

## NUMERICAL MODEL FOR SIMULATING MOVEMENT OF WATER, HEAT AND MULTIPLE SOLUTES IN VARIABLY SATURATED POROUS MEDIA

JIŘÍ ŠIMŮNEK

This paper presents the model for simulating the movement of variably saturated water flow, heat transport, and the transport of volatile solutes involved in sequential first-order decay reactions in one-dimensional porous media. The model numerically solves the Richards' equation for saturated-unsaturated water flow and the convection-dispersion equation for heat and solute transport. The solute transport equations consider convective-dispersive transport in the liquid phase, convective-diffusive transport in the gaseous phase, nonlinear equilibrium sorption/exchange, linear equilibrium reaction between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions: one which is independent of other solutes, and one which provides the coupling between solutes involved in the sequential first-order decay reactions. Freundlich or Langmuir adsorption isotherms are used to describe the nonlinear equilibrium sorption/exchange. The governing partial differential equations are solved numerically using Galerkin-type linear finite elements schemes. Examples are presented to illustrate several applications of the code.

**KEY WORDS:** Solute Transport, Nonlinear Adsorption, First-Order Decay Reactions, Finite Elements.

Jiří Šimůnek: Numerický model pro simulování proudění vody a transportu tepla a rozpuštěných látek v nenasyceném pórovitém prostředí. *Vodohosp. Cas.*, 42, 1994, 1; 27 lit., 5 obr., 3 tab.

Tento článek přináší popis modelu pro simulaci nenasyceného proudění vody, transportu tepla a transportu těkavých rozpuštěných látek podléhajících sekvenčnímu rozpadu prvního řádu v jednorozměrném pórovitém prostředí. Model řeší numericky Richardsovu rovnici pro nasycené-nenasycené proudění vody a konvektivně-disperzní rovnici pro transport tepla a rozpuštěných látek. Řídící rovnice pro transport rozpuštěných látek uvažuje konvektivně-disperzní transport v kapalně fázi, konvektivně-difúzní transport v plynné fázi, nelineární rovnovážnou sorpci, lineární reakci mezi kapalnou a plynnou fází, produkci nultého řádu a dvě rozkladné reakce prvního řádu: první, která je nezávislá na ostatních chemických rozpuštěných látkách a druhá, která představuje spojení mezi rozpuštěnými látkami podléhajícími

Ing. Jiří Šimůnek, CSc., Research Institute for Soil Reclamation and Protection, Žabovřeská 250, 156 00 Prague, Czech Republic.

sekvenčnímu řetězovému rozkladu prvního řádu. Freundlichova nebo Langmuirova adsorpční isoterma je použita k popisu nelineární rovnovážné sorpce. Řídící parciálně diferenciální rovnice jsou řešeny numericky použitím Galerkinovy verze lineárních konečných elementů. Některé aplikace modelu jsou ukázány na dvou příkladech.

**KLÍČOVÁ SLOVA:** transport rozpuštěných látek, nelineární adsorpce, rozklad prvního řádu, konečné prvky.

Иржи Шимунек: Нумерическая модель симуляции переноса воды и тепла в водой ненасыщенной пористой среде. *Водохоз. Ж.*, 42, 1994, 1; 27 лит., 5 рис., 3 табл.

Статья содержит математическую модель для симуляции переноса воды, тепла и растворимых веществ в пористых средах. Распад растворенных веществ первого порядка происходит в одномерной пористой среде. Основой модели уравнение Ричардса для конвективно-дисперсионного транспорта тепла и растворимых веществ. Уравнение включает: конвективно-дисперсионный транспорт жидкости и газа, нелинейную равновесную сорпцию, линейную реакцию между жидкостью и газом, продукцию нулевого порядка и две реакции распада первого порядка. Первая реакция независима на остальных растворенных веществах, вторая соединяет реакции между растворенными веществами, которые подвергаются постепенному распаду первого порядка. Нелинейная равновесная сорпция описана адсорпционной изотермой Фрейндлиха или Лангмура. Дифференциальные уравнения с частными производными решены чисерически методом линейных конечных элементов в модификации Галеркина. Использование предложенной модели показано на двух примерах.

**КЛЮЧЕВЫЕ СЛОВА:** перенос растворенных веществ, нелинейная адсорпция, распад первого порядка, конечные элементы.

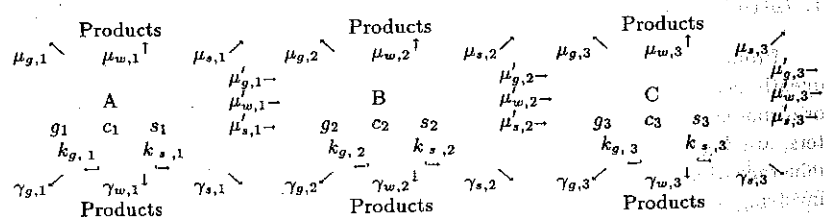
### 1. Introduction

Problems of solute transport involving sequential first-order reactions frequently occur in soil and groundwater systems. Most chemical substances applied or disposed of on soil, such as for example pesticides, herbicides and organic matters, are degraded or volatilized in the soil profile with ultimate detoxification or mineralization (Angelakis et al. [1]). Often quoted example of solute transport involving sequential first-order reactions is that of the migration of various radionuclides (Lester et al. [11], Rogers [15], Gureghian [5], Gureghian and Jansen [6], van Genuchten [24]). Other examples are concerned with the simultaneous movement of interacting nitrogen species (Cho [4], Misra et al. [14], Wagenet et al. [25], Tillotson et al. [21], Gureghian [5], Wagenet and Hutson [26]), organic phosphates (Castro and Rolston [3]) or pesticides (Bromilow and Leistra [2], Wagenet and Hutson [26]).

The solute transport models mostly considered only one solute and simplified different chemical processes (Huyakorn et al. [9], Yeh and Huff [27]). The complex processes of adsorption and cation exchange are usually accounted for by a linear (Huyakorn et al. [9]) or nonlinear Freundlich isotherms (Yeh and Huff [27]), where all reactions between solid and liquid phases are lumped into the distribution coefficient  $Kd$  (Liu and Narasimhan [12]) and possibly into the nonlinear exponent. Several models were developed which simulate several solutes involved in sequential first-order decay reactions (Gureghian [5], Wagenet and Hutson [26], Huyakorn et al. [9]). However, transport of solute species, their transformations and simultaneous transport of their gaseous products under transient water flow conditions has not yet been considered (Angelakis et al. [1]).

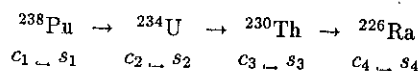
The purpose of this paper is to present the model CHAIN\_1D for simulating water flow, heat transport and movement of solutes involved in sequential first-order decay reactions in one-dimensional variably saturated media. The program numerically solves the Richard's equation for saturated-unsaturated water flow and the convection-dispersion equation for heat and solute transport. The governing convection-dispersion equation is written in a general form and provides provisions for nonlinear equilibrium reactions between the solid and liquid phases and linear equilibrium reaction between liquid and gaseous phases. Further the solute transport equation incorporates zero-order production, first-order degradation independent of other solutes and first-order decay/production that provides the coupling between the solutes involved in sequential first-order reactions. Both convection and dispersion in the liquid phase, as well as diffusion in the gas phase are considered. The heat transport is included into the model since almost all transport and reaction parameters are strongly temperature dependent.

General structure of the whole system of solutes is as follows:

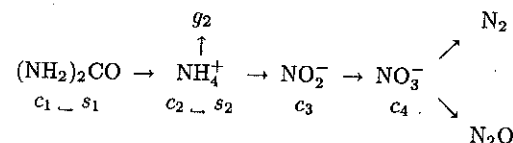


where  $c$ ,  $s$ , and  $g$  represent the concentrations in the liquid, solid, and gaseous phases, respectively; straight arrows ( $\gamma, \mu, \mu'$ ) represent the zero- and first-order rate reactions and circular arrows ( $k_g, k_s$ ) the equilibrium distribution between phases. More detail is given later. Typical examples of sequential first-order chains are as follows:

1. Radionuclides (van Genuchten [24])

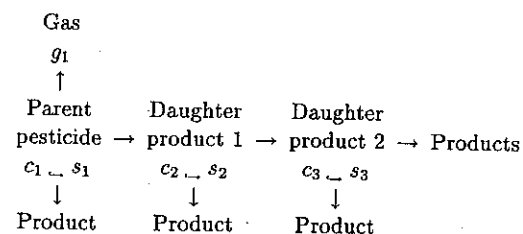


2. Nitrogen (Tillotson et al. [21])

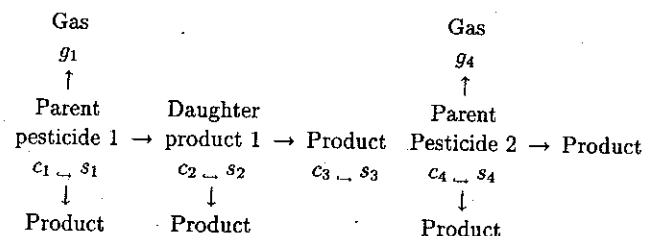


3. Pesticides (Wagenet and Hutson [26]):

a) Uninterrupted chain - one reaction path:



b) Interrupted chain - two independent reaction path:



In this paper I will not give the descriptions of the variably saturated water flow and heat transport, since relatively standard procedures are used (Šimůnek and Suarez [18]), and I will concentrate mainly on the theoretical formulation and numerical solution of governing solute transport equations. At the end of the paper several examples which verify the code are presented.

## 2. Governing solute transport equations

We assume that the solutes can exist in all three phases (liquid, solid, and gaseous) and that the decay and production processes are generally different in each phase. Further we assume that the solutes are transported by four different mechanisms: by the convection and dispersion in the liquid phase and by the convection and diffusion in the gaseous phase. Then the partial differential equations governing one-dimensional chemical transport of solutes involved in a sequential first-order decay chain during transient water flow in a variably saturated rigid porous medium is taken as

$$\begin{aligned} \frac{\partial \theta c_1}{\partial t} + \frac{\partial \rho s_1}{\partial t} + \frac{\partial a g_1}{\partial t} = \frac{\partial}{\partial x} \left( \theta D_1^w \frac{\partial c_1}{\partial x} \right) + \frac{\partial}{\partial x} \left( a D_1^g \frac{\partial g_1}{\partial x} \right) - \\ - \frac{\partial q^w c_1}{\partial x} - \frac{\partial q^g g_1}{\partial x} - \mu_{w,1} \theta c_1 - \mu_{s,1} \rho s_1 - \mu_{g,1} a g_1 - \\ - \mu'_{w,1} \theta c_1 - \mu'_{s,1} \rho s_1 - \mu'_{g,1} a g_1 + \gamma_{w,1} \theta + \gamma_{s,1} \rho + \gamma_{g,1} a - S c_{r,1}, \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{\partial \theta c_k}{\partial t} + \frac{\partial \rho s_k}{\partial t} + \frac{\partial a g_k}{\partial t} = \frac{\partial}{\partial x} \left( \theta D_k^w \frac{\partial c_k}{\partial x} \right) + \frac{\partial}{\partial x} \left( a D_k^g \frac{\partial g_k}{\partial x} \right) - \\ - \frac{\partial q^w c_k}{\partial x} - \frac{\partial q^g g_k}{\partial x} - \mu_{w,k} \theta c_k - \mu_{s,k} \rho s_k - \mu_{g,k} a g_k + \\ + \mu'_{w,k-1} \theta c_{k-1} + \mu'_{s,k-1} \rho s_{k-1} + \mu'_{g,k-1} a g_{k-1} - \mu'_{w,k} \theta c_k - \mu'_{s,k} \rho s_k - \\ - \mu'_{g,k} a g_k + \gamma_{w,k} \theta + \gamma_{s,k} \rho + \gamma_{g,k} a - S c_{r,k} \quad k \in (2, n_s), \end{aligned} \quad (2)$$

where  $c$  is the solution concentration [ML<sup>-3</sup>],  $s$  is the adsorbed concentration [MM<sup>-1</sup>],  $g$  is the concentration of solute in the gaseous phase [ML<sup>-3</sup>],  $\theta$  is the water content [L<sup>3</sup>L<sup>-3</sup>],  $q^w$  and  $q^g$  are the Darcy's volumetric fluxes in liquid and gaseous phases [LT<sup>-1</sup>], respectively;  $\mu_w, \mu_s$ , and  $\mu_g$  are first-order rate constants for solutes in the liquid, solid, and gas phases [T<sup>-1</sup>], respectively;  $\gamma_w, \gamma_s$ , 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 from the water flow equation,  $c_r$  is the concentration of the sink term [ML<sup>-3</sup>],  $D^w$  is the dispersion coefficient [L<sup>2</sup>T<sup>-1</sup>] for the liquid phase, and  $D^g$  is the diffusion coefficient [L<sup>2</sup>T<sup>-1</sup>] for the gas phase. The subscripts  $w, s$ , and  $g$  correspond with the liquid, solid and gas phases, respectively; the subscript  $k$  represents the  $k$ -th chain number,  $n_s$  is the number of solutes involved in the chain reaction and  $\mu'_w, \mu'_s$ , and  $\mu'_g$  are the first-order rate constants for solutes in the liquid, solid and gas phases [T<sup>-1</sup>], respectively, which provide the connection between individual chain species. The nine zero- and first-order rate constants in (1) and (2) may be used to represent a variety of reactions or transformations including biodegradation, volatilization, precipitation etc. The variable  $c_r$  is considered in

the model to be equal to the solution concentration up to some limit above which  $c_r$  is kept constant.

The dispersion coefficient in both liquid and gaseous phases are defined as

$$\begin{aligned} D_k^w &= D_k^{w0} \tau_w + \lambda_w \frac{|q^w|}{\theta}, \\ D_k^g &= D_k^{g0} \tau_g + \lambda_g \frac{|q^g|}{a}, \end{aligned} \quad (3)$$

where  $D^{w0}$  and  $D^{g0}$  represent the molecular diffusion coefficients in free water and air [L<sup>2</sup>T<sup>-1</sup>], respectively;  $\lambda_w$  and  $\lambda_g$  are the longitudinal dispersivities in liquid and gaseous phases, respectively; and  $\tau_w$  and  $\tau_g$  are tortuosity factors in liquid and gaseous phases [-], respectively, evaluated as a function of the water and gas content using the relationship of Millington and Quirk [13]:

$$\begin{aligned} \tau_w &= \frac{\theta^{7/3}}{\theta_s^2}, \\ \tau_g &= \frac{a^{7/3}}{\theta_s^2}. \end{aligned} \quad (4)$$

The model assumes equilibrium interactions between the solution ( $c$ ), adsorbed ( $s$ ), and gas ( $g$ ) concentrations of the solute in the soil system. The adsorption isotherm relating  $s_k$  and  $c_k$  is described either by a nonlinear Freundlich equation of the form (e.g. van Genuchten and Cleary [22])

$$\begin{aligned} s_k &= k_{s,k} c_k^{\eta_k} \quad k \in (1, n_s) \\ \frac{\partial s_k}{\partial t} &= k_{s,k} \eta_k c_k^{\eta_k-1} \frac{\partial c_k}{\partial t} + c_k^{\eta_k} \frac{\partial k_{s,k}}{\partial t} + k_{s,k} c_k^{\eta_k} \ln c_k \frac{\partial \eta_k}{\partial t} \quad k \in (1, n_s) \end{aligned} \quad (5)$$

or by a nonlinear Langmuir equation (e.g. Millington and Cleary [22])

$$\begin{aligned} s_k &= \frac{k_{s,k} c_k}{1 + \eta_k c_k} \quad k \in (1, n_s), \\ \frac{\partial s_k}{\partial t} &= \frac{k_{s,k}}{(1 + \eta_k c_k)^2} \frac{\partial c_k}{\partial t} + \frac{c_k}{1 + \eta_k c_k} \frac{\partial k_{s,k}}{\partial t} - \frac{k_{s,k} c_k^2}{(1 + \eta_k c_k)^2} \frac{\partial \eta_k}{\partial t} \quad k \in (1, n_s), \end{aligned} \quad (6)$$

where  $k_{s,k}$  [L<sup>3</sup> M<sup>-1</sup>] and  $\eta_k$  ([-] or [L<sup>3</sup>M<sup>-1</sup>]) are empirical constants. Note that both nonlinear Freundlich and Langmuir adsorption isotherms can be simplified by selecting proper values of the parameter  $\eta_k$  into a linear adsorption isotherm.

Similarly the concentrations  $g_k$  and  $c_k$  are related by a linear relation

$$g_k = k_{g,k} c_k, \quad k \in (1, n_s), \quad (7)$$

where  $k_{g,k}$  is an empirical constant [-].

Substituting (5), (6), and (7) into (1) and (2) gives the following equation

$$-\frac{\partial \theta R_k^1 c_k}{\partial t} - \theta R_k^2 \frac{\partial c_k}{\partial t} - \frac{\partial q c_k}{\partial x} + \frac{\partial}{\partial x} \left( \theta D_k \frac{\partial c_k}{\partial x} \right) + F_k c_k + G_k = 0, \quad (8)$$

$$k \in (1, n_s),$$

where  $D$  is the effective dispersion coefficient tensor in the soil matrix [ $L^2 T^{-1}$ ]

$$\theta D_k = \theta D_k^w + a D_k^g k_{g,k} \quad k \in (1, n_s) \quad (9)$$

and  $q$  is the effective fluid velocity in the soil matrix [ $LT^{-1}$ ].

$$q = q^w + q^g k_{g,k} - a D_k^g \frac{\partial k_{g,k}}{\partial x} \quad k \in (1, n_s). \quad (10)$$

The last term of (10) represents the contribution of spatial derivation of distribution constant  $k_g$  to coefficient  $q$ . The coefficients  $F_k$  and  $G_k$  in (8) are defined as follows

$$F_k(c_k) = -(\mu_{w,k} + \mu'_{w,k})\theta - (\mu_{s,k} + \mu'_{s,k})\rho k_{s,k} c_k^* -$$

$$-(\mu_{g,k} + \mu'_{g,k})a k_{g,k} - \rho c_k^* \frac{\partial k_{s,k}}{\partial t} + \rho k_{s,k} c_k^- \frac{\partial \eta_k}{\partial t}, \quad k \in (1, n_s),$$

$$G_1 = \gamma_{w,1}\theta + \gamma_{s,1}\rho + \gamma_{g,1}a - S_{c,r,1},$$

$$G_k = (\mu'_{w,k-1}\theta + \mu'_{s,k-1}\rho k_{s,k-1} c_{k-1}^* + \mu'_{g,k-1}a k_{g,k-1}) c_{k-1} +$$

$$+ \gamma_{w,k}\theta + \gamma_{s,k}\rho + \gamma_{g,k}a - S_{c,r,k}, \quad k \in (2, n_s), \quad (11)$$

where variables  $c_k^*$  and  $c_{k-1}^*$  for Freundlich isotherm are given as

$$c_k^* = c_k^{\eta_k - 1}, \quad k \in (1, n_s),$$

$$c_{k-1}^* = c_{k-1}^{\eta_{k-1} - 1}, \quad k \in (1, n_s) \quad (12)$$

and for Langmuir equation are equal to

$$c_k^* = \frac{1}{1 + \eta_k c_k}, \quad k \in (1, n_s),$$

$$c_{k-1}^* = \frac{1}{1 + \eta_{k-1} c_{k-1}}, \quad k \in (1, n_s). \quad (13)$$

Variables  $c_k^-$  for Freundlich isotherm is given as

$$c_k^- = -c_k^{\eta_k - 1} \ln c_k, \quad k \in (1, n_s) \quad (14)$$

and for Langmuir equation is equal to

$$c_k^- = \frac{c_k}{(1 + \eta_k c_k)^2}, \quad k \in (1, n_s). \quad (15)$$

The retardation factor in eq. (8) is divided into two parts  $R_k^1$  and  $R_k^2$  [-]. The reason for this division will be discussed in Chapter 3. The particular retardation factors are defined as follows

$$R_k^1 = 1 + \frac{a k_{g,k}}{\theta}, \quad k \in (1, n_s),$$

$$R_k^2(c_k) = \frac{\rho k_{s,k} c_k^*}{\theta}, \quad k \in (1, n_s), \quad (16)$$

where variable  $c_k^+$  for Freundlich isotherm is equal to

$$c_k^+ = \eta_k c_k^{\eta_k - 1}, \quad k \in (1, n_s) \quad (17)$$

and for Langmuir equation is given as

$$c_k^+ = \frac{1}{(1 + \eta_k c_k)^2}, \quad k \in (1, n_s). \quad (18)$$

In order to solve eq. (8), it is necessary to know the water contents  $\theta$  and the volumetric fluxes in liquid and gaseous phases,  $q^w$  and  $q^g$ , respectively. First two variables are obtained from solutions of the Richards' equation. The volumetric flux in the gaseous phase is calculated using the simple model proposed by Šimůnek and Suarez [18]. Assuming that  $\mu'_w$ ,  $\mu'_s$ ,  $\mu'_g$ , and  $k_g$  are zero and  $\eta_k$  is equal to one for Freundlich isotherm or equal to zero for Langmuir isotherm, the whole system of equations (1) through (18) simplifies into a system of mutually independent solutes as described in two-dimensional code SWMS.2D (Šimůnek et al. [19]).

Most of the diffusion ( $D^{w0}$ ,  $D^{g0}$ ), distribution ( $k_s$ ,  $k_g$ ), and reaction rate ( $\gamma_w$ ,  $\gamma_s$ ,  $\gamma_g$ ,  $\mu'_w$ ,  $\mu'_s$ ,  $\mu'_g$ ,  $\mu_w$ ,  $\mu_s$ , and  $\mu_g$ ) coefficients are strongly temperature dependent. Model assumes, that this dependence can be generally expressed by the Arrhenius equation (Stumm and Morgan [17]). After simple modification we get (Šimůnek and Suarez [18])

$$a_T = a_r \exp \left[ \frac{E(T^A - T_r^A)}{RT^A T_r^A} \right] \quad (19)$$

where  $a_r$  and  $a_T$  are the values of the respective coefficient at a reference absolute temperature  $T_r^A$  and absolute temperature  $T^A$ , respectively, and  $E$  is the activation energy of the reaction or process [ $ML^2 T^{-2} M^{-1}$ ].

### 3. Numerical Solution of Governing Solute Transport Equations

#### 3.1 Spatial Discretization

Galerkin finite element method is used for spatial discretization of equation (8). The upstream weighting variant of the method of finite elements is used to overcome the problems connected with numerical oscillations. Since the description of this method for the solution of transport equation is described in detail elsewhere (e.g. Huyakorn and Pinder [8], van Genuchten [23]) only the basic assumptions and results of approximation process will be given here.

The flow region is divided in finite elements by defining the nodal points. The dependent variable, the concentration  $c(x, t)$ , is approximated by a function  $c'(x, t)$ , which is defined as:

$$c'(x, t) = \sum_{m=1}^N \phi_m(x) c_m(t), \quad (20)$$

where  $\phi_m$  are the selected linear basis functions, which fulfill the condition  $\phi_m(x_n) = \delta_{nm}$ ,  $\delta_{nm}$  is Kronecker delta ( $\delta_{nm} = 1$  for  $m = n$ , and  $\delta_{nm} = 0$  for  $m \neq n$ ),  $c_m$  are the unknown time dependent coefficients which represent solution of (8) at the finite elements nodal points and  $N$  is the total number of nodal points. Linear basis functions have the following form:

$$\begin{aligned} \phi_1 &= 1 - \xi, \\ \phi_2 &= \xi, \end{aligned} \quad (21)$$

where  $\xi$  is the coordinate in the local coordinate system [-]. In the global coordinate system  $\xi$  is defined as

$$\xi = \frac{x - x_1}{\Delta x}, \quad x_1 \leq x \leq x_2, \quad (22)$$

where  $\Delta x (= x_2 - x_1)$  is the size of finite element [L], which is defined as distance of two neighboring nodal points. Approximated solution  $c'(x, t)$  converges to the correct solution  $c(x, t)$  for great number of basis functions  $N$ .

By application of Galerkin method, which postulates that the differential operator associated with the transport equation is orthogonal to each of the  $N$  basis functions, we get the system of  $N$  time dependent differential equations with  $N$  unknown values  $c_n(t)$ .

$$\int_0^L \left[ -\frac{\partial(\theta R^1 c)}{\partial t} - \theta R^2 \frac{\partial c}{\partial t} + \frac{\partial}{\partial x} \left( \theta D \frac{\partial c}{\partial x} - qc \right) + Fc + G \right] \phi_n dx = 0. \quad (23)$$

Index  $k$  is dropped throughout this section. By integrating "per partes" the terms with spatial derivatives we get the following equation

$$\begin{aligned} & \int_0^L \left[ -\frac{\partial(\theta R^1 c)}{\partial t} - \theta R^2 \frac{\partial c}{\partial t} + Fc + G \right] \phi_n dx - \\ & - \int_0^L \left( \theta D \frac{\partial c}{\partial x} - qc \right) \frac{\partial \phi_n}{\partial x} dx - q_{sL} \phi_n(L) + q_{s0} \phi_n(0) = 0 \end{aligned} \quad (24)$$

and by substituting variable  $c_m(t)$  for  $c(x, t)$  we obtain

$$\begin{aligned} & \int_0^L \left[ -\frac{\partial(\theta R^1 c_m)}{\partial t} \phi_m - \theta R^2 \frac{\partial c_m}{\partial t} \phi_m - Fc_m \phi_m + G \right] \phi_n dx - \\ & - \int_0^L \left( \theta D c_m \frac{\partial \phi_m}{\partial x} - qc_m \phi_m \right) \frac{\partial \phi_n}{\partial x} dx - q_{sL} \phi_n(L) + q_{s0} \phi_n(0) = 0. \end{aligned} \quad (25)$$

Eq. (25) can be rewritten in matrix form

$$\frac{d([Q^1]\{c\})}{dt} + [Q^2] \frac{d\{c\}}{dt} + [S]\{c\} = \{f\}, \quad (26)$$

where vector  $\{c\}$  contains unknown values of nodal point concentrations and where

$$Q_{nm}^1 = \int_0^L \theta R^1 \phi_m \phi_n dx, \quad (27)$$

$$Q_{nm}^2 = \int_0^L \theta R^2 \phi_m \phi_n dx, \quad (28)$$

$$S_{nm} = \int_0^L \left[ \theta D \frac{d\phi_m}{dx} \frac{d\phi_n}{dx} - q \frac{d\phi_n}{dx} \phi_m - F\phi_m \phi_n \right] dx, \quad (29)$$

$$f_n = \int_0^L G \phi_n dx - q_{sL} \phi_n(L) + q_{s0} \phi_n(0), \quad (30)$$

$$q_s = -\theta D \frac{\partial c'}{\partial x} + qc'. \quad (31)$$

In addition to basic assumptions involved in Galerkin method it is possible to use additional assumptions (van Genuchten [23]). First, inside each element and given time the coefficients (or groups of coefficients) from equations (27) through (30)  $\theta R, \theta D, q, F, G$  change linearly in agreement with following expressions:

$$\theta R(t, x) = \sum_{n=1}^N \theta R(t, x_n) \phi_n(x),$$

$$\theta D(t, x) = \sum_{n=1}^N \theta D(t, x_n) \phi_n(x),$$

$$q(t, x) = \sum_{n=1}^N q(t, x_n) \phi_n(x), \quad (32)$$

$$G(t, x) = \sum_{n=1}^N G(t, x_n) \phi_n(x),$$

$$F(t, x) = \sum_{n=1}^N F(t, x_n) \phi_n(x).$$

Advantage of this approach is that it is not necessary to use numerical integration to calculate coefficients from eq. (26). Particular matrixes have following contribution from individual elements.

$$Q_{nm}^e = \int_{x_1}^{x_2} \theta R \phi_m \phi_n dx \Rightarrow \frac{\Delta x}{12} \begin{vmatrix} 3\theta_1 R_1 + \theta_2 R_2 & \theta_1 R_1 + \theta_2 R_2 \\ \theta_1 R_1 + \theta_2 R_2 & \theta_1 R_1 + 3\theta_2 R_2 \end{vmatrix}, \quad (33)$$

$$S_{nm1}^e = \int_{x_1}^{x_2} \theta D \frac{d\phi_m}{dx} \frac{d\phi_n}{dx} dx \Rightarrow \frac{1}{2\Delta x} \begin{vmatrix} \theta_1 D_1 + \theta_2 D_2 & -\theta_1 D_1 - \theta_2 D_2 \\ -\theta_1 D_1 - \theta_2 D_2 & \theta_1 D_1 + \theta_2 D_2 \end{vmatrix}, \quad (34)$$

$$S_{nm2}^e = \int_{x_1}^{x_2} q \frac{d\phi_n}{dx} \phi_m dx \Rightarrow \frac{1}{6} \begin{vmatrix} 2q_1 + q_2 & q_1 + 2q_2 \\ -2q_1 - q_2 & -q_1 - 2q_2 \end{vmatrix}, \quad (35)$$

$$S_{nm3}^e = \int_{x_1}^{x_2} F \phi_m \phi_n dx \Rightarrow \frac{\Delta x}{12} \begin{vmatrix} 3F_1 + F_2 & F_1 + F_2 \\ F_1 + F_2 & F_1 + 3F_2 \end{vmatrix}, \quad (36)$$

$$f_n^e = \int_{x_1}^{x_2} G \phi_n dx \Rightarrow \frac{\Delta x}{6} \begin{vmatrix} 2G_1 + G_2 \\ G_1 + 2G_2 \end{vmatrix}. \quad (37)$$

As I already mentioned in Chapter 3.1, above given method can cause significant numerical oscillations in cases when convection is a dominant transport process. This problem can be overcome when during the integration of the terms with spatial derivations the higher weight is given to the upstream nodes. This method is in english literature called upstream weighting. In the following test I will perform this type of weighting only for convective term of transport equation. Huyakorn and Nilkuha [7] proposed following nonorthogonal basis functions

$$\varphi_1 = \phi_1 - 3\alpha \phi_1 \phi_2; \quad (38)$$

$$\varphi_2 = \phi_2 + 3\alpha \phi_1 \phi_2.$$

After calculating the integral from the convective term we get the following contributions to matrix [S]

$$S_{nm2}^e = \int_{x_1}^{x_2} q \frac{d\varphi_n}{dx} \phi_m dx \Rightarrow \frac{1}{6} \begin{vmatrix} q_1(2+3\alpha) + q_2 & q_1 + q_2(2-3\alpha) \\ -q_1(2+3\alpha) - q_2 & -q_1 - q_2(2-3\alpha) \end{vmatrix}. \quad (39)$$

### 3.2 Time Discretization

Numerical solution of eq. (26) is obtained by replacing continuous time coordinate by discrete consequence of times and time derivatives by finite differences. Time differential scheme may be selected with the temporal weighting factor  $\epsilon$  ( $= 0$  : explicit scheme,  $= 0.5$  : Crank-Nicholson scheme,  $= 1$  : fully implicit scheme)

$$\frac{[Q^1]^{k+1} \{c\}^{k+1} - [Q^1]^k \{c\}^k}{\Delta t} + [Q^2]^{k+\epsilon} \frac{\{c\}^{k+1} - \{c\}^k}{\Delta t} + \epsilon [S]^{k+1} \{c\}^{k+1} + (1-\epsilon) [S]^k \{c\}^k = \epsilon \{f\}^{k+1} + (1-\epsilon) \{f\}^k, \quad (40)$$

where  $k$  and  $k+1$  indicate previous and actual time level and  $\Delta t$  is time step. Eq. (40) can be rewritten:

$$[P] \{c\}^{k+1} = [T] \{c\}^k + \{R\}, \quad (41)$$

where

$$\begin{aligned} [P] &= \frac{1}{\Delta t} ([Q^1]^{k+1} + [Q^2]^{k+\epsilon}) + \epsilon [S]^{k+1}, \\ [T] &= \frac{1}{\Delta t} ([Q^1]^k + [Q^2]^{k+\epsilon}) - (1-\epsilon) [S]^k, \\ \{R\} &= \epsilon \{f\}^{k+1} + (1-\epsilon) \{f\}^k. \end{aligned} \quad (42)$$

Division of the retardation factor  $R$  into two parts  $R^1$  and  $R^2$  which leads to two matrixes  $[Q^1]$  and  $[Q^2]$ , each of them evaluated at different time level, causes much faster convergence rate when nonlinear adsorption isotherm is considered.

Higher-order approximations for the time derivative in the transport equation were derived by van Genuchten [23] (for Crank-Nicholson integration scheme). This higher-order effect may be incorporated into the transport equation by introducing time-dependent dispersion corrections as follows:

$$\begin{aligned} D^- &= D - \frac{q^2 \Delta t}{6\theta^2 (R^1 + R^2)}, \\ D^+ &= D + \frac{q^2 \Delta t}{6\theta^2 (R^1 + R^2)}, \end{aligned} \quad (43)$$

where the superscripts  $+$  and  $-$  indicate evaluation at the old and the new time levels, respectively.

By calculating the integrals mentioned above we got the tridiagonal matrixes

[P] and [T] in the form:

$$[P] = \begin{pmatrix} d_1 & e_1 & 0 & & & 0 \\ b_2 & d_2 & e_2 & 0 & & 0 \\ 0 & b_3 & d_3 & e_3 & 0 & 0 \\ & & & & & \\ & & & & & \\ 0 & 0 & b_{n-2} & d_{n-2} & e_{n-2} & 0 \\ 0 & & 0 & b_{n-1} & d_{n-1} & e_{n-1} \\ 0 & & & 0 & b_n & d_n \end{pmatrix} \quad (44)$$

where particular elements of the matrix [P] are given in Table 1. In Table 1:  $a = x_i - x_{i-1}$ ;  $b = x_{i+1} - x_i$ ;  $\Delta x = (a + b)/2$ ;  $\Delta t = t_{j+1} - t_j$ ;  $i$  is index of a node (increasing in the direction of axes  $x$ ;  $i = 1, 2, \dots, n$ ) and  $j$  is time index. Particular elements of vector {R} have following form

$$\begin{aligned} r_1 &= a(2s_1 + s_2) + \epsilon q_s(0, t^{j+1}) + (1 - \epsilon)q_s(0, t^j), \\ r_i &= a(s_{i-1} + 2s_i) + b(2s_i + s_{i+1}), \\ r_n &= b(s_{n-1} + 2s_n) - \epsilon q_s(L, t^{j+1}) - (1 - \epsilon)q_s(L, t^j), \\ s_i &= \frac{1}{6} [\epsilon G_i^{j+1} + (1 - \epsilon)G_i^j]. \end{aligned} \quad (45)$$

From eq. (42) it follows that matrixes [P] and [T] are identical under the assumption that the variables  $D^-$ ,  $F$ ,  $q$  and  $\epsilon$  are replaced by  $-D^+$ ,  $-F$ ,  $-q$  and  $(1 - \epsilon)$ .

### 3.3 Solution Process

The solution process at each time step proceeds as follows. First, an iterative procedure is used to obtain the solution of the Richards' equation. After achieving convergence, the solution of the solute transport equation is implemented. This is done by first determining the nodal values of the fluid flux from nodal values of the pressure head by applying Darcy's law. Nodal values of the water content and the fluid flux at the previous time level are already known from the solution at the previous time step. Values for the water content and the fluid flux are subsequently used as input to the solute transport equation leading to the system of linear algebraic equations given by (41). If a linear equilibrium reaction between solid and liquid phases is considered then since transport is assumed to be independent of changes in the fluid density, one may proceed directly to the next solute or next time level once the transport equation is solved for the current time level. On the other side if a nonlinear equilibrium reaction between solid and liquid phase is

Table 1. Coefficients of matrix [P] for the finite element method with nonorthogonal upstream weighting. Tabulka 1. Matice koeficientů [P] pro metodu konečných elementů s neortogonálním horním vážením.

$d_1 = \frac{b}{12\Delta t} (3\theta_1 R_1 + \theta_2 R_2) + \frac{\epsilon}{2b} (\theta_1 D_1^- + \theta_2 D_2^-) + \frac{\epsilon}{6} [q_1(2 + 3\alpha^+) + q_2] + \frac{cb}{12} (3F_1 + F_2)$	(50)
$b_i = \frac{a}{12\Delta t} (\theta_{i-1} R_{i-1} + \theta_i R_i) - \frac{\epsilon}{2a} (\theta_{i-1} D_{i-1}^- + \theta_i D_i^-) - \frac{\epsilon}{6} [q_{i-1}(2 + 3\alpha^-) + q_i] + \frac{ca}{12} (F_{i-1} + F_i)$	(51)
$d_i = \frac{a}{12\Delta t} (\theta_{i-1} R_{i-1} + 3\theta_i R_i) + \frac{b}{12\Delta t} (3\theta_i R_i + \theta_{i+1} R_{i+1}) + \frac{\epsilon}{2a} (\theta_{i-1} D_{i-1}^- + \theta_i D_i^-) + \frac{\epsilon}{2b} (\theta_i D_i^- + \theta_{i+1} D_{i+1}^-) + \frac{\epsilon}{6} [q_{i-1} + 3q_i(\alpha^+ + \alpha^-) - q_{i-1}] + \frac{ca}{12} (F_{i-1} + 3F_i) + \frac{cb}{12} (3F_i + F_{i+1})$	(52)
$e_i = \frac{b}{12\Delta t} (\theta_i R_i + \theta_{i+1} R_{i+1}) - \frac{\epsilon}{2b} (\theta_i D_i^- + \theta_{i+1} D_{i+1}^-) + \frac{\epsilon}{6} [q_{i+1}(2 - 3\alpha^+) + q_i] + \frac{cb}{12} (F_i + F_{i+1})$	(53)
$d_n = \frac{a}{12\Delta t} (\theta_{n-1} R_{n-1} + 3\theta_n R_n) + \frac{\epsilon}{2a} (\theta_{n-1} D_{n-1}^- + \theta_n D_n^-) - \frac{\epsilon}{6} [q_{n-1} + q_n(2 - 3\alpha^-)] + \frac{ca}{12} (F_{n-1} + 3F_n)$	(54)

considered, iteration procedure similar to that for the water flow is used to solve the transport equations. After the first iteration, the coefficients in (41) are re-evaluated using the first solution, and the new equations are again solved. The iterative process continues until a satisfactory degree of convergence is obtained, i.e., until at all nodes the absolute change in concentrations between two successive iterations becomes less than some small value determined by the imposed relative and absolute concentration tolerances.

4. Example 1 – Solute Transport with Nitrification Chain

This example was used to verify the mathematical accuracy of the solute transport part of the model. Van Genuchten [24] published analytical solution for one-dimensional convective-dispersive transport of solutes involved in a sequential first-order decay reactions. This solution holds for solute transport in a homogeneous, isotropic porous medium during steady-state unidirectional groundwater flow. The solute transport equations (1) and (2) for this situation reduce to

$$R_1 \frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} - v \frac{\partial c_1}{\partial x} - \mu_1 R_1 c_1, \tag{46}$$

$$R_i \frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x} + \mu_{i-1} R_{i-1} c_{i-1} - \mu_i R_i c_i, \quad i = 2, 3, \tag{47}$$

where  $\mu$  is a first-order degradation constant,  $D$  is the dispersion coefficient,  $v$  is the average pore water velocity ( $q/\theta$ ) in the flow direction, and  $x$  the spatial coordinate parallel to the direction of flow. The initially solute-free medium is subjected to a source of the first solute,  $c_0$ , of unit concentration. The boundary conditions may be written as:

$$\begin{aligned} \left(-D \frac{\partial c_1}{\partial x} + v c_1\right) &= v c_{0,1}(0, t), \\ \left(-D \frac{\partial c_i}{\partial x} + v c_i\right) &= 0, \quad i = 2, 3, \\ \lim_{x \rightarrow \infty} \frac{\partial c_i}{\partial x} &= 0, \quad i = 1, 2, 3. \end{aligned} \tag{48}$$

The extensive form of the analytical solution of the above transport problem is presented by van Genuchten [24].

The example applies to the three-species nitrification chain



Table 2. Input parameters for example 1.  
Tabulka 2. Vstupní parametry pro příklad 1.

Parameter Parametr	Value Hodnota
$q$ [cm/hour]	1.0
$D$ [cm <sup>2</sup> /hour]	0.18
$\mu_1$ [hour <sup>-1</sup> ]	0.005
$\mu_2$ [hour <sup>-1</sup> ]	0.1
$\mu_3$ [hour <sup>-1</sup> ]	0.0
$R_1$ [-]	2.0
$R_2$ [-]	1.0
$R_3$ [-]	1.0
$c_{0,1}$ [-]	1.0

Table 3. Input parameters for example 2.  
Tabulka 3. Vstupní parametry pro příklad 2.

Parameter Parametr	Value Hodnota
$q$ [cm/hour]	0.271
$D$ [cm <sup>2</sup> /hour]	1.167
$\rho$ [g/cm <sup>3</sup> ]	0.884
$\theta$ [-]	0.633
$c_0$ [mmol <sub>e</sub> /L]	10.0
$k_s$ [cm <sup>3</sup> /g]	1.687
$\gamma$ [-]	1.615

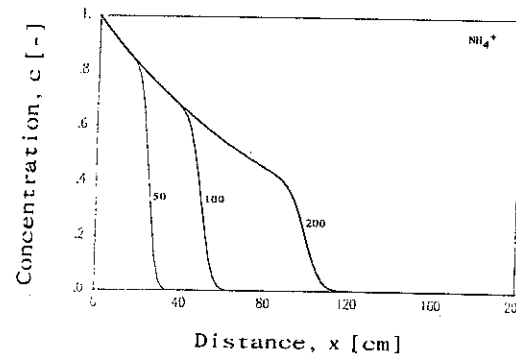


Fig. 1. Concentration profiles for NH<sub>4</sub><sup>+</sup> at 50, 100 and 200 hours for example 1.  
Obr. 1. Koncentrační profily pro NH<sub>4</sub><sup>+</sup> v čase 50, 100 a 200 hodin pro příklad 1.

and is the same as described earlier by van Genuchten [24]. The input transport parameters for the simulation are listed in Table 2.

Figures 1, 2, and 3 show the concentration profiles at three different times (50, 100, and 200 hours) for NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, respectively. Figure 4 shows concentration profiles of all three solutes at time 200 hours. Because of relatively fine discretization of both space and time (Peclet number is equal to 1 and Courant number is 0.2 (Šimůnek et al. [19])), the analytical and numerical results are visually identical.



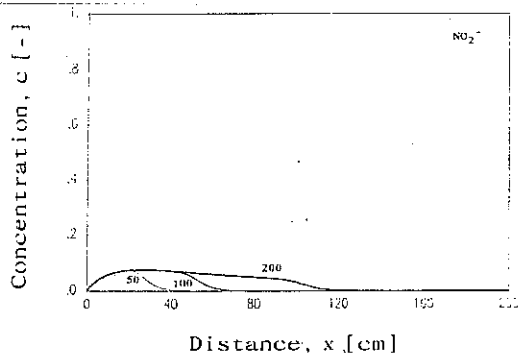


Fig. 2. Concentration profiles for  $\text{NO}_2^-$  at 50, 100 and 200 hours for example 1.  
Obr. 2. Koncentrační profily pro  $\text{NO}_2^-$  v čase 50, 100 a 200 hodin pro příklad 1.

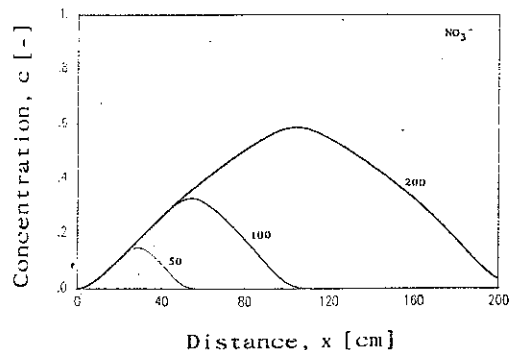


Fig. 3. Concentration profiles for  $\text{NO}_3^-$  at 50, 100 and 200 hours for example 1.  
Obr. 3. Koncentrační profily pro  $\text{NO}_3^-$  v čase 50, 100 a 200 hodin pro příklad 1.

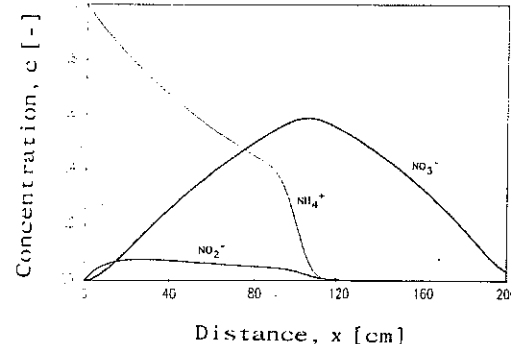


Fig. 4. Concentration profiles for  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  at 200 hours for example 1.  
Obr. 4. Koncentrační profily pro  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  a  $\text{NO}_3^-$  v čase 200 hodin pro příklad 1.

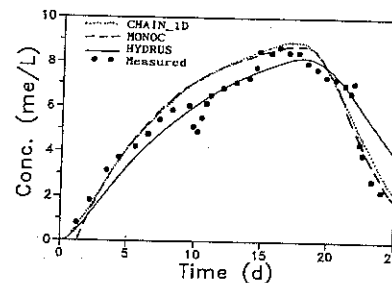


Fig. 5. Mg breakthrough curve for Abist loam (data points from Selim et al. [16]) for example 2.  
Obr. 5. Průniková křivka pro Mg pro půdu „Abist loam“ pro příklad 2 (body z Selim et al. [16]); ●●● naměřeno.

### 5. Example 2 – Solute Transport with Nonlinear Cation Adsorption

The experiment used for this example was conducted by Selim et al. [16] and was used for the verification of the model HYDRUS (Kool and van Genuchten [10]). The soil in this experiment was Abist loam. A 10.75 cm long soil column was first saturated with a  $10 \text{ mmol}_c\text{L}^{-1}$   $\text{CaCl}_2$  solution. The experiment consisted of applying a 14.26 pore volume pulse ( $t = 358.05$  hours) of  $10 \text{ mmol}_c\text{L}^{-1}$   $\text{MgCl}_2$  solution, followed by the original  $\text{CaCl}_2$  solution. The measured magnesium breakthrough curve provided data for verifying the CHAIN\_1D transport solution. The adsorption isotherm was determined with the help of batch experiments (Selim et

al. [16]) and was fitted with the Freundlich eq. (5) (Kool and van Genuchten [10]). The Freundlich isotherm parameters, as well as other transport parameters for this problem, are listed in Table 3.

The observed Mg breakthrough curve is shown in Figure 5, together with the simulated breakthrough curves obtained with CHAIN\_1D and programs MONOC (Selim et al. [16]) and HYDRUS (Kool and van Genuchten [10]). The results indicate that the breakthrough curve predicted by CHAIN\_1D described the measured data reasonably well and that there is a very high correspondence between the simulated results of models CHAIN\_1D and MONOC. Slightly worse correspondence is between these two models and model HYDRUS. However, the correspondence between models CHAIN\_1D and MONOC and measured data seems to be better than correspondence between model HYDRUS and data.

## 6. Summary and Conclusion

The model for simulating the movement of variably saturated water flow, heat transport, and the transport of volatile solutes involved in sequential first-order decay reactions in one-dimensional porous media is presented in this paper. The model numerically solves the Richards' equation for saturated-unsaturated water flow and the convection-dispersion equation for heat and solute transport. The solute transport equations consider convective-dispersive transport in the liquid phase, convective-diffusive transport in the gaseous phase, nonlinear equilibrium sorption/exchange, linear equilibrium reaction between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions: one which is independent of other solutes, and one which provides the coupling between solutes involved in the sequential first-order decay reactions. Freundlich or Langmuir adsorption isotherms are used to describe the nonlinear equilibrium sorption/exchange. The governing partial differential equations are solved numerically using Galerkin-type linear finite element schemes with the option for upstream weighting in order to overcome the numerical oscillations.

Two examples are presented to verify and illustrate applications of the code. The first example represents the solute transport with nitrification chain and the numerical results are compared with the analytical solution. Solute transport with nonlinear cation adsorption is used to verify the possibility to simulate the nonlinear adsorption. The numerical results were compared with the experimental data and with the results of two other computer models.

Two dimensional version of this program is under preparation at U. S. Salinity Laboratory in Riverside (Šimůnek and van Genuchten [20]).

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NUMERICKÝ MODEL PRO SIMULOVÁNÍ PROUDĚNÍ VODY  
A TRANSPORTU TEPLA A ROZPUŠTĚNÝCH LÁTEK  
V NENASYCENĚM PÓROVITĚM PROSTŘEDÍ

Jiří Šimůnek

Tento článek přináší popis modelu pro simulaci nenasyčeného proudění vody, transportu tepla a transportu těžkých rozpuštěných látek podléhajících sekvenčnímu rozpadu prvního řádu v jednorozměrném pórovitém prostředí. Model řeší numericky Richardsovu rovnici pro nasycené-nenasycené proudění vody a konvektivně-disperzní rovnici pro transport tepla a rozpuštěných látek. Řídící rovnice pro transport rozpuštěných látek uvažuje konvektivně-disperzní transport v kapalně fázi, konvektivně-difúzní transport v plynné fázi, nelineární rovnovážnou sorpci, lineární reakci mezi kapalnou a plynnou fází, produkci nultého řádu a dvě rozkladné reakce prvního řádu: první, která je nezávislá na ostatních chemických rozpuštěných látkách a druhá, která představuje spojení mezi rozpuštěnými látkami podléhajícími sekvenčnímu řetězovému rozkladu prvního řádu. Freundlichova nebo Langmuirova adsorpční isoterma je použita k popisu nelineární rovnovážné sorpce. Řídící parciálně diferenciatní rovnice jsou řešeny numericky použitím Galerkinovy verze lineárních konečných elementů. Metoda horního vážení je použita k překonání numerických oscilací pro transportní problémy s dominující konvekcí.

Aplikace modelu jsou ukázány na dvou příkladech. První příklad simuluje transport rozpuštěných dusíkatých látek podléhajících rozpadovému procesu (nitrifikaci). Příklad je použit ke srovnání numerických výsledků s výsledky analytického řešení. Druhý příklad je použit k verifikaci možnosti modelovat transport chemických látek podléhajících nelineární adsorpci. Numerické výsledky jsou srovnány s experimentálními daty a s výsledky modelů HYDRUS a MONOC.

Seznam použitých symbolů

- $a$  – objemový obsah plynné fáze [ $L^3L^{-3}$ ],  
 $b_i$  – prvky matice  $[P]$  [ $LT^{-1}$ ],  
 $c$  – koncentrace rozpuštěné látky [ $ML^{-3}$ ],  
 $c'$  – aproximativní řešení transportní rovnice [ $ML^{-3}$ ],  
 $c_m$  – uzlové koncentrace, které reprezentují řešení transportní rovnice [ $ML^{-3}$ ],  
 $c_r$  – koncentrace propadového členu [ $ML^{-3}$ ],  
 $\{c\}$  – vektor obsahující neznámé hodnoty koncentrace v uzlových bodech [ $ML^{-3}$ ],  
 $D$  – disperzní koeficient [ $L^2T^{-1}$ ],  
 $D^+$ ,  $D^-$  – korekce disperzního koeficientu [ $L^2T^{-1}$ ],  
 $D^g$  – disperzní koeficient v plynné fázi [ $L^2T^{-1}$ ],  
 $D^{g0}$  – molekulární difúzní koeficient v plynné fázi [ $L^2T^{-1}$ ],  
 $D^w$  – disperzní koeficient v kapalně fázi [ $L^2T^{-1}$ ],  
 $D^{w0}$  – molekulární difúzní koeficient v kapalně fázi [ $L^2T^{-1}$ ],  
 $d_i$  – prvky matice  $[P]$  [ $LT^{-1}$ ],  
 $e$  – číslo elementu [-],  
 $e_i$  – prvky matice  $[P]$ , [ $LT^{-1}$ ],  
 $E$  – aktivační energie reakce [ $ML^2T^{-2}M^{-1}$ ],  
 $\{f\}$  – vektor v globální soustavě lineárních rovnic pro transport [ $ML^{-2}T^{-1}$ ],  
 $g$  – koncentrace v plynné fázi [ $ML^{-3}$ ],  
 $i$  – index uzlu (stoupající ve směru orientace osy  $x$ ;  $i = 1, 2, \dots, n$ ) [-],  
 $j$  – časový index [-],  
 $k_g$  – distribuční koeficient, který vztahuje koncentrace v kapalně a plynné fázi [-],  
 $k_s$  – distribuční koeficient, který vztahuje koncentrace v kapalně a pevně fázi [ $L^3M^{-1}$ ],  
 $L$  –  $x$ -ová souřadnice půdního povrchu [ $L$ ],  
 $N$  – počet konečných elementů [-],  
 $[P]$  – matice v globální soustavě lineárních rovnic pro transport [ $LT^{-1}$ ],  
 $q$  – objemová rychlost [ $LT^{-1}$ ],  
 $q^g$  – Darcyovská rychlost v plynné fázi [ $LT^{-1}$ ],  
 $q^w$  – Darcyovská rychlost v kapalně fázi [ $LT^{-1}$ ],  
 $[Q]$  – matice v globální soustavě lineárních rovnic pro transport [ $L$ ],  
 $R$  – retardační faktor [-],  
 $R^1, R^2$  – složky retardačního faktoru [-],  
 $R_1, R_2$  – retardační faktory v koncových bodech elementu  $e$  [-],  
 $r_i$  – prvky vektoru  $\{R\}$  [ $ML^{-2}T^{-1}$ ],  
 $\{R\}$  – vektor v globální soustavě lineárních rovnic pro transport [ $ML^{-2}T^{-1}$ ],  
 $s$  – adsorbovaná koncentrace [-],  
 $S$  – propadový (extrakční) člen [ $T^{-1}$ ],  
 $[S]$  – matice v globální soustavě lineárních rovnic pro transport [ $LT^{-1}$ ],  
 $t$  – čas [ $T$ ],  
 $T^A$  – absolutní teplota [ $K$ ],  
 $T_r^A$  – referenční absolutní teplota [ $K$ ] ( $293.15 K = 20^\circ C$ ),  
 $[T]$  – matice v globální soustavě lineárních rovnic pro transport [ $LT^{-1}$ ],  
 $x$  – prostorová vertikální souřadnice orientovaná kladně směrem vzhůru [ $L$ ],  
 $\Delta x$  – velikost konečného elementu [ $L$ ],  
 $\Delta t$  – časový krok [ $T$ ],

$\alpha$	- vázicí faktor [-],
$\gamma_g$	- rychlostní konstanta nultého řádu pro zdroj v plynné fázi [ $ML^{-3}T^{-1}$ ],
$\gamma_s$	- rychlostní konstanta nultého řádu pro zdroj v pevné fázi [ $T^{-1}$ ],
$\gamma_w$	- rychlostní konstanta nultého řádu pro zdroj v kapalně fázi [ $ML^{-3}T^{-1}$ ],
$\delta_{nm}$	- Kroneckerovo delta [-],
$\epsilon$	- parametr určující typ časového diskretizačního schématu [-],
$\eta$	- empirický koeficient v adsorpční isothermě, [-] nebo [ $L^3M^{-1}$ ],
$\lambda_g$	- disperzivita v plynné fázi [L],
$\lambda_w$	- disperzivita v kapalně fázi [L],
$\phi_m$	- lineární básová funkce [-],
$\mu_g, \mu'_g$	- rychlostní konstanta prvního řádu pro propad plynné fázi [ $T^{-1}$ ],
$\mu_s, \mu'_s$	- rychlostní konstanta prvního řádu pro propad v pevné fázi [ $T^{-1}$ ],
$\mu_w, \mu'_w$	- rychlostní konstanta prvního řádu pro propad v kapalně fázi [ $T^{-1}$ ],
$\xi$	- souřadnice v lokální souřadnicové soustavě [-],
$\theta$	- objemová vlhkost [ $L^3L^{-3}$ ],
$\theta_s$	- nasycená vlhkost [ $L^3L^{-3}$ ],
$\theta_1, \theta_2$	- vlhkosti v koncových bodech elementu $e$ [ $L^3L^{-3}$ ],
$\rho$	- objemová hmotnost porézního prostředí [ $ML^{-3}$ ],
$\tau_g$	- faktor tortuozity v plynné fázi [-],
$\tau_w$	- faktor tortuozity v kapalně fázi [-].