

Two Dimensional Numerical Simulation of Solute Transport in Chemically Heterogeneous Porous Media

By

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Abstract

In recent years, many hydrogeochemical models have appeared for simulating subsurface solute transport in homogeneous and heterogeneous porous media. Most of these models deal with the porous media are chemically homogeneous. The hydrological transport of solute can be described by a set of linear partial differential equations, and the chemical equilibrium reactions are described by a set of nonlinear algebraic equations. In this paper a reacting nonlinear adsorbing solute transport in chemically heterogeneous soils is studied. The adsorption is assumed to be adequately described with the Freundlich equation. Random variation of the adsorption coefficient is assumed to describe the chemical heterogeneity of the porous media. The mass action, transport, and site constraint equations are expressed in a differential/algebraic form and solved simultaneously. In the mass action equations describing complexation and sorption process, the activities of the species in the aqueous phase are approximated using the Davies equation. The efficiency of several algorithms for solving the problem of solute transport in chemically heterogeneous porous medium has been studied. In particular, the relative efficiency of competing algorithms is evaluated as a function of the nature of the chemistry.

المخلص العربي

أصبحت عملية تلوث البيئة تشغل بال الكثير من الباحثين في الآونة الأخيرة لما لها من تأثير كبير على عمليات التنمية وصحة الإنسان. ففي المناطق ذات النمو السكاني أو الصناعي أو الزراعي المرتفع لأنها العديد من الملوثات من العناصر الثقيلة وغيرها يصل إلى التربة ومنها ينتقل إلى الخزان الجوفي

مما يؤثر على نوعية المياه الجوفية بهذه الخزانات. وتعتبر عملية محاكاة سريان هذه الملوثات في الخزان الجوفي وخصوصا المتفاعل منها أمرا غاية في التعقيد حيث تتحكم كثير من العوامل في سريان تلك الملوثات. وحيث أن معادلة سريان المياه الجوفية عبارة عن معادلة تفاضلية ومعادلة وصف التفاعلات الكيميائية عبارة عن معادلات جبرية غير خطية فإنه يجب اختيار الطريقة المناسبة لحل كلا من نظامي سريان المياه الجوفية والتفاعلات الكيميائية التي تحدث للملوثات أثناء السريان في آن واحد. وقد ظهرت في الآونة الأخيرة بعض الطرق لتمثيل سريان الملوثات المتفاعلة كيميائية غير أن هذه النماذج لم تأخذ في الاعتبار عدم التجانس الكيميائي للوسط المنفذ في الخزان الجوفي وإنما أخذت فقط في الاعتبار عدم التجانس في الخواص الهيدروليكية للخزان الجوفي. وتهدف هذه الدراسة إلى تطوير نموذج يمكن استخدامه لتمثيل حركة الملوثات المتفاعلة كيميائيا في وسط منفذ غير متجانس كيميائيا. وقد تمت دراسة العديد من طرق الحل للاختيار أفضل الطرق لحل نظامي معادلات حركة المياه الجوفية والتفاعلات الكيميائية التي تحدث أثناء حركة الملوثات في وقت واحد بكفاءة عالية وتوفير الوقت والجهد والتكلفة. وتساهم هذه الدراسة في حماية الموارد المائية وإمكانية التنبؤ بسلوك الملوثات في الخزان الجوفي ومن ثم طرح الحلول اللازمة لحماية الخزانات الجوفية من انتشار هذه الملوثات.

Introduction

The contamination of the environment has become a matter of considerable concern. In areas with high intensity of industry and agriculture, large concentrations of heavy metals or organic contaminants may reach the soil by atmospheric deposition or by waste disposal. These contaminated sites are a potential risk for groundwater quality, for the quality of agricultural production, and for the quality of the drinking water supply. In order to manage our soil and groundwater resources properly, modeling tools are necessary to understand and predict movement of contaminants in the environment.

During the past decades much attention has been given to the theory and modeling of solute transport. This development has been accelerated and increased by the difficulty and high costs of field scale measurements. Much attention has been given to the monocomponent solute transport in homogeneous media. Monocomponent models may adequately describe situations where nonreacting solutes or solutes at trace levels are present [van der Zee, 1990b]. A number of analytical solutions for these cases for different boundary conditions, were given by van Genuchten and Alves [1982], who considered linear adsorption and zero and first-order production and decay. Extensions were developed, taking into account the nonequilibrium aspect of the adsorption process, by van Genuchten et al. [1974] and Rao et al. [1979].

Many transport models concern homogeneous media, but in practice soils and groundwater systems appear to be heterogeneous. One of the first efforts to describe heterogeneity as achieved by making use of the dual-porosity concept [Coats and Smith, 1964; van Genuchten and Wierenga, 1976] and of the two sites surface adsorption concept [Cameron and Klute, 1977].

The studies concerning heterogeneity of porous media mainly involve variable soil hydraulic properties caused by spatially variable porosity, dispersion and hydraulic conductivity. *Boekhold et al.* [1990] have shown that chemical properties which play a role in the process of adsorption, such as pH and organic matter content, may show highly variable distributions. Studies concerning reactive solute transport with random sorption parameters were performed by *van der Zee and van Riemsduik* [1986, 1987], *Cvetkovic and Shapiro* [1990], *Destouni and Cvetkovic* (1991), *Jury et al.* [1986] and *Chrysikopoulos et al.* [1990]. *Cvetkovic and Shapiro* [1990] studied the mass arrival of transporting solute taking into account spatial variability of hydraulic conductivity, the linear adsorption coefficient, and of adsorption and desorption rate parameters. *Destouni and Cvetkovic* [1991] showed a double peak behavior for the mass arrival of solute into groundwater considering random hydraulic conductivity and random adsorption and desorption rate parameters. *Jury et al.* [1986] extended the transfer function model for solutes that undergo physical, chemical and biological transformations in heterogeneous systems. *Van der Zee and van Riemsduik* [1987] used a random distribution of chemical parameters to simulate solute transport in a heterogeneous field. They found that variation of the retardation factor and the water velocity causes non-Fickian front shapes for the average field concentration front. *Chrysikopoulos et al.* [1990] studied the effect of a spatially variable retardation factor on linearly adsorbing one-dimensional solute transport, focusing on column scale heterogeneity.

Governing Equations

Several researchers have developed methods to solve the problem of transport of multicomponent in groundwater as mentioned in the literature review. Most of these approaches are powerful in one dimensional, but for two or three dimensional problem the solution of the system is very computationally intensive, since the coupled of ordinary differential equation and nonlinear algebraic equations resulted in a very large matrix (Yeh and Tripathi, 1989). In this study a two dimensional powerful model for solving the problem of transport of multicomponent in groundwater is developed based on the direct substitution method. The definition of component and species of Westall et al., (1976) have been adopted. The components of a chemical system are a set of linearly independent chemical entities such that every chemical species can be uniquely represented as a linear combination of those components. A component is an aqueous component if its component species exists in solution. Similarly a

component is an adsorbed component if its component species exists at the surface of a solid. The total concentration of a component is the sum of the concentrations of the species that contain the component multiplied by the stoichiometric coefficients. The aqueous, adsorbed, and precipitated concentrations of a component are the aqueous, adsorbed and precipitated fractions of the total concentration of the component, respectively.

The two dimensional, advection dispersion transport equation subjected to nonlinear equilibrium adsorption for a steady state flow in the groundwater is expressed as follows:

$$\theta D_L \left(\frac{\partial^2 C_j}{\partial x^2} \right) + \theta D_T \left(\frac{\partial^2 C_j}{\partial y^2} \right) - \theta v_x \left(\frac{\partial C_j}{\partial x} \right) = \theta \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} \quad (1)$$

Where:

- C = The pollution concentration (mol m⁻³).
- q = The adsorbed concentration in volumetric basis (mol m⁻³).
- θ = The volumetric water fraction.
- D_L = The longitudinal pore scale dispersion coefficient (m² yr⁻¹).
- D_T = The transverse pore scale dispersion coefficient (m² yr⁻¹).
- v = The flow velocity (m yr⁻¹).

The nonlinear adsorption is described by the Freundlich equation as follows:

$$q = kC^n \quad 0 < n < 1 \quad (2)$$

For studying the transport of solute through a chemically heterogeneous soil, k is considered to be a random space function. Depending on the nonlinearity of the adsorption, *Van Duijn and Kanabner* (1990) have shown that a traveling wave front develops in a homogeneous porous medium. These considerations indicate that due to the nonlinearity of adsorption, the lower concentration experiences a large retardation than higher concentrations. Consequently, a relatively steep front develops as adsorption nonlinearity opposes the front spreading effect due to pore scale dispersion. If both effects, due to nonlinear adsorption and due to pore scale dispersion, are of equal force, the front shape and front velocity remain constant.

Initial and Boundary Condition

The initial and boundary conditions used for the derivation of the analytical solution are given by

$$C(x, y, t) = 0 \quad \text{when } x > 0, y > 0 \text{ and } t = 0 \quad (3)$$

$$C(x, y, t) = C_0 \quad \text{when } x = 0, y = 0 \text{ and } t > 0 \quad (4)$$

Bosma and van der Zee [1992b] gave the transformation to describe the concentration with respect to a moving coordinate system by:

$$\eta_x = x - \left(\frac{v_x t}{R} \right) \text{ and} \quad (4a)$$

$$\eta_y = y - \left(\frac{v_y t}{R} \right) \quad (4b)$$

Where:

η = Transformed coordinate (m).

x, y = Cartesian coordinates (m).

v_x, v_y = Flow velocities in x and y directions (m yr^{-1}).

R = Nonlinear retardation factor.

R_l = Nonlinear retardation factor.

The retardation factor R can be expressed as follows:

$$R = 1 + \left(\frac{\Delta q(c)}{\theta \Delta C} \right) \quad (5)$$

where $\Delta C = C_0 - C_i$, C_0 is the feed concentration (mol m^{-3}), C_i is the initial concentration (mol m^{-3}), and Δq is the corresponding change in the adsorbed amount. When the traveling wave front has formed the initial and boundary conditions will be as follows:

$$C(\eta) = C(x, y, t) \quad (6a)$$

$$q(\eta) = q(x, y, t) \quad (6b)$$

The transformed boundary condition for the infinite system can be expressed as follows:

$$C(\eta) = C_0, \quad \frac{\partial C}{\partial \eta} = 0, \quad \frac{\partial q}{\partial \eta} = 0 \text{ and } \eta = -\infty \quad (7a)$$

$$C(\eta) = 0, \quad \frac{\partial C}{\partial \eta} = 0, \quad \frac{\partial q}{\partial \eta} = 0 \text{ and } \eta = \infty \quad (7b)$$

The analytical solution for the two dimensional nonlinear adsorption for equation (1) and (2) can given for the main flow direction and transverse direction as follows:

$$\bar{C}(\eta_x) = \left(\frac{C(\eta_x)}{C_0} \right) = \left\{ 1 - \exp \left[\frac{v_x (R-1)}{D_l R} \cdot (1 - \eta_x)(\eta_x - \eta_x^*) \right] \right\}^{1/(1-n)} \text{ where } \eta_x \leq \eta_x^* \quad (8a)$$

$$\bar{C}(\eta_x) = 0 \text{ where } \eta_x > \eta_x^* \quad (8b)$$

$$\bar{C}(\eta_y) = \left(\frac{C(\eta_y)}{C_0} \right) = \left\{ 1 - \exp \left[\frac{v_y(R-1)}{D_t R} \cdot (1 - \eta_y)(\eta_y - \eta_y^*) \right] \right\}^{1/(1-n)} \quad \text{where } \eta_y \leq \eta_y^* \quad (8c)$$

$$\bar{C}(\eta_y) = 0 \quad \text{where } \eta_y > \eta_y^* \quad (8d)$$

Where:

\bar{C} = Relative concentration (mol m⁻³).

η^* = Reference point value for transformed coordinates (m).

n = Freundlich sorption parameter.

If solute transport subjected to nonlinear adsorption is considered, it is possible to derive an analytical expression for the variance of the front from equations (8a), (8b), (8c) and (8d) when k is constant and not a random space function (for chemically homogeneous porous media). The traveling wave is characterized by a constant front shape and a constant velocity. The constant front shape implies that the front variance is also invariant with time and moving distance in the two directions. This suggests that an expression for the front variance can be derived that depends only on pore scale dispersion and on the degree of nonlinear adsorption.

Using the substitution $\bar{\eta} = \eta - \eta^*$ into equations (8a) and (8c) will yield:

$$\bar{C}(\bar{\eta}_x) = [1 - \exp(P_x \bar{\eta}_x)]^m \quad \text{where } \bar{\eta}_x \in (-\infty, 0) \quad (9a)$$

$$\bar{C}(\bar{\eta}_y) = [1 - \exp(P_y \bar{\eta}_y)]^m \quad \text{where } \bar{\eta}_y \in (-\infty, 0) \quad (9b)$$

Where:

$$m = \frac{1}{1-n} \quad (10)$$

$$P_x = \frac{v_x(R-1)}{D_l R m} \quad (11a)$$

$$P_y = \frac{v_y(R-1)}{D_T R m} \quad (11b)$$

Numerical Solution

(a) Distribution of soil chemical heterogeneity

In order to describe solute spreading in heterogeneous porous media one must account for the often irregular variation of transport and adsorption parameters [Mackay et al., 1986a, b]. To study the effect of column scale heterogeneity on solute transport, the transport and adsorption parameters may be considered variable in the vertical direction. Bosma and van der Zee [1992a] have shown the effect of layering on solute transport with nonlinear adsorption. Considering

linearly and nonlinearly adsorbing layers, the layering order was found to be important in order to describe the downstream concentration front. Whereas a soil consisting of two different layers was considered [Bosma and van der Zee, 1992a], here it is our aim to show the effect of multilayered soils.

In accordance with van der Zee [1990a], only variation of the adsorption parameters was considered in order to describe the effect of chemical heterogeneity, whereas variation of physical parameters such as flow velocity and dispersivity is not taken into account. The latter effects have been studied by Dagan and Bresler [1979], Bresler and Dagan [1979, 1981, 1983] and Amoozegar-Fard et al. [1982]. In view of the often rather constant n value [de Haan et al., 1987; Boekhold et al., 1991], we have considered only the Freundlich adsorption coefficient k to be random, characterized by a probability density function (PDF). The variation of the adsorption coefficient k is given by a normal distribution. Similar to Black and Freyberg [1987] and Chrysikopoulos et al., [1990], who used a spatial correlation of their random variable, we assumed the Freundlich adsorption coefficient k to be spatially correlated according to the exponential autocorrelation function given as:

$$r(\zeta) = \exp\left(\frac{-\zeta}{\lambda}\right) \quad (12)$$

Where:

- ζ = The separation distance.
- r = The autocorrelation scale.
- λ = The correlation scale.

To assess the effect of a spatially variable adsorption coefficient, Monte Carlo simulations were performed. The random columns were finely discretized with different values for the adsorption coefficient k at each node. The columns had a prescribed probabilistic structure and each column is considered an equally likely configuration for the actual spatial pattern of the adsorption coefficient. A one-dimensional random generator has been used to construct one-dimensional random fields of a normally distributed parameter with autocorrelation described by the first-order exponential autocorrelation function given by (12). Use was made of a generator, creating uncorrelated normally distributed random numbers. To improve the accuracy of the reproduction of the autocorrelation structure in the random columns, more points per correlation scale were generated than actually used in the numerical transport calculations. The remaining points were not considered during the rest of the calculations. This technique, used by Bellin [1991], has been shown to improve the results.

The variable adsorption coefficient k at each discrete generation point is

evaluated by:

$$k = m_k + \varepsilon \quad (13)$$

where m_k is the average adsorption coefficient and ε is the random fluctuation of m_k with zero mean. With the fluctuations ε the autocorrelation of the adsorption coefficient can be created. Using the first order exponential autocorrelation function, the adsorption coefficient k at node i is determined by node $i - 1$ as follows:

$$k_i = \beta k_{i-1} + \varepsilon_{i-1} \quad (13)$$

where β is the autocorrelation coefficient for two subsequent generation points.

With the random generator 600 possible chemically heterogeneous soil columns can be generated. At each generation point of each column the k value is determined by the expected value m_k and the fluctuation ε .

(b) Solving transport equations

A numerical solution of equation (1) and (2) has been developed to perform the calculations with the random columns. The numerical solution is based on a finite difference Crank-Nicolson approximation of equation (1) in combination with a Newton-Raphson iteration scheme. In order to prevent oscillation the increments in the two direction x , y and time t were chosen to satisfy the criteria for linear adsorption, given by *van Genuchten and Wierenga* [1974]. The discretization makes it possible to specify a different adsorption coefficient for each node. A first type boundary condition was used at the inlet of the column, whereas at the outlet a flux type boundary was imposed:

$$C = C_0 \text{ when } x=0 \text{ and } t \geq 0 \quad (14a)$$

$$C = C_0 \text{ when } y=0 \text{ and } t \geq 0 \quad (14b)$$

$$\frac{\partial C}{\partial x} = \text{constant when } x \rightarrow \infty \text{ and } t > 0 \quad (14c)$$

$$\frac{\partial C}{\partial y} = \text{constant when } y \rightarrow \infty \text{ and } t > 0 \quad (14d)$$

The initial condition for the numerical calculation can be expressed as follows:

$$C = C_i \text{ when } x, y > 0 \text{ and } t = 0 \quad (15)$$

where C_i is the initial value and must be taken negligibly small.

The analytical solution for equations (8a), (8b), (8c) and (8d) was derived for a zero initial concentration. The numerical approximation for that case is involved, as due to the infinite derivative of equation (2) with respect to c at $c = 0$, we must deal with a moving boundary problem. We have taken the initial concentration negligibly small (but not zero) for the numerical approximation and to avoid any numerical floating errors. This yields small deviations from the solution method proposed by *Dawson and Wheeler* [1990] for the same problem. These deviations are, for the chosen parameter values and the present context, insignificant.

Discretization of the soil columns is required for the numerical approximation and the implementation of chemical heterogeneity. Preliminary calculations for homogeneous columns illustrated that discretization should be done with extreme care.

(c) Assessment of spreading mechanisms

Concentration distributions, calculated with the random distribution for k using the numerical solution, give an indication of the effect of chemical heterogeneity. However, effects on the front shapes are difficult to distinguish by observing only the fronts. By computing the moments of the fronts in a chemically heterogeneous column and comparing these with the analytical moments of a homogeneous case, with the same spatially averaged k value for the heterogeneous and homogeneous column with length (L), the effect of heterogeneity can be demonstrated more clearly. The adsorption coefficient k determines the front shape and the front velocity (through retardation factor R). Hence, randomness of k causes a variation in both front shape and front velocity.

Incorporation of heterogeneity of the adsorption coefficients causes several mechanisms to play a role in solute spreading. These spreading mechanisms can be characterized as follows: (1) thickness of the individual traveling wave front; (2) porous media heterogeneity of the adsorption coefficient; and (3) different average retardation factors for an ensemble consisting of all porous media.

The thickness of the individual traveling wave front can be assessed by considering a homogeneous porous media. The front width due to dispersion and, in this case, nonlinear adsorption, may play a role in all transport cases considered in this study. If, however, an individual heterogeneous porous media is taken into account, both thickness of the individual front and porous media heterogeneity play a role in solute spreading. The front velocity and front variance give an impression of the impact of the heterogeneity of the adsorption coefficient. Averaging over all realizations of the velocity and variance, both as a function of depth, yields the expected behavior of a heterogeneous porous media.

Additionally, an average front can be considered, representing an ensemble average front, assuming that the flow domain consists of an ensemble of heterogeneous porous media. In addition to the first two spreading mechanisms, extra spreading of the ensemble average front is caused by the variable average retardation factors for different porous media. The latter spreading mechanism is caused by the numerical generation of the random porous media. The fluctuation imposed on the mean value of the adsorption coefficient causes slightly different average adsorption coefficients for each porous media.

Numerical Model Verification

In an integration approach of laboratory experiments and numerical simulations both physical and physico-chemical aquifer heterogeneities were investigated. For verification of numerical simulations an analytical calculations of solute transport through chemically heterogeneous porous media for transport of cadmium in a one-dimensional column test has been tested. This column test has been previously solved by *Bosma and van der Zee* [1993]. *De Haan et al.* [1987] have shown that contaminants like copper and cadmium show Freundlich adsorption behavior, and parameter values were available for Cd from *van der Zee* [1990b]. We have simulated transport of Cd with an initial concentration of 0 mol m^{-3} and a feed concentration of 0.02 mol m^{-3} . Table (1) show the flow and transport parameters for this column test. The effect of spatially variable hydraulic conductivity and porosity values on the expected plume velocity are shown in figure (1) and (2) respectively for the travelling wave and negative derivative of concentrations.

Table 1. Column test parameters values.

<i>Parameter</i>	<i>Unit</i>	<i>Value</i>
Volumetric water fraction (θ)		0.445
Soil dry bulk density (ρ)	Kg m^{-3}	1335
Column length (l)	m	4
Flow velocity (v)	myr^{-1}	1.9
Longitudinal dispersion coefficient (D_l)	myr^{-1}	0.057
Transverse dispersion coefficient (D_T)	myr^{-1}	0.035
Initial concentration (C_i)	mol m^{-3}	0.000001
Feeding concentration (C_0)	mol m^{-3}	0.02
Average adsorption coefficient (m_k)	$\text{mol}^{1-n} \text{ m}^{3(n-1)}$	4.40
Freundlich sorption parameter (n)		0.65
Node distance for numerical calculation (Δx)	m	2.2×10^{-2}

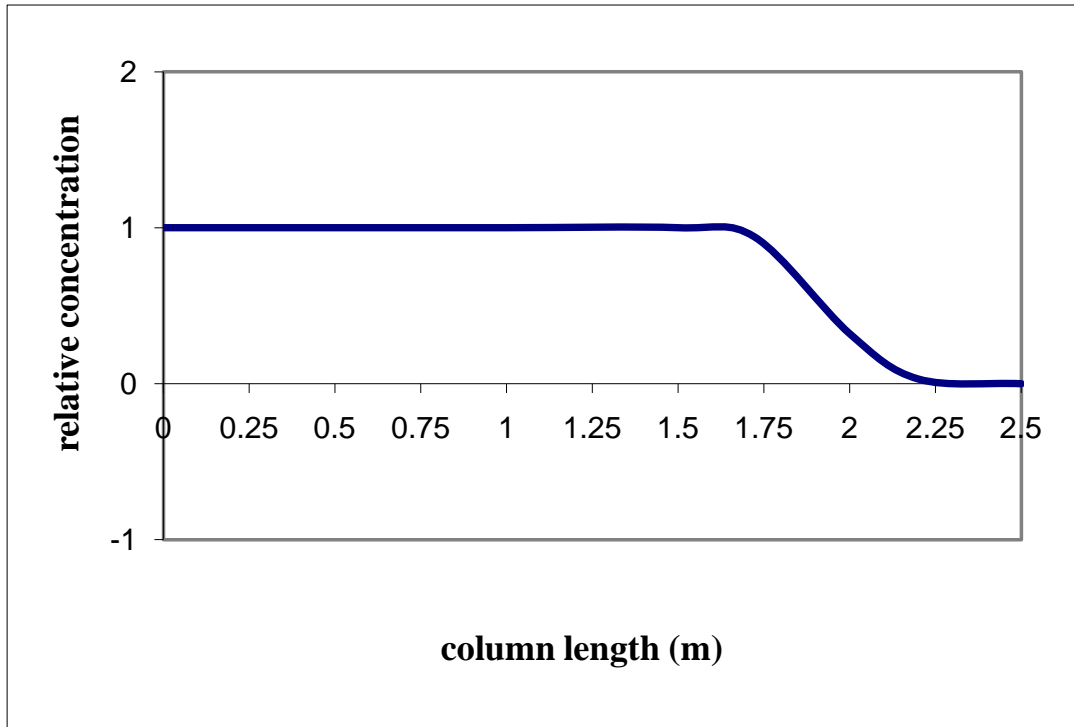


Figure 1. The traveling wave front at time (t= 42 year).

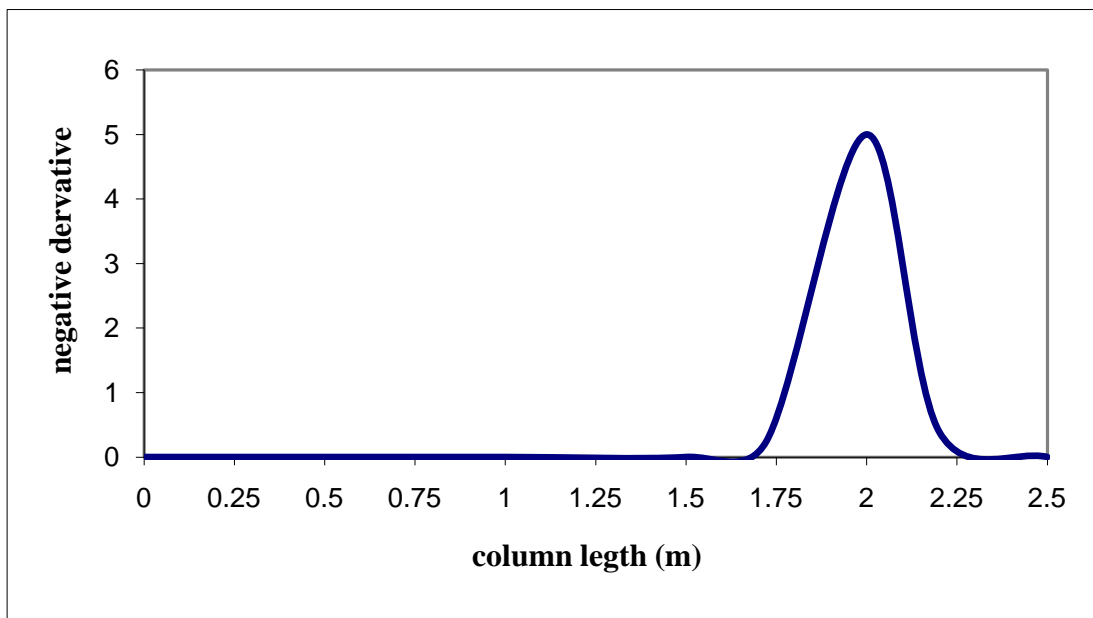


Figure 2. The negative derivative of concentration at time (t = 42 year).

Conclusions and Recommendations

The prediction of one dimensional transport of multichemical compounds in groundwater was simulated for a hydraulically and hydrochemically

heterogeneous aquifer system. The effect of spatially varying sorption parameters on the expected second order spatial moment of the solute plume was observed using one dimensional column tests and compared with the numerical results. The study based on detailed sedimentological, hydraulic and hydrochemical analysis of the parameters and the laboratory test lead to one dimensional data set of unsurpassed resolution and quality which is believed to very close to the reality. Although the effect of heterogeneity in chemical parameters of the aquifer system could be considered in these investigations, there was still a large discrepancy between simulations and the real plume transport monitored in the column test. Most significant for the tracer tests was a constant mass loss of the tracer, which in its order of magnitude can neither be attributed to physical nor sorption heterogeneity. From the laboratory observations we rather think that chemical reactions processes such as nonequilibrium sorption or some degree of non-reversibility are the dominating solute transport processes.

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