

**NUMERICAL MODEL FOR SIMULATING  
MULTIPLE SOLUTE TRANSPORT IN  
VARIABLY-SATURATED MEDIA**

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*Invited Paper*

## **Numerical model for simulating multiple solute transport in variably-saturated soils**

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### **Abstract**

**In** this paper we discuss a two-dimensional model, **CHAIN\_2D**, for simulating the variably-saturated movement of water, heat, and multiple solutes involved in sequential first-order decay reactions. The model assumes that the solutes can reside in all three phases, i.e., liquid, solid, and gaseous. The solute transport equations consider convective-dispersive transport in the liquid phase, diffusion in the gaseous phase, nonlinear equilibrium or nonequilibrium sorption, linear equilibrium volatilization, zero-order production, and first-order degradation reactions which provide the necessary coupling between solutes involved in the sequential first-order decay reactions. Nonlinear sorption is described by a generalized formulation which can be simplified to either a Freundlich or Langmuir equation. Nonequilibrium sorption may be described using both one-site or two-site kinetic reactions. The model considers temperature dependence of all transport and reaction parameters. Typical examples of first-order decay scenarios are the simultaneous movement of interacting nitrogen species, radionuclides, organic phosphates, and pesticides and their metabolites.

### **1 Introduction**

Once released into the subsurface environment, industrial and agricultural chemicals are generally subjected to a large number of simultaneous physical, chemical, and biological processes, including sorption-desorption, volatilization, photolysis, and biodegradation, as well as their kinetics. The extent of degradation, sorption and volatilization largely determines the persistence of a pollutant in the subsurface (Chiou [2]). For example, the

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fate of organic chemicals in soils is known to be strongly affected by the kinetics of biological degradation. Alexander & Scow [1] gave a review of some of the equations used to represent biodegradation kinetics. These equations include zero-order, half-order, first-order, three-half-order, mixed-order, logistic, logarithmic, Michaelis-Menton, and Monod type (with or without growth) expressions. While most of these expressions have a theoretical bases, they are commonly used only in an empirical fashion by fitting the equations to observed data. Zero- and first-order kinetic equations remain the most popular for describing biodegradation of organic compounds, mostly because of their simplicity and the ease in which they can be incorporated in solute transport models. Conditions for the application of these two equations are described by Alexander & Scow [1].

One special group of degradation reactions involves decay chains in which solutes are subject to sequential (or consecutive) decay reactions. Problems of solute transport involving sequential first-order decay 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, and the transport of certain pesticides and their metabolites.

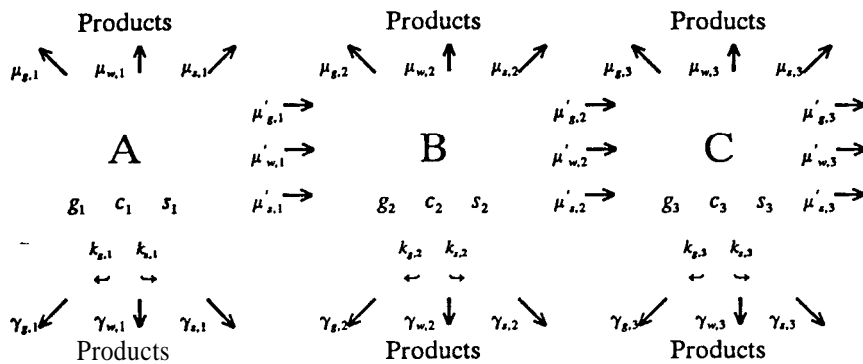
While in the past most pesticides were regarded as involatile, volatilization is now increasingly recognized as an important process affecting the fate of pesticides in field soils (Glotfelty & Schomburg [3], Spencer [11]). Another process affecting pesticide fate and transport is the relative reactivity of solutes in the sorbed and solution phases. Several processes such as gaseous and liquid molecular diffusion, and convective-dispersive transport, act only on solutes that are not adsorbed. Degradation of organic compounds likely occurs mainly, or even exclusively, in the liquid phase (Pignatello [7]). On the other side, radioactive decay takes place equally in the solution and adsorbed phases, while other reactions may occur only in the sorbed phase. To be useful, the invoked mathematical model must allow for different reaction rates to take place in the solid, liquid, and gaseous phases, as well as for a correct distribution of the solutes among the different phases.

The purpose of this paper is to given an overview of the solute transport part of the CHAIN 2D computer program (Šimůnek & van Genuchten [10]) simulating two-dimensional variably-saturated water flow, heat movement, and the transport of solutes involved in sequential first-order decay reactions.

### 2 Nonequilibrium transport of solutes involved in sequential first-order decay reactions

We assume that solutes can exist in all three phases (liquid, solid, and gaseous) and that the decay and production processes can be different in

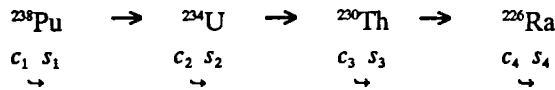
each phase. Interactions between the solid and liquid phases may be described by nonlinear nonequilibrium equations, while interactions between the liquid and gaseous phases are assumed to be linear and instantaneous. We further assume that the solutes are transported by convection and dispersion in the liquid phase, as well as by diffusion in the gas phase. A general structure of the system of first-order decay reactions for three solutes (A, B and C) is as follows (Šimůnek & van Genuchten [10]):



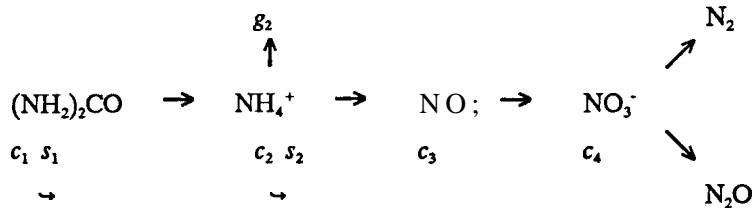
where  $c, s,$  and  $g$  represent concentrations in the liquid, solid, and gaseous phases, respectively; the subscripts  $w, s,$  and  $g$  similarly refer to solid, liquid and gaseous phases, respectively; straight arrows represent the different zero-order ( $\gamma$ ) and first-order ( $\mu, \mu'$ ) rate reactions, and circular arrows ( $k_g, k_s$ ) indicate equilibrium distribution coefficients between phases.

Typical examples of sequential first-order decay chains are:

- a. Radionuclides (Higashi & Pigford [4])

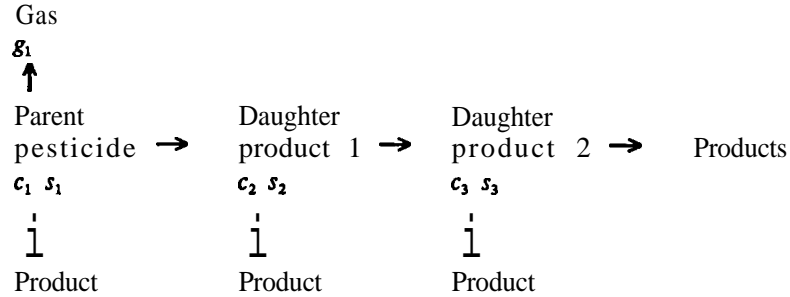


- b. Nitrogen (Tillotson et al. [12])



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### c. Pesticides (Wagenet & Hutson [16])



The partial differential equations governing two-dimensional nonequilibrium chemical 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 (Šimůnek & van Genuchten [10])

$$\begin{aligned}
 \frac{\partial \theta c_k}{\partial t} + \frac{\partial \rho s_k}{\partial t} + \frac{\partial a_v g_k}{\partial t} = & \frac{\partial}{\partial x_j} (\theta D_{ij}^w \frac{\partial c_k}{\partial x_j}) + \frac{\partial}{\partial x_i} (a_v D_{ij}^g \frac{\partial g_k}{\partial x_j}) - \frac{\partial q_i c_k}{\partial x_i} - \\
 & - (\mu_{w,k} + \mu'_{w,k}) \theta c_k - (\mu_{s,k} + \mu'_{s,k}) \rho s_k - (\mu_{g,k} + \mu'_{g,k}) a_v g_k + \mu'_{w,k-1} \theta c_{k-1} \\
 & + \mu'_{s,k-1} \rho s_{k-1} + \mu'_{g,k-1} a_v g_{k-1} + \gamma_{w,k} \theta + \gamma_{s,k} \rho + \gamma_{g,k} a_v - S c_{r,k} \quad k \in (2, n_s)
 \end{aligned} \quad (1)$$

where  $c$ ,  $s$ , and  $g$  are solute concentrations in the liquid [ML<sup>-3</sup>], solid [MM<sup>-1</sup>], and gaseous [ML<sup>-3</sup>], phases, respectively;  $q_i$  is the  $i$ -th component of the volumetric flux density [LT<sup>-1</sup>],  $\mu_w$ ,  $\mu_s$ , and  $\mu_g$  are first-order rate constants for solutes in the liquid, solid, and gas phases [T<sup>-1</sup>], respectively;  $\mu'_w$ ,  $\mu'_s$ , and  $\mu'_g$  are similar first-order rate constants providing connections between individual chain species,  $\gamma_w$ ,  $\gamma_s$ , and  $\gamma_g$  are zero-order rate constants for the liquid [ML<sup>-3</sup>T<sup>-1</sup>], solid [T<sup>-1</sup>], and gas [ML<sup>-3</sup>T<sup>-1</sup>] phases, respectively;  $\rho$  is the soil bulk density [ML<sup>-3</sup>],  $a$  is the air content [L<sup>3</sup>L<sup>-3</sup>],  $S$  is the sink term in the water flow equation,  $c_r$  is the concentration of the sink term [ML<sup>-3</sup>],  $D_{ij}^w$  is the dispersion coefficient tensor [L<sup>2</sup>T<sup>-1</sup>] for the liquid phase, and  $D_{ij}^g$  is the diffusion coefficient tensor [L<sup>2</sup>T<sup>-1</sup>] for the gas phase. As before, the subscripts  $w$ ,  $s$ , and  $g$  correspond with the liquid, solid and gas phases, respectively; while the subscript  $k$  represents the  $k$ th chain number, and  $n_s$  is the number of solutes involved in the chain reaction. The indicial notation used in this report assumes summations over indices  $i$  and  $j$  ( $ij = 1,2$ ), but not over index  $k$ . 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 eqn (1), except that all terms containing the subscript  $k-1$  ( $= 0$ ) must be removed. To simplify the notation, the subscript  $k$  will not be

further used in this paper, except when needed for clarity.

CHAIN\_2D assumes nonequilibrium interactions between the solution (c) and adsorbed (s) concentrations, and equilibrium interactions between the solution (c) and gas (g) concentrations of the solute in the soil system. The adsorption isotherm relating s and c is described by a generalized nonlinear equation of the form

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

where  $k_s$ , [ $L^3M^{-1}$ ],  $\beta$  [-] and  $\eta$  [ $L^3M^{-1}$ ] are empirical coefficients. The Freundlich, Langmuir, and linear adsorption equations are all special cases of eqn (2). When  $\beta = 1$ , eqn (2) becomes the Langmuir equation, when  $\eta = 0$ , eqn (2) reduces to the Freundlich equation, and when both  $\beta = 1$  and  $\eta = 0$ , eqn (2) leads to a linear adsorption isotherm. Solute transport without adsorption is described with  $k_s = 0$ . While the coefficients  $k_s$ ,  $\beta$ , and  $\eta$  in eqn (2) are assumed to be independent of concentration, they are permitted to change as a function of time through their dependency on temperature. This feature will be discussed later.

The concept of two-site sorption (Selim et al. [8], van Genuchten & Wagenet [15]) is implemented in CHAIN\_2D to permit consideration of nonequilibrium adsorption-desorption reactions. The two-site sorption concept assumes that the sorption sites can be divided into two fractions:

$$s = s^e + s^k \quad (3)$$

Sorption,  $s^e$  [MM'], on one fraction of the sites (the type-1 sites) is assumed to be instantaneous, while sorption,  $s^k$  [MM'], on the remaining (type-2) sites is considered to be time-dependent. At equilibrium we have for the type-1 (equilibrium) and type-2 (kinetic) sites, respectively

$$s^e = fs \quad (4)$$

$$s^k = (1 - f)s \quad (5)$$

where  $f$  is the fraction of exchange sites assumed to be in equilibrium with the solution phase [-]. Because type-1 sorption sites are always at equilibrium, differentiation of eqn (4) gives immediately the sorption rate for the type-1 equilibrium sites:

$$\frac{\partial s^e}{\partial t} = f \frac{\partial s}{\partial t} \quad (6)$$

Sorption on the type-2 nonequilibrium sites is assumed to be a first-order kinetic rate process. Following Toride et al. [13], the mass balance equation for the type-2 sites in the presence of production and degradation is given by

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$$\frac{\partial s^k}{\partial t} = \omega[(1-f) \frac{k_s c^\beta}{1 + \eta c^\beta} - s^k] - (\mu_s + \mu'_s) s^k + (1-f) \gamma_s \quad (7)$$

where  $\omega$  is a first-order rate constant [ $T^{-1}$ ].

The concentrations  $g$  and  $c$  are related by a linear expression of the form

$$g = k_g c \quad (8)$$

where  $k_g$  is an empirical constant [-].

Substituting eqns (2) through (8) into eqn (1), and using the continuity equation describing isothermal Darcian flow of water in a variably saturated porous medium, leads to the following equation

$$-\theta R \frac{\partial c}{\partial t} - q_i \frac{\partial c}{\partial x_i} + \frac{\partial}{\partial x_i} (\theta D_{ij} \frac{\partial c}{\partial x_j}) + Fc + G = 0 \quad (9)$$

in which  $D_{ij}$  [ $L^2 T^{-1}$ ] is an effective dispersion coefficient tensor given by

$$\theta D_{ij} = \theta D_{ij}^w + a_v D_{ij}^g k_g \quad (10)$$

The coefficients  $F$  and  $G$  in eqn (9) are defined as

$$F(c) = -(\mu_w + \mu'_w) \theta - (\mu_s + \mu'_s) \rho f \frac{k_s c^{\beta-1}}{1 + \eta c^\beta} - (\mu_g + \mu'_g) a_v k_g + \quad (11)$$

$$+ S + k_g \frac{\partial \theta}{\partial t} - a_v \frac{\partial k_g}{\partial t} - \omega \rho \frac{(1-f) k_s c^{\beta-1}}{1 + \eta c^\beta} - g(c)$$

$$G_k(c_k) = (\mu'_{w,k-1} \theta + \mu'_{s,k-1} f \rho \frac{k_{s,k-1} c_{k-1}^{\beta_{k-1}-1}}{1 + \eta_{k-1} c_{k-1}^{\beta_{k-1}}} + \mu_{g,k-1} a_v k_{g,k-1}) c_{k-1} + \quad (12)$$

$$+ \mu'_{s,k-1} \rho s_{k-1}^k + \gamma_{w,k} \theta + \gamma_{s,k} f \rho + \gamma_{g,k} a_v - S c_{r,k} + \omega_k \rho s_k^k \quad k \in (2, n_s)$$

where the variable  $g$  accounts for possible changes in the adsorption parameters caused by temperature changes in the system as follows:

$$g(c) = \rho f \left[ \frac{c^{\beta-1}}{1 + \eta c^\beta} \frac{\partial k_s}{\partial t} - \frac{k_s c^{2\beta-1}}{(1 + \eta c^\beta)^2} \frac{\partial \eta}{\partial t} + \frac{k_s \ln c c^{\beta-1}}{(1 + \eta c^\beta)^2} \frac{\partial \beta}{\partial t} \right] \quad (13)$$

Equation (12) also holds for the first solute in the decay chain, provided that all terms containing the subscript  $k-1$  ( $=0$ ) are removed. The retardation factor  $R$  [-] in eqn (9) is given by

$$R(c) = 1 + \frac{\rho}{\theta} \frac{fk_s \beta c^{\beta-1}}{(1 + \eta c^\beta)^2} + \frac{a_v k_g}{\theta} \quad (14)$$

#### Effective Dispersion Coefficient

The components of the effective dispersion tensor,  $D_{ij}$  in the soil are given by

$$\theta D_{ij} = D_T |q| \delta_{ij} + (D_L - D_T) \frac{q_j q_i}{|q|} + \theta D_w \tau_w \delta_{ij} + a_v D_g k_g \tau_g \delta_{ij} \quad (15)$$

where  $D_w$  and  $D_g$  are the molecular diffusion coefficients in free water and the gas phase, respectively [ $L^2 T^{-1}$ ];  $\tau_w$  and  $\tau_g$  are tortuosity factors in the liquid and gas phases, respectively [-];  $|q|$  is the absolute value of the Darcian fluid flux density [ $L T^{-1}$ ],  $\delta_{ij}$  is the Kronecker delta function, and  $D_L$  and  $D_T$  are the longitudinal and transverse dispersivities, respectively [L].

The tortuosity factors for both phases are evaluated in CHAIN\_2D as a function of the water and gas contents using the relationship of Millington & Quirk [5]:

$$\tau_w = \frac{\theta^{7/3}}{\theta_s^2} \quad (16)$$

$$\tau_g = \frac{a_v^{7/3}}{\theta_s^2}$$

#### Temperature Dependence of Transport and Reaction Coefficients

Several of the diffusion ( $D_w, D_g$ ), zero-order production ( $\gamma_w, \gamma_s, \gamma_g$ ), first-order degradation ( $\mu_w', \mu_s', \mu_g', \mu_w, \mu_s, \mu_g$ ), and adsorption ( $k_s, k_g, \beta, \eta, \omega$ ) coefficients may be strongly dependent upon temperature. CHAIN 2D assumes that this dependency can be expressed by the Arrhenius equation. After some modification, this equation can be expressed in the general form (Šimůnek & Suarez [9])

$$a_r = a_r \exp \left[ \frac{E_a (T^A - T_r^A)}{R_u T^A T_r^A} \right] \quad (17)$$

where  $a_r$  and  $a_r$  are the values of the coefficient being considered at a certain reference absolute temperature  $T_r^A$ , and at absolute temperature  $T^A$ , respectively;  $R_u$  is the universal gas constant [ $MM^{-1} L^2 T^{-2} K^{-1}$ ], and  $E_a$  [ $MM^{-1} L^2 T^{-2}$ ] is the activation energy of the particular reaction or process being modeled.



### 3 Example: Movement of water and dissolved organic compounds

We present one example here to illustrate possible applications of the CHAIN 2D code. The example concerns the transient infiltration of water and a dissolved solute of unit concentration from a single-ring infiltrometer into a soil profile consisting of two layers: a 40-cm thick A-horizon, and an underlying B/C- horizon (Šimůnek & van Genuchten [10]). Because of axisymmetry, the calculations were carried out only for the radial half-plane  $r > 0$ . A steady-state profile for water flow was obtained after about 2 or 3 days. The infiltrated water contained during the first five days of infiltration an organic parent compound, the pesticide aldicarb, which is known to degrade in the soil profile by oxidation into two sequential daughter products, sulfone and sulfoxide (Ou et al. [6]), such that  $\mu'_w$  equals 0.36, 0.024, and 0.0024 day<sup>-1</sup> for the three consecutive chain members. The three solutes also undergo hydrolytical first-order decay ( $\mu'_w = 0.2, 0.01, 0.005$  day<sup>-1</sup>) that leads to products (i.e., oxime, sulfone oxime, and sulfoxide oxime; see Ou et al. [6]) which are not further considered here. All three solutes were subject to adsorption onto the solid phase ( $k_s = 0.0001, 0.00005, 0.0002$  m<sup>3</sup>/kg, whereas volatilization was considered only for the first and the third solutes ( $k_g = 1.33 \cdot 10^{-7}, 0.0, 1.33 \cdot 10^{-3}$ ). The above solute transport parameters were taken from Wagenet & Hutson [16]; all other model parameters are given elsewhere (Šimůnek & van Genuchten, [10]).

Figures 1 and 2 show concentration profiles for the three solutes after irrigating for 5 and 10 days, respectively. Subsequent to its application in the infiltrating water during the first five days of the simulation (Fig. 1a), the first (parent) solute moves further into the soil profile by convective-dispersive transport and gaseous diffusion. The parent organic is also degraded by two first-order decay reactions such that the soil profile is practically free of this solute after 10 days (Fig. 2a). The second solute exists exclusively because of first-order degradation of the parent solute. Hence, its distribution in the soil profile initially corresponds closely to that of the first solute, but subsequently moves faster through the soil profile because of a lower retardation factor (less sorption). Similar features as for the second solute also apply to the third solute. In particular, notice that the highest concentrations of the third solute are reached at the end of the simulation (Fig. 2c).

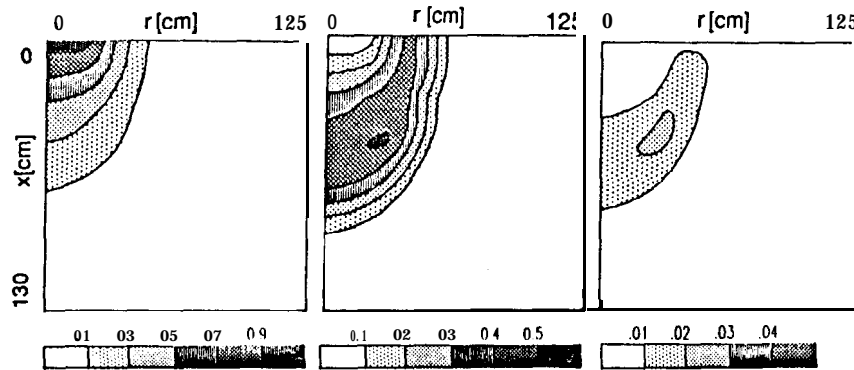


Figure 1: Concentration profiles [-] for aldicarb, sulfone and sulfoxide after 5 days of irrigation.

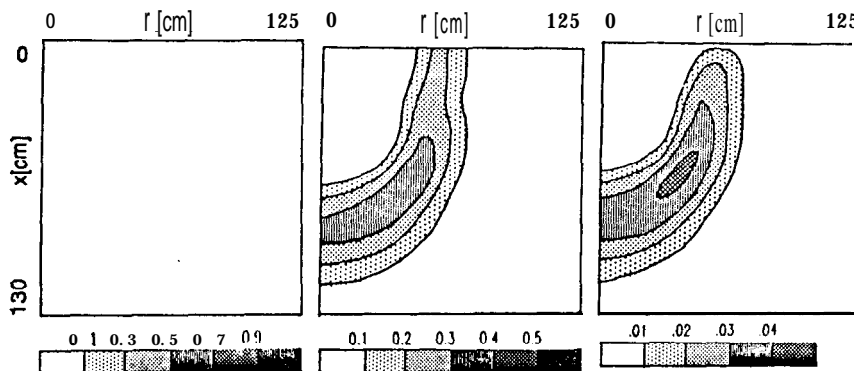


Figure 2: Concentration profiles [-] for aldicarb, sulfone and sulfoxide after 10 days of irrigation.

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