Modelling multiple solute transport in variably saturated soils

JIRÍ ŠIMŮNEK, MARTINUS TH. VAN GENUCHTEN & DONALD L. SUAREZ
US Salinity Laboratory, USDA-ARS, 4500 Glenwood Drive, Riverside, California 92501, USA

Abstract This paper presents two models typical of two different approaches often used for modelling the advective-dispersive transport of multiple ions in variably-saturated porous media. The first approach assumes that all solute reactions can be incorporated directly into the governing transport equations (the one-step method), while the second approach divides the mathematical solution process into two separate steps: one for transport, and one for most or all chemical reactions (the two-step method). The two approaches are illustrated using the one-step CHAIN_2D code which simulates the nonlinear nonequilibrium transport of solutes involved in sequential first-order decay reactions, and the two-step UNSATCHEM-2D code which considers equilibrium and kinetic non-equilibrium chemistry of major ions.

INTRODUCTION

The fate and transport of a variety of chemicals migrating from industrial and municipal waste disposal sites, or intentionally applied to agricultural lands, is increasingly becoming a concern. Once released into the subsurface environment, these chemicals are often subjected to a large number of simultaneous physical, chemical, and biological processes, including sorption-desorption, volatilization, photolysis, precipitation-dissolution, complexation, and biodegradation. While many models have been developed which quantify some of these processes, most models usually consider only one solute by severely simplifying the different chemical interactions. For example, the complex processes of adsorption and cation exchange are often accounted for by invoking simplified linear (Huyakorn et al., 1991) or nonlinear Freundlich isotherms (Yeh & Huff, 1985) which lump all reactions between the solid and liquid phases into a single distribution coefficient $K_D$ (Liu & Narasimhan, 1989), either with or without a Freundlich type exponent. Other processes such as precipitation, biodegradation, volatilization or radioactive decay are frequently simulated by means of simple first- or zero-order rate equations. Only recently has there been a significant effort to develop models that consider multiple-species solute transport as well as variably-saturated water flow.

Two approaches may be used for modelling the transport of multiple ions which undergo a number of simultaneous and often interactive chemical reactions (Zysset et al., 1994). One approach (the one-step method) assumes that all chemical reactions in the simulated system can be included directly into the governing transport equations, while a second approach (the two-step method) divides the numerical solution into two
independent steps which are solved separately. The first step provides solutions of the partial differential equations governing advective-dispersive transport, whereas the second step involves algebraic equations describing the different chemical equilibrium reactions, as well as ordinary differential equations describing kinetic reactions. In this paper we present two models that serve as examples for the above two modelling approaches.

The one-step approach is illustrated using the CHAIN_2D (Šimůnek & Van Genuchten, 1994) which simulates the nonlinear nonequilibrium transport of solutes involved in sequential first-order decay reactions. Problems of solute transport involving sequential first-order reactions frequently occur in soil and groundwater systems. Examples are the migration of various radionuclides, the simultaneous movement of interacting nitrogen species, organic phosphate transport, or the transport of selected pesticides and their degradation products.

The two-step method is illustrated by means of the UNSATCHEM-2D (Šimůnek & Suarez, 1994a) which models equilibrium and kinetic non-equilibrium chemistry of major ions. This model accounts for a variety of equilibrium chemical reactions (e.g. complexation, cation exchange, precipitation-dissolution) and chemical-kinetic reactions (precipitation-dissolution of selected solid phases). The model in its present form may be used to simulate the behaviour and transport of major ions in the subsurface, such as occurs during salinization of soils in arid regions due to irrigation practices, or during reclamation of sodic soils. Only relatively small changes are needed to make the model also applicable to the transport of selected minor ions such as radionuclides and oxyanions.

The CHAIN2D and UNSATCHEM-2D models were coupled with variably-saturated water flow using subroutines taken from the SWMS_2D model of Šimůnek et al. (1994), as well as with heat transport; these additional features will not be discussed in this paper.

THEORY

Solute transport in CHAIN_2D

This code assumes that solutes can reside in all three phases, i.e., the liquid, solid, and gaseous phases. Interaction between solid and liquid phase concentrations may be described by nonlinear nonequilibrium reactions, while interactions between liquid and gaseous phase concentrations is represented by linear equilibrium reactions. The code also assumes that degradation and production processes are often different in each phase, and that there are two types of first-order decay: first-order degradation independent of other solutes, and first-order decay (or production) that provides the required coupling with other solutes involved in the sequential first-order reactions. The model considers advective-dispersive transport in the liquid phase, as well as diffusive transport in the gas phase. The general structure of the system of first-order decay reactions for three solutes (A, B, and C) is as follows (Šimůnek & Van Genuchten, 1994):
in which $\gamma$ and $\mu$ are zero-order production and first-order degradation rate coefficients, respectively, $\mu'$ represents first-order rate constants which provide connections between individual chain species, and where the symbols and subscripts $w$, $s$ and $g$ refer to the liquid, solid and gaseous phases, respectively. This above general structure allows one to simulate various solute transport scenarios by selecting or deleting certain rate constants. Typical examples of sequential first-order chains are:

1. Radionuclides (Van Genuchten, 1985)

   \[ ^{238}\text{Pu} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra} \]

2. Nitrogen (Tillotson et al., 1980)

   \[ (\text{NH}_2)_2\text{CO} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \]


   \[
   \text{Parent pesticide} \rightarrow \text{Daughter product 1} \rightarrow \text{Daughter product 2} \rightarrow \text{Products}
   \]

The partial differential equations governing the two-dimensional nonequilibrium transport of solutes involved in a sequential first-order decay chain during transient water flow in a variably saturated rigid porous medium are taken as (Simůnek & Van Genuchten, 1994):

\[
\frac{\partial \theta c_k}{\partial t} + \frac{\partial \rho s_k}{\partial t} + \frac{\partial a g_k}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta \frac{\partial c_k}{\partial x_j} \right) + \frac{\partial}{\partial x_i} \left( \alpha \rho g_k \frac{\partial g_k}{\partial x_j} \right) - \mu' \frac{\partial c_k}{\partial x_i} - (\mu_{w,k} + \mu'_{w,k}) \theta c_k - (\mu_{s,k} + \mu'_{s,k}) \rho s_k - (\mu_{g,k} + \mu_{g,k}') a g_k + \mu'_{w,k-1} \theta c_{k-1} + \mu_{g,k-1} \rho s_{k-1} + \gamma_{w,k} \theta + \gamma_{s,k} \rho + \gamma_{g,k} a - S c_{r,k} \quad k \in (2, n_s)
\]
where $c$, $s$, and $g$ are the solute concentrations in the solution, adsorbed, and gaseous phases, respectively; $q_i$ is the $i$th component of the volumetric flux, $\rho$ is the soil bulk density, $a$ is the air content, $S$ is a sink term (e.g. root water uptake), $c_r$ is the concentration of the sink term, $D_{ij}^w$ is the dispersion coefficient tensor for the liquid phase, $D_{ij}^g$ is the diffusion coefficient tensor for the gas phase, the subscript $k$ represents the $k$th chain number, and $n_r$ is the number of solutes involved in the chain reaction. The nine zero- and first-order rate constants in (1) may be used to represent a variety of reactions or transformations including biodegradation, volatilization, and precipitation. The governing equation for the first solute in the chain is the same as (1), except that all terms containing the subscript $k-1$ ($=0$) must be removed. For simplicity, the subscript $k$ will be not be used further in this paper.

CHAIN_2D assumes nonequilibrium interaction between the solution ($c$) and adsorbed ($s$) concentrations, and equilibrium interaction between the solution ($c$) and gas ($g$) concentrations. The equilibrium adsorption isotherm relating $s$ and $c$ is described by a generalized nonlinear empirical equation:

$$s = \frac{k_s c^\beta}{1 + \eta c^\beta}$$  \hspace{1cm} (2)

where $k_s$, $\beta$, and $\eta$ are constants. The Freundlich, Langmuir, and linear adsorption equations are special cases of equation (2). The concept of two-site sorption (Van Genuchten & Wagenet, 1989) is used in CHAIN_2D to account for nonequilibrium sorption. The sorption sites of the solid phase are, for this purpose, divided into two fractions:

$$s = s^e + s^k$$ \hspace{1cm} (3)

Sorption, $s^e$, on one fraction ($f$) of the sites is assumed to be instantaneous, while sorption, $s^k$ on the remaining fraction is considered to be time dependent using the first-order rate law:

$$\frac{\partial s^k}{\partial t} = \omega \left[ (1 - f) \frac{k_s c^\beta}{1 + \eta c^\beta} - s^k \right] - (\mu_s + \mu_s') s^k + (1 - f) \gamma_s$$ \hspace{1cm} (4)

where $\omega$ is a first-order rate constant. In addition, we used a linear equilibrium equation to relate the concentrations $g$ and $c$ as follows

$$g = k_g c$$ \hspace{1cm} (5)

where $k_g$ is an empirical distribution coefficient.

Substituting (2) through (5) into (1) and invoking the continuity equation for isothermal water flow in a variably saturated porous medium leads to

$$-\theta R_k \frac{\partial c_k}{\partial t} - q_i \frac{\partial c_k}{\partial x_j} + \frac{\partial}{\partial x_j} \left( \theta D_{ij} \frac{\partial c_k}{\partial x_j} \right) + F_k c_k + G_k = 0 \hspace{1cm} k \in (1, n_r)$$ \hspace{1cm} (6)

where the coefficients $F$ and $G$ are given in Šimůnek & Van Genuchten (1994), $D_{ij}$ is the effective dispersion coefficient tensor, and $R$ is a retardation factor given by

$$R(c) = 1 + \frac{\rho}{\theta} \frac{f k_s c^\beta - 1}{(1 + \eta c^\beta)^2} + \frac{ak_g}{\theta}$$ \hspace{1cm} (7)
The solution of equation (6) requires knowledge of the water content $\theta$ and the volumetric flux $q_i$. These two variables are obtained from numerical solutions of the Richards’ equation. Assuming that $\mu_v, \mu_s, \mu_g, \eta$, and $k_g$ are zero, and $f$ and $\beta$ are equal to one, the above system of equations given by (1) through (7) reduces to a set of mutually independent solute transport equations as described in the SWMS_2D code (Šimůnek et al., 1994).

Solute transport and chemical reactions in UNSATCHEM-2D

The second model, UNSATCHEM-2D (Šimůnek & Suarez, 1994a), simulates solute, CO$_2$ and heat transport, as well as major ion equilibrium and nonequilibrium chemistry, in a variably-saturated porous medium. We included CO$_2$ and heat transport since these variables can significantly affect the solution chemistry, including most thermodynamic constants and reaction rates. Table 1 lists the species accounted for in the chemical submodel. While a total of 33 chemical species were considered, transport equations were written only for the first six species in the first group of Table 1, as well as for total alkalinity.

<table>
<thead>
<tr>
<th>Table 1 Species considered in the chemical submodel of UNSATCHEM-2D.</th>
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<tbody>
<tr>
<td>1 Aqueous components</td>
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<tr>
<td>2 Complexed species</td>
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<tr>
<td>3 Precipitated species</td>
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<tr>
<td>4 Sorbed species</td>
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<tr>
<td>5 Additional species</td>
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</tbody>
</table>

The partial differential equation governing two-dimensional advective-dispersive chemical transport of the $k$th solute component during transient water flow in a variably-saturated medium is taken as (Šimůnek & Suarez, 1994a):

$$
\frac{\partial (\theta c_k)}{\partial t} + \rho \frac{\partial \tilde{c}_k}{\partial t} + \rho \frac{\partial \hat{c}_k}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta D_{ij} \frac{\partial c_k}{\partial x_j} - q_j c_k \right) \quad k = 1, 2, \ldots, n_s
$$

where $c_k$, $\tilde{c}_k$, and $\hat{c}_k$ are the total dissolved, sorbed and precipitated concentrations, respectively, and $n_s$ is the number of aqueous components. Solute uptake by plant roots is not considered in (8) since plants usually take up only a negligible fraction of the salts present in soil water. The second and third terms of equation (8) are zero for components that do not undergo ion exchange or precipitation/dissolution reactions. The total concentration of a component $k$, defined as the sum of the dissolved, sorbed and precipitated concentrations, is influenced only by transport processes which act on the solution concentration $c_k$, but not by chemical reactions (Zysset et al., 1994). However, the relative fraction of a component in each of the three phases (solution, sorbed, precipitated) depends strongly on the specific chemical processes in the system.
Therefore, equation (8) must be augmented with a set of equations describing the various
equilibrium or nonequilibrium chemical reactions such as complexation, cation
exchange, adsorption/desorption, and precipitation/dissolution.

Complexation reactions for species in the second group of Table 1 were represented
by equilibrium expressions of the type

$$K_{ij} = \frac{(c_i) (c_j)}{(c_y)}$$

where $K_{ij}$ is the equilibrium constant for the complexed species $c_{ij}$ and where
parentheses denote ion activities. Ion activities were calculated by either using an
extended version of the Debye-Hückel equation, or by means of the Pitzer expressions
(Šimůnek & Suarez, 1994a).

Partitioning between the solution and solid phases (the fourth group in Table 1) was
described with the Gapon equation (White & Zelazny, 1986)

$$c_y + (c_x)^{1/3} c_x^{1/3}$$

where $y$ and $x$ are the valences of species $i$ and $j$, respectively, $K_{ij}$ is the Gapon
selectivity coefficient. The adsorbed concentration is expressed in mol$_c$ kg$^{-1}$ soil. We
assumed that the cation exchange capacity $c_T$ (mol$_c$ kg$^{-1}$ soil) was constant and
independent of pH.

UNSATCHEM-2D considered three solid phases (gypsum, nesquehonite and
hydromagnesite) which constrain the solution to equilibrium whenever the solids were
specified or approached from oversaturation. Precipitation-dissolution of calcite was
optionally treated using either equilibrium or kinetic expressions. Dissolution of
dolomite was always treated as a kinetic process. The precipitation of equilibrium solids
was expressed in terms of solubility products $K_{SP}$

$$K_{SP}^{i} = \prod_j (c_j)$$

in which the stoichiometric coefficient $\nu_{ij}$ gives the molar fraction of component $j$ in
solid $i$. The rate equations for precipitation/dissolution of calcite and dolomite are given
by Šimůnek & Suarez (1994a). Finally, the species in the last group of Table 1 are
represented by Henry’s law, the first and second dissociation equation for carbonic acid,
and the dissociation equation for water.

**EXAMPLES**

Figure 1 illustrates an application of the CHAIN_2D code to the transport of a nitrogen
decay chain involving ammonium, nitrite, and nitrate in a soil profile during
unidirectional steady-state water flow at a rate of 1 cm h$^{-1}$ (Van Genuchten, 1985).
Ammonium, applied at unit concentration to an initially solute-free medium, is being
nitrified sequentially into nitrite ($\mu_1 = 0.005$ h$^{-1}$) and nitrate ($\mu_2 = 0.1$ h$^{-1}$). Ammonium
ions adsorbed onto the soil matrix such that the retardation factor was equal to 2. Nitrite
and nitrate, on the other hand, did not undergo any sorption ($R = 1$). A more detailed
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![Dimensionless concentration profiles for ammonium, nitrite, and nitrate after 200 h of steady-state irrigation with at a rate of 1 cm h⁻¹.](image)

Figure 1 shows concentration profiles of the three solutes at time 200 h as calculated with CHAIN_2D; the results were found to be the same as those generated with the analytical solution of Van Genuchten (1985).

Figure 2 gives an example showing how the UNSATCHEM_2D code may be applied to the reclamation of a sodic soil (Simunek & Suarez, 1994b). The example assumes three different reclamation scenarios involving a furrow irrigation system in which every other furrow is flooded with water. The solution composition of the water initially in the soil profile was that of highly sodic water with $C_{a_T} = 0.2$, $Na_T = 4.8$, $Cl_T = 4.6$, and $Alkalinity = 0.4 \text{ mmol}_c \text{ L}^{-1}$. The cation exchange capacity was equal to 100 mmol$_c$ kg$^{-1}$, and divided into exchangeable calcium and sodium ($Ca = 5.0$, $Na = 95.0 \text{ mmol}_c \text{ kg}^{-1}$). Two different irrigation water compositions were used. One type of irrigation water was almost gypsum saturated ($Ca_T = 32.6$, $Na_T = 4.8$, $Cl_T = 5.0$, $SO_4T = 32.0$, $Alkalinity = 0.4 \text{ mmol}_c \text{ L}^{-1}$), while the second irrigation water had the following composition: $Ca_T = 1.5$, $Na_T = 2.0$, $Cl_T = 1.0$, $SO_4T = 2.0$, and $Alkalinity = 0.5 \text{ mmol}_c \text{ L}^{-1}$. Reclamation was attempted in three different ways. The first two cases used either the gypsum saturated or the high-quality irrigation water without consideration of calcite dissolution, while the third case involved the application of high-
quality water to a soil profile whose soil solution was in equilibrium with calcite. Figure 2 presents the exchangeable concentration of calcium for each of the three reclamation scenarios after five days of irrigation. The results demonstrate important differences in the reclamation rate, as well as in the sharpness of the exchange front, among the three reclamation methods.

REFERENCES


