

## ANALYSIS OF MODELS FOR THE TRANSPORT OF SOLUTES IN SOIL COLUMNS

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**Abstract.** *Three mathematical models for the transport of KBr in a soil column are examined in this paper. The models are for: (a) Linear equilibrium adsorption in a finite column, (b) Linear equilibrium adsorption in a semi-infinite column and (c) Linear non-equilibrium adsorption in a semi-infinite column. The inverse problem of parameter estimation for each of the three models is solved with the Levenberg-Marquardt method of minimization of the least squares norm. The inverse analysis was applied to experimental data obtained for a saturated breakthrough column. A comparison of the residuals obtained with the parameter estimation technique showed that model c performed best.*

**Keywords:** *solute transport properties, inverse problems, mathematical models*

### 1. INTRODUCTION

Numerical simulations of the transport of pollutants, such as mining residues, fertilizers, pesticides, heavy metals and radioactive waste, in soils or in engineered barriers play an important role in safety analyses. Accurate simulations of these processes require reliable values for the different parameters in the governing solute transport equations. Several studies in the literature deal with the identification of solute transport properties obtained with different experimental techniques, including van Genuchten (1981), Gillham et al. (1984), Shackelford and Daniel (1991.a,b), Barone et al. (1989), Simunek et al. (1995), Pereira et al. (1999, 2001), Shackelford and Redmond (1995), Moreira et al (2003), and Nascimento et al (2004), among others.

An important aspect of the numerical simulation of pollutant transport in soils is the selection of an appropriate mathematical model for the problem. The model must be able to account for the different geochemical processes affecting transport, such non-linearities, non-equilibrium conditions, chemical reactions, and radioactive decay (van Genuchten, 1981). An effective way to select an appropriate mathematical model for physical problems is the use of *inverse analysis techniques*. Inverse analyses do not only allow a comparison a posteriori between the numerical simulations and the experimental data in qualitative terms, but also facilitate a closer synergism between the experimental and theoretical work during the study in order to obtain the maximum of information of the physical problem being considered (Beck, 1999). Using this approach, parameters and/or functions in the mathematical formulation are estimated from the experimental data being measured. An analysis of the residuals (defined as the difference between measured and estimated variables), or of the parameters estimated sequentially, further permits verification of the adequacy of the mathematical model assumed to hold for the physical problem. In fact, with minimization of the maximum likelihood objective function, residuals are expected to be small and non-correlated (i.e., without a characteristic *signature*) if the mathematical model is appropriate. Similarly, with the use of a sequential parameter estimation technique, estimated quantities are expected to asymptotically converge with the use of an appropriate mathematical model (Beck and Arnold, 1977, Beck, 1999).

In this paper we examine three different mathematical models as applied to the transport of Potassium Bromide (KBr) in a breakthrough column packed with a saturated soil. The models hold for advective-dispersive transport of solutes subject: (a) Linear equilibrium adsorption in a finite column (Nascimento et al, 2004); (b) Linear equilibrium adsorption in a semi-infinite column (van Genuchten, 1981); and (c) Linear non-equilibrium adsorption in a semi-infinite column (van Genuchten, 1981). The experiments were run on a saturated breakthrough column. The inverse problem of parameter estimation was solved with the Levenberg-Marquardt Method of minimization of the least-squares norm (Beck and Arnold, 1977; Ozisik and Orlande, 2000).

### 2. EXPERIMENTAL APPARATUS

The experimental apparatus consisted of a plexiglass column having an internal diameter of 0.095 mm and a length of 380 mm. The column base was closed with a plexiglass plate. An electrical conductivity cell was placed in a flexible nylon tube at the column outlet in order to measure the solution concentration. The cell was connected to a data-acquisition system to record the measurements in a computer for posterior use in the inverse analysis. A valve in the outlet tubing was used to control flow through the column. The flow rate itself was kept constant by maintaining a

constant level of the solution above the soil surface. The tracer solution was injected continuously into the constant-level reservoir from a separate tracer reservoir. A schematic of the experimental apparatus is shown in figure 1.

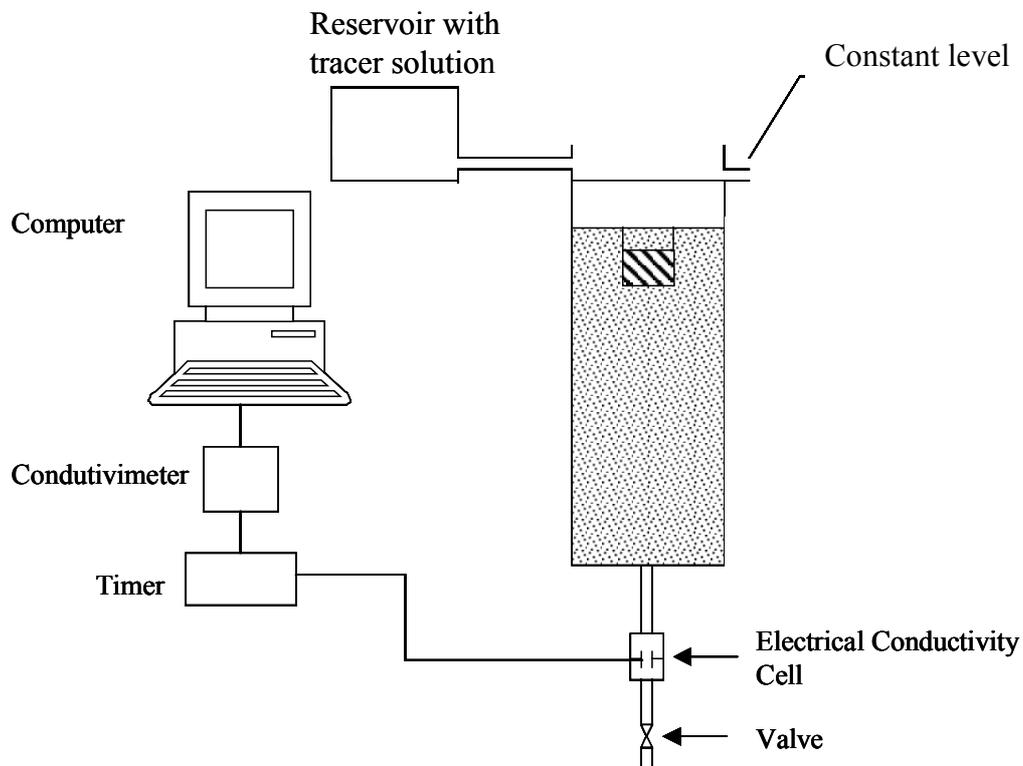


Figure 1. Schematic of experimental setup

For the experiments, the column was carefully packed under saturated conditions with a sandy loam up to a level of 5.4 cm, as illustrated in figure 2. The soil bulk density and porosity were  $1.452 \text{ g/cm}^3$  and 0.457, respectively. The soil granulometry is presented in figure 3. The column above the soil was filled with a tracer solution up to the level of 30 cm. Opening the valve established a constant flow rate at a pore water velocity of  $0.587 \text{ cm}$ . The solution was obtained by diluting a 500 ml solution of KBr at 2.5 g/l in 20 liters of distilled water.



Figure 2. Column with soil

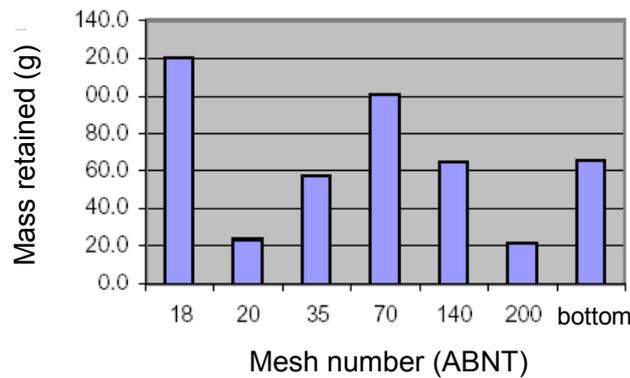


Figure 3. Soil granulometry

### 3. MATHEMATICAL MODELS

This section briefly describes the three mathematical models examined in this study:

- Model a: Linear equilibrium adsorption model for a finite column
- Model b: Linear equilibrium adsorption model for a semi-infinite column
- Model c: Linear non-equilibrium adsorption model for a semi-infinite column

#### 3.a. Linear equilibrium adsorption model for a finite column

This model accounts for a finite length  $L$  of the column. Transport is assumed to be one-dimensional along the longitudinal direction of the column, while the relation between adsorbed and solution concentrations is described by a linear isotherm (van Genuchten, 1981). The advection-dispersion equation describing solute transport through the column is then given by:

$$R \frac{\partial C(z,t)}{\partial t} = D \frac{\partial^2 C(z,t)}{\partial z^2} - V \frac{\partial C(z,t)}{\partial z} \quad \text{in } 0 \leq z \leq L \text{ and } t > 0 \quad (1.a)$$

with initial condition:

$$C(z,0) = C_0 \quad \text{in } 0 \leq z \leq L \text{ for } t = 0 \quad (1.b)$$

and the boundary conditions:

$$C(0,t) = C_{in} \quad \text{at } z = 0 \text{ and } t > 0 \quad (1.c)$$

$$D \frac{\partial C(L,t)}{\partial z} + h_m C(L,t) = h_m C_0 \quad \text{at } z = L \text{ and } t > 0 \quad (1.d)$$

where  $C_0$  is the background concentration in the column,  $C_{in}$  is the concentration of the injected solution,  $D$  is the dispersion coefficient,  $R$  is the retardation factor and  $V$  is the pore water velocity. Note in Eq. (1.c) that the boundary condition at  $z = 0$  is taken to be of the first type by assuming that the advective effects are locally dominant. Also, note in Eq. (1.d) that the boundary condition at  $z = L$  is taken to be of the third type, where  $h_m$  is a mass transfer coefficient between the column and the outflow plenum. Such may be the case because a stainless steel screen was used to hold the porous medium inside the column. Any retention of solute on this screen would be mathematically accounted for through some non-zero value of the mass transfer coefficient  $h_m$ .

The dispersion coefficient  $D$  can be written as:

$$D = \alpha V^n + \tau D_{dm} \quad (2)$$

where  $\alpha$  is the dispersivity,  $\tau$  is the tortuosity,  $D_{dm}$  is the molecular diffusion coefficient and  $n$  is an empirical constant usually taken between 1 and 2.

By assuming a linear isotherm between the adsorbed and solution concentrations, the retardation factor can be written as

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (3)$$

where  $\rho_b$  is the soil bulk density on a dry basis,  $K_d$  is the distribution coefficient and  $\theta$  is the porosity.

For the solution of the problem given by Eqs. (1) we used finite-differences with the McCormack predictor-corrector scheme (Anderson, 1984) given by:

$$\textbf{Predictor:} \quad C_j^{n+1} = C_j^n - \nu(C_{j+1}^n - C_j^n) + r(C_{j+1}^n - 2C_j^n + C_{j-1}^n) \quad (4.a)$$

$$\textbf{Corrector:} \quad C_j^{n+1} = \frac{1}{2} \left[ C_j^n + C_j^{n+1} - \nu(C_j^{n+1} - C_{j-1}^{n+1}) + r(C_{j+1}^{n+1} - 2C_j^{n+1} + C_{j-1}^{n+1}) \right] \quad (4.b)$$

The Levenberg-Marquardt method was used for solution of the inverse problem of parameter estimation (Beck and Arnold, 1977; Ozisik and Orlande, 2000). Consider for this purpose the vector of parameters in the physical model formulation as:

$$\mathbf{P}^T \equiv [P_1, P_2, \dots, P_N] \quad (5)$$

where  $N$  is the number of parameters. The iterative procedure of the Levenberg-Marquardt Method for minimization of the maximum likelihood objective function:

$$S(\mathbf{P}) = [\mathbf{Y} - \mathbf{C}(\mathbf{P})]^T \mathbf{W} [\mathbf{Y} - \mathbf{C}(\mathbf{P})] \quad (6)$$

is given by:

$$\mathbf{P}^{k+1} = \mathbf{P}^k + (\mathbf{J}^T \mathbf{W} \mathbf{J} + \lambda^k \mathbf{\Omega}^k)^{-1} \mathbf{J}^T \mathbf{W} [\mathbf{Y} - \mathbf{C}(\mathbf{P}^k)] \quad (7)$$

where  $k$  denotes the number of iterations,  $\mathbf{J}$  is the sensitivity matrix,  $\mathbf{\Omega}$  is a diagonal matrix and  $\lambda$  is a scalar named the damping parameter (Beck and Arnold, 1977; Ozisik and Orlande, 2000). In objective function (6),  $\mathbf{Y}$  is the vector of measured concentrations and  $\mathbf{C}(\mathbf{P})$  is the vector of estimated concentrations. We note that the following statistical hypothesis are presumed valid (Beck and Arnold, 1977): errors in the measured variables are additive, uncorrelated, and normally distributed with a zero mean and known constant standard-deviation; only the measured variables in the objective function contain errors; and there is no prior information regarding the values and uncertainties of the unknown parameters.

With the model given by Eqs. (1.a-d), the estimated concentrations  $\mathbf{C}(\mathbf{P})$  are obtained from the solution of the forward problem at  $z = L$ .

### 3.b. Linear equilibrium adsorption model for a semi-infinite column

For this case we used the same mathematical formulation as above, except that the column is treated as a semi-infinite medium. Hence, the mathematical formulation is now given by:

$$R \frac{\partial C(z,t)}{\partial t} = D \frac{\partial^2 C(z,t)}{\partial z^2} - V \frac{\partial C(z,t)}{\partial z} \quad \text{in } z \geq 0 \text{ and } t > 0 \quad (8.a)$$

$$C(z,0) = C_0 \quad \text{in } z > 0 \text{ for } t = 0 \quad (8.b)$$

$$C(0,t) = C_m \quad \text{at } z = 0 \text{ and } t > 0 \quad (8.c)$$

The analytical solution of Eqs. (8.a-c) at  $z=L$  was used for the estimated concentrations in the inverse problem. We used the CFITIM code within the windows-based STANMOD software package (Simunek et al, 1995) for the forward and inverse problems, using the Levenberg-Marquardt method as described above for estimation of the parameters.

### 3.c. Linear non-equilibrium adsorption model for a semi-infinite column

The models given by Eqs (1.a-d) and (8.a-c) assume that all of the porous medium (soil and water) in the column participates equally in the transport process of the tracer and that adsorption is homogeneous in the entire medium. As a result, curves of the outflow concentration should be symmetric or sigmoid. On the other hand, experimental results for the outflow concentration from columns in many situations do not exhibit such characteristics.

Several approaches have been used to account for the observed asymmetry and tailing in experiments (van Genuchten, 1981). One such approach involves the concept of solute transfer between mobile and immobile soil-water phases. Advective-dispersive solute transport in that case is assumed to be confined only to the mobile water phase, while solute transfer between the mobile and immobile soil-water regions is assumed to be controlled by diffusion. By assuming linear adsorption for both the mobile and immobile regions, the governing equations for this model can be written as (van Genuchten, 1981):

$$[\theta_m + \rho_b f K_d] \frac{\partial C_m}{\partial t} + [\theta_{im} + \rho_b (1-f) K_d] \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial z^2} - \theta_m V_m \frac{\partial C_m}{\partial z} \quad (9.a)$$

$$[\theta_{im} + \rho_b (1-f) K_d] \frac{\partial C_{im}}{\partial t} = \alpha [C_m - C_{im}] \quad (9.b)$$

where the subscripts *m* and *im* refer to the mobile and immobile regions, respectively,  $\alpha$  is the mass transfer coefficient between the two liquid phases, while the factor *f* defines the solid mass fraction of the mobile region. A retardation factor can also be defined for the non-equilibrium model in the same form as given by equation (3) where:

$$\theta = \theta_m + \theta_{im} \quad (10)$$

Other non-equilibrium models can also be found in the literature, including one- and two-site non-equilibrium formulations that assume non-uniform sorption. Such models lead to formulations that are mathematically analogous to Eqs. (9.a,b) (van Genuchten, 1981).

Equations (9.a,b) were solved for a semi-infinite column, with initial and boundary condition given by equations (8.b,c), respectively. As for the equilibrium model, the forward solution at  $z=L$  was used for the estimated concentrations for solution of the inverse problem. We again used STANMOD (Simunek et al, 1995) for solving the forward and inverse problems.

#### 4. RESULTS AND DISCUSSIONS

Figures 4.a-c show normalized concentrations obtained from the experiments, as well as those calculated with models *a-c*. A comparison of these figures reveals that agreement between measured and estimated concentrations is generally better with models *a* and *c* than with model *b*. Note that in model *b* only *R* and *D* are estimated, while in model *a* the parameters *R*, *D* and  $h_m$  are estimated and in model *c* the parameters *R*, *D*, *f* and  $\alpha$ . Hence, the models that accounted for the effects of retention in the outflow boundary (model *a*) or of non-equilibrium adsorption (model *c*) produced better agreement between measured and estimated concentrations. Note in figure 1.a that model *a*, which deals with a finite column, leads to concentrations at steady state (large times) that are smaller than those measured. This is due to the third-type condition used for the outflow boundary (see equation 1.d). By comparison, estimated and measured concentrations are in excellent agreement during the whole time domain for model *c*.

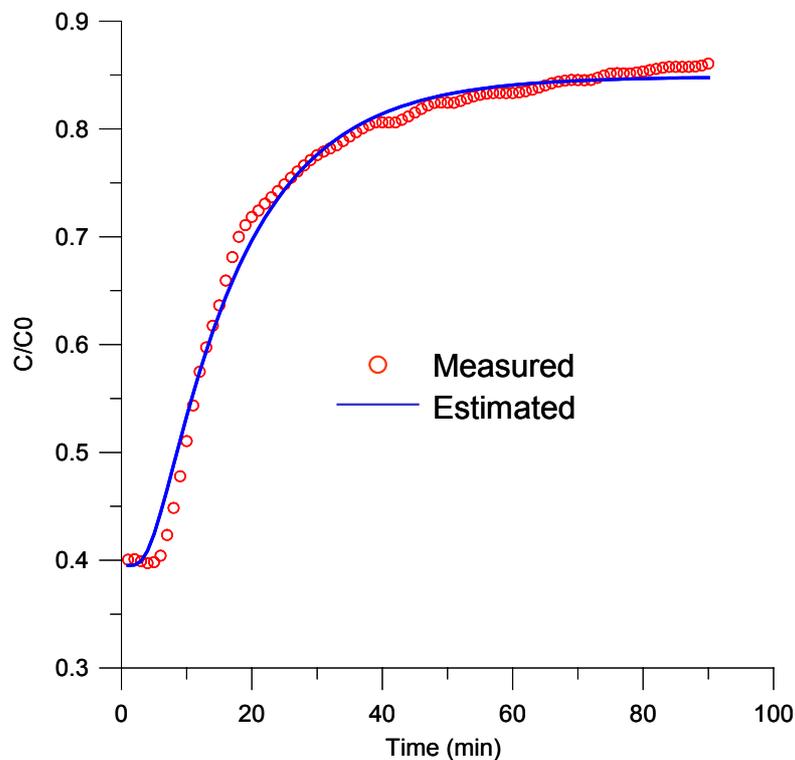


Figure 4.a. Measured and estimated concentrations – model *a*

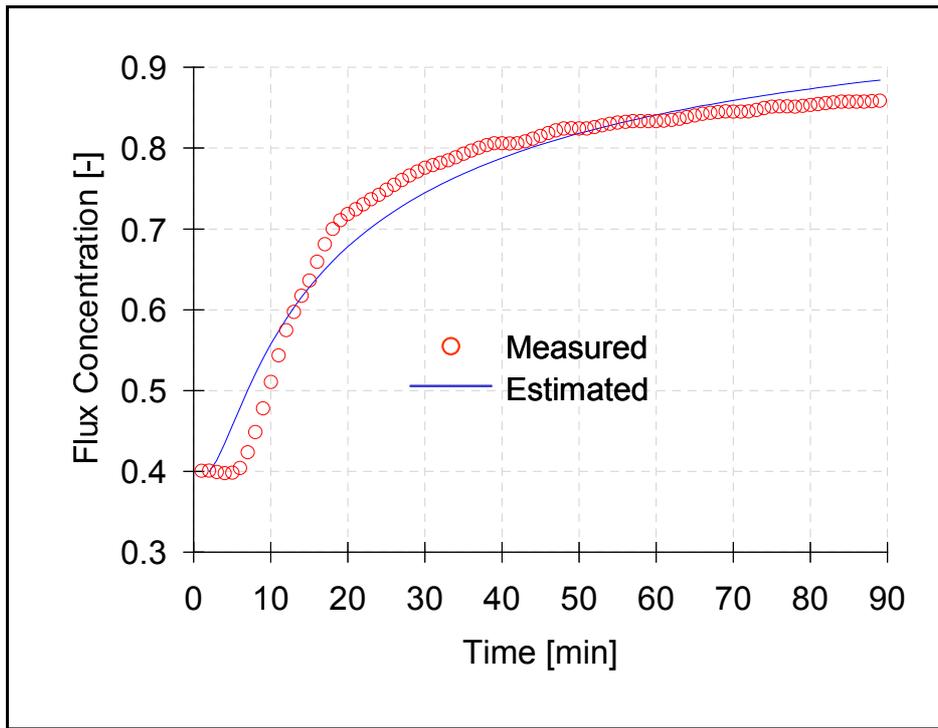


Figure 4.b. Measured and estimated concentrations – model *b*

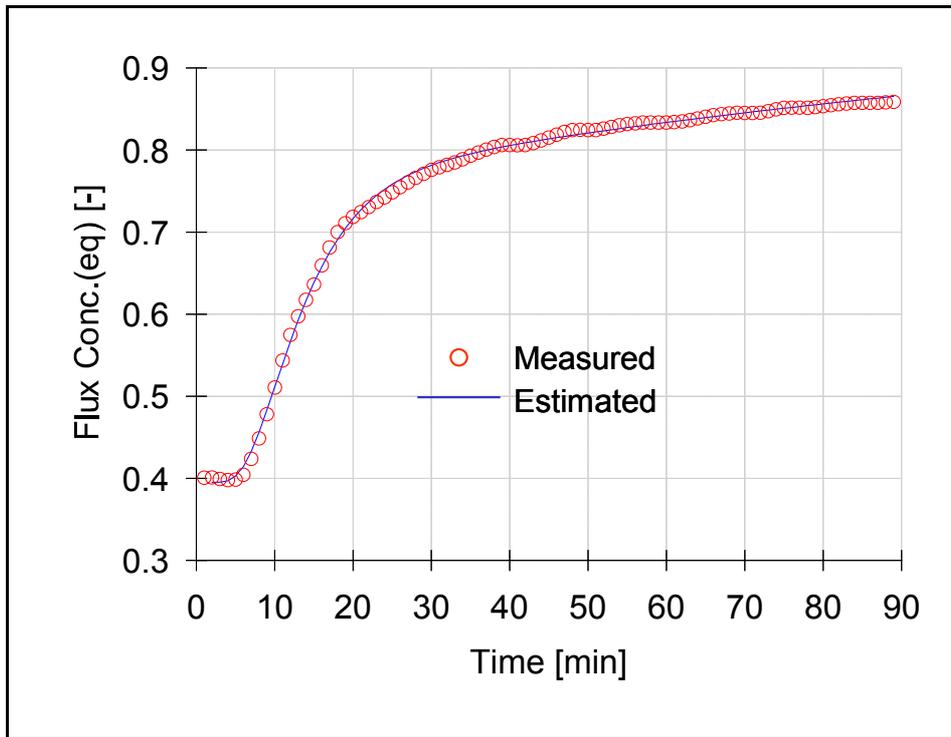


Figure 4.c. Measured and estimated concentrations – model *c*

Similar conclusions can also be obtained from an analysis of the residuals obtained with the three models. Results are presented in figure 5. Notice that the residuals obtained with model *c* are much smaller and less correlated than those obtained with models *a* and *b*. Figure 6 presents values of the objective function given by equation (6) (with  $\mathbf{W}=\mathbf{I}$ , that is, the objective function is of the least-squares norm) for models *a-c*. The smallest value of the objective function was obtained with model *c*, which again shows that this model provides the best agreement between measured and estimated concentrations. The values of the objective function could not be reduced further for models *a* and *b* since these models are apparently not capable of appropriately representing the physical phenomena of the experiments. We

hence conclude that the non-equilibrium model is the most appropriate to represent the physical phenomena that govern the transport of KBr for the soil and transport conditions adopted in this study.

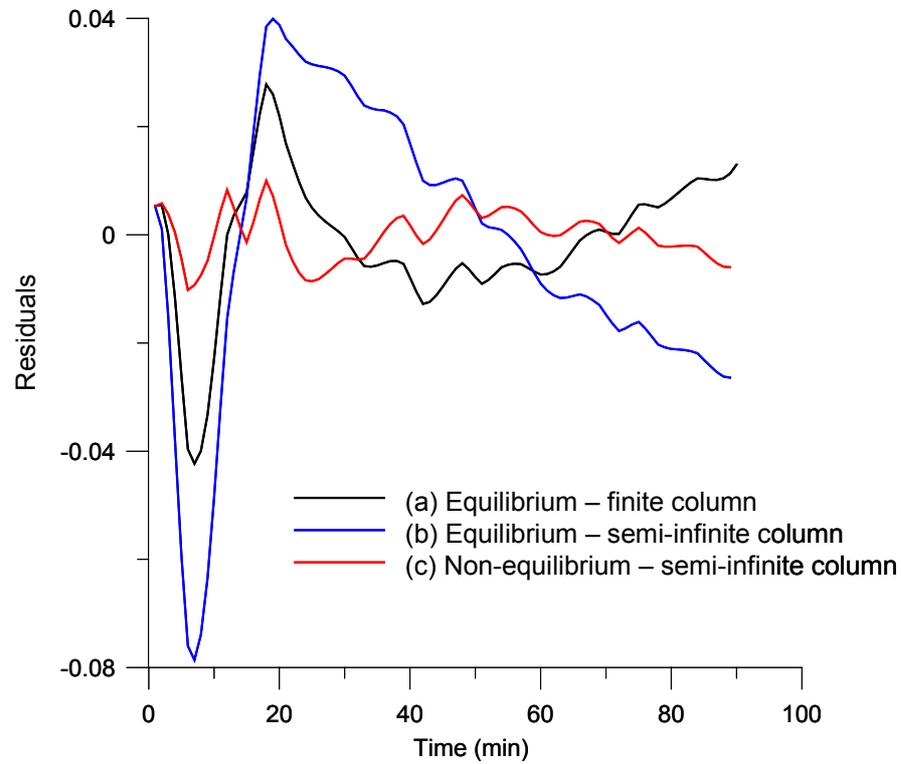


Figure 5. Residuals obtained with models *a*, *b* and *c*

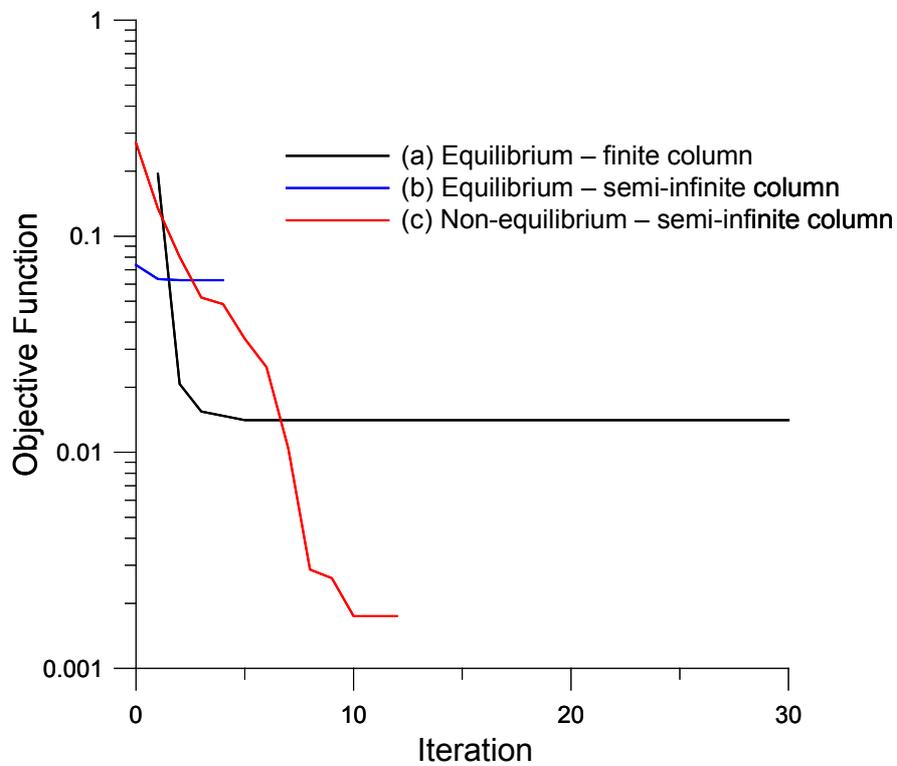


Figure 6. Objective function

Table 1 presents values estimated for the retardation factor and the dispersion coefficient using the three models examined in this study. It is interesting to notice in this table that the value of the retardation factor is not sensitive to the type of model used. On the other hand, the value of the dispersion coefficient is strongly affected by the invoked mathematical model. Numerical experiments revealed that the values presented in table 2 were not affected by the initial estimates used for the iterative procedure of the Levenberg-Marquardt method.

Using the value of the retardation factor as estimated with model *c*, the distribution coefficient calculated for KBr in the soil was 6.5 cm<sup>3</sup>/g. Literature values for K and for Br fall within 15 cm<sup>3</sup>/g and 75 cm<sup>3</sup>/g for sandy and clay soils, respectively (Sheppard and Thibault, 1990). Therefore, the results obtained in this paper are less than those available in the literature. Possible causes for the observed discrepancy are uncertainty in soil porosity, a non-homogeneous distribution of the soil in the column and perhaps pH effects on the transport properties.

Table 1. Values estimated for the retardation factor and the dispersion coefficient.

	Model a	Model b	Model c
<i>R</i>	7.43	7.87	7.22
<i>D</i> (cm <sup>2</sup> /min)	3.89	7.707	0.43

## 5. CONCLUSIONS

In this study we examined the use of three different mathematical models as applied to the transport of KBr in columns with a saturated soil. The models examined assumed: (a) Linear equilibrium adsorption in a finite column; (b) Linear equilibrium adsorption in a semi-infinite column; and (c) Linear non-equilibrium adsorption in a semi-infinite column. The Levenberg-Marquardt method of minimization of the least-squares norm was used for estimation of the parameters in the three models. Actual experimental data were used for solution of the parameter estimation problem and for comparison of the models.

An analysis of the residuals revealed that only the non-equilibrium adsorption model for a semi-infinite column (model *c*) was capable of appropriately describing the physical phenomena governing the transport of KBr in saturated soil column being studied. This model also produced the smallest value of the objective function. The values estimated for the retardation factor were found to be relatively insensitive to the type of mathematical model used in the analysis.

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