soil water. The cause of supersaturation has been shown to be due to poisoning of crystal surfaces by dissolved organic matter (Lebron and Suarez, 1996). Lebron and Suarez (1996) developed a precipitation rate model which considers the effects of dissolved organic carbon both on crystal growth and heterogeneous nucleation. The combined rate expression is given by

$$R_T = R_{CG} + R_{HN} \qquad \textbf{(8)}$$

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

$$R_{HN} = k_{HN}\ f\,(SA)\,[\log(\Omega - 2.5)]\,(3.37 \times 10^{-4}\ DOC^{-1.14}) \qquad \textbf{(9)}$$

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

Gypsum. The model allows specification of the initial presence of gypsum, requiring input of the quantity present (mmol_c /kg). If gypsum is present in any soil layer at the given time step, the model forces the solution to gypsum equilibrium. The program tracks changes in the amount of gypsum present. In all cases gypsum precipitates wherever supersaturation is indicated by solution calculations.For the objectives of this model it appears reasonable to assume that kinetics of gypsum dissolution/precipitation are sufficiently fast that the equilibrium condition can be used.

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

The model considers that Mg precipitation can occur as a carbonate or as a silicate. Since this is a predictive model, it considers only phases that either precipitate under earth surface conditions or occur frequently and are reactive under earth surface conditions. These need not necessarily be the thermodynamically most stable phases. With this consideration, magnesite is neglected.The model will allow precipitation of the metastable phases nesquehonite or hydromagnesite when saturation is reached. These phases will occur very infrequently. The Mg carbonate precipitated, combined with calcite precipitation, will represent the mixed Ca-Mg precipitate, called protodolomite, that is observed in hypersaline environments. However, the resulting solution composition is much different than that produced by simply forcing equilibrium with respect to dolomite. The precipitation of calcite+ magnesium carbonate results in solutions of approximately three orders of magnitude supersaturation with respect to dolomite. This result is consistent with the high levels of dolomite supersaturation maintained in high Mg waters (Suarez, unpublished data). Precipitation (or dissolution, if present in the soil) of poorly crystallized sepiolite is also considered by the model.

4.4 *Cation exchange*

Cation exchange is generally the dominant *chemical* process for the major cations in solution in the unsaturated zone. The model uses a Gapon-type expression.It is assumed that the cation exchange capacity c_T(mol$_c$/kg), is constant, Experimentally determined selectivity values are not constant, nor is the cation exchange capacity which varies as a function of pH, due to variable charge materials such as organic matter. Suarez and Wood (1993) developed a mixing model which is able to approximate the nonconstant values of the soil selectivity coefficient by taking into account the organic matter content of the soil and using the published constant selectivity values for clay and organic matter. UNSATCHEM uses this approach by solving 2 sets of equations for cation exchange (clay and organic matter).

4.5 *Boron adsorption*

Boron adsorption is predicted using the constant capacitance model and a generalized set of equations that predict the model parameters based on commonly available soil properties. The following equations are used from Goldberg et al., 2000:

$$\mathrm{Log}K_{B-} = -8.98 + 0.00351\mathrm{CEC} - 0.00609\mathrm{SA} + 0.263\mathrm{OC} + 0.340\mathrm{IOC} + 0.401\mathrm{Fe} \quad \textbf{(10)}$$

$$\mathrm{Log}K_{+} = 9.42 - 0.00495\mathrm{CEC} + 0.00514\mathrm{SA} - 0.132\mathrm{OC} - 0.586\mathrm{IOC} - 8.51\mathrm{Al} \quad \textbf{(11)}$$

$$\mathrm{Log}K_{-} = -12.51 + 0.00156\mathrm{SA} + 0.312\mathrm{OC} + 0.237\mathrm{IOC} - 4.85\mathrm{Al} \quad \textbf{(12)}$$

where SA is the surface area, IOC is inorganic carbon C is organic carbon aaand Al and Fe are readily extractible Fe and Al.

Silicate weathering

The kinetics of silicate is represented by rate equations that account for surface area, ligand concentration, surface OH groups (based on surface charge) as related to pH. , SOH equations of the type .

$$R_t = a(\Gamma)^{4.0} + a'(\Gamma')^{4.0} + b_1(\mathrm{SOH}) + b_2(\mathrm{S-L}) \quad \textbf{(13)}$$

$$R_t = b_1(\mathrm{SOH}) + b_2(\mathrm{S-L}) \qquad \textbf{(14)}$$

$$R = k_H + \frac{\left[\mathrm{H}^+\right]^n}{\left[\mathrm{M}\right]^x \left[\mathrm{Al}^{3+}\right]^y} + \frac{k\mathrm{H_2O}}{\left[\mathrm{Al}^{3+}\right]^u} + k_{CO_2} p_{CO_2} + k_{org}\left[\mathrm{org}\right]^{0.5} \qquad \textbf{(15)}$$

where SA is surface area

5 CONCLUSIONS

The model contains representation of important processes relating to major ions and selected trace ions. The predictive capability has been demonstrated in studies involving, carbon dioxide, water flow, major ion chemistry including gypsum and calcite dissolution cation exchange, B transport and adsorption. A simplified version of the model with a more user friendly interface was developed for distribution by FAO as FAO-SWS.

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