J. Mater. Environ. Sci. 7 (6) (2016) 2082-2093
ISSN : 2028-2508
CODEN: JMESC

Investigation of Conservative and Non-Conservative Solute Transport in Soil and Comparison of Three Adsorption Models Using HYDRUS-2D

F. Taran*, A. H. Nazemi, A. A. Sadraddini, Y. Dinpazhuh
Department of Water Engineering, University of Tabriz, Tabriz, Iran

Received 10 Feb 2016, Revised 24 Mar 2016, Accepted 09 Apr 2016

**Corresponding author. E-mail: farshidtaran@gmail.com (F.Taran); Phone: +98 912 067 6455*

Abstract

In this study, transport of two conservative (sodium chloride) and non-conservative (mono-potassium phosphate) solutes in soil was investigated under laboratory conditions. The experiments were implemented with separately injection of these solutes in a sloping soil bulk. The results showed that the concentration distribution of the both solutes in various parts of the sampling box slope was different and solute outflows from the beginning of the slope earlier than the end of it. Because of the adsorption of the non-conservative solute by the soil particles, not only its transport velocity was slower than the conservative solute, but also its peak concentration was less than that of the conservative solute. The HYDRUS-2D model was used to simulate the solutes transport. The concentration of the conservative solute was satisfactorily simulated with high values of the coefficient of determination (R^2=0.907), Nash–Sutcliffe efficiency coefficient (EF=0.907) and a low value of root mean square error (RMSE=0.351 g/L). In the simulation of the non-conservative solute transport, a linear adsorption isotherm and the two non-linear Freundlich and Langmuir models were individually used. The results of the Freundlich model (R^2=0.951, EF=0.920 and RMSE=0.064 g/L) were better than those of the Langmuir (R^2=0.811, EF=0.802 and RMSE=0.101 g/L) and the linear (R^2=0.762, EF=0.761 and RMSE=0.111 g/L) models. The results indicated that the conservative and non-conservative solutes had different transport behavior in the soil. The Freundlich model was found to be the most appropriate adsorption isotherm for investigation of a non-conservative solute transport in soil.

Keywords: Freundlic model, HYDRUS-2D, Langmuir model, Linear adsorption isotherm, Non-linear adsorption isotherms, solute transport.

1. Introduction

Soil and groundwater contamination is an important environmental issue to which the concern and research about the behavior of contaminants in these resources have been increased in recent years. In order to prevent the soil and groundwater resources deterioration and manage the contaminated soils, a clear understanding of the solute transport processes in soil is essential. Typically, the solutes moving in soil are non-conservative; i.e. do not move in the soil with the same velocity as water does and some of them, while moving, are adsorbed on the soil particles [1]. To estimate the adsorption of solutes by soil particles, various isothermal linear and non-linear models have been used. The Freundlich and the Langmuir are the most common models that have been applied in many studies such as the assessment of the phosphorus and heavy metals adsorption [2, 3] and the nature of adsorption for removing contaminants from water [4]. Aslam *et al*. [5] used the Freundlich isotherm for determining the need of some soils under rice cultivation to phosphorus. This model described well the phosphorus adsorption with correlation coefficient value more than 0.96. Pang and Hunt [6] assuming a linear adsorption isotherm, proposed an analytical solution for one-dimensional transport equation in which the breakthrough curves had a high compliance with observations related to the transport of tritium in a sandy soil column. Hussain *et al*. [2] used the Freundlich and Langmuir adsorption isotherm models to investigate the phosphorus adsorption in saline-sodic soils. In their study, the results indicated that the Freundlich model with a correlation coefficient of 0.97 was better than the Langmuir model with a correlation coefficient of 0.64. Charm and Abdollahi [7] fitted the adsorption data to the Freundlich and Langmuir models in the study of the adsorption properties of zinc in soils under sugarcane cultivation. They found that the results of the Freundlich model with R^2=0.979 were better than those of the Langmuir model with R2=0.893. Branger *et al*. [8] used the linear adsorption isotherm and satisfactorily simulated the water flow and pesticide transport in order to investigate the pesticides transport in a field with subsurface drainage, assuming an instantaneous equilibrium between solid and liquid concentrations. Khan *et al*. [9] observed that the fitting of the adsorption data to the Freundlich model (R^2=0.99) was better than that to the Langmuir model (R^2=0.97) in their investigation on phosphate adsorption in various saline soils. Shafqat and Pierzynski [3] examined the amount of phosphorus available to plants in two soil types and fitted the adsorption data to the Freundlich model. They concluded that for better understanding the ability of this model in predicting the phosphorus availability, more research would be needed on most soils with various physical and chemical properties.

Often, the use of field technologies is not common to study solute transport in soil, due to their temporal and spatial limitations and high cost. Hence, usually, laboratory experiments and modeling are used [10, 11, 12]. However, in many cases, analytical solutions cannot be used and, thus, numerical models are preferred due to their flexibility to the initial and boundary conditions [13, 14]. The HYDRUS-2D model [15] is one of the most powerful computer models, which numerically solves the equations of the water flow and solute transport in soil. Previous researches have confirmed the ability of this model for simulating the solute transport in the soil [10, 16, 17, 18].

In the previous studies, the laboratory experiments of solute transport have been conducted in small horizontal or vertical soil tanks or columns, the solute has been injected at a certain point on the soil surface, and sampling has been done only through one output point. In this study, the solute was injected through entire surface of the soil surface using a rainfall simulator. Also, the samplings were done through some subsurface drains. Therefore, condition of this study was closer to field conditions. Also, most of the studies related to the solute adsorption on soil particles are based on the batch experiments. Therefore, the adsorption has less been taken into account during the solute flow through the soil. In this study, the adsorption was investigated during the flow, which better estimates the field conditions comparing with the batch experiments [19]. In the simulation of the non-conservative solute (KH_2PO_4) transport, a linear adsorption isotherm and two non-linear Freundlich and Langmuir models were used.

The objectives of this study were: (1) investigation of the differences between the conservative and non-conservative solutes behavior in the soil, (2) comparison of the accuracy of the linear and non-linear adsorption isotherms to describe the behavior of the non-conservative solute during its movement, and (3) simulation of solutes transport processes using the HYDRUS-2D model.

2. Materials and Methods

2.1. Laboratory model, Solutes and Soil

The experiments were conducted in a physical model at Water Resources Lab of University of Tabriz, Tabriz, Iran. The model had a cube-shaped soil box, with dimensions of 200 cm length, 100 cm width and 45 cm height. Four cylindrical drainage pipes with 2 cm diameter and 80 cm length were installed in the bottom of the box. The slope of the box was adjustable. A rainfall simulator as installed on top of the box at a 60 cm height. This simulator consisted of 4 laterals, each of them equipped with 2 sprayers (ProMax QPHA-35, Spraying Systems Co., 0.02 L/sec, 10 psi) to produce a uniform rainfall on the soil surface. The model had two reservoirs to supply water and solution; each of them had its own pump and flow meter. Figure 1 shows a scheme of the soil box and the location of the drains.

The experiments were conducted by individual injection of the sodium chloride (NaCl) and mono-potassium phosphate (KH_2PO_4) as conservative and non-conservative solutes, respectively. In each experiment, 1000 g of both NaCl and KH_2PO_4 separately was completely dissolved in 200 L of tap water (both solutes with the concentration of 5 g/L). The concentration of salts in tap water (0.225 g/L) was lower than the solute concentration and so, it did not have a significant effect on the experimental results. Therefore, it was ignored in the measurements.

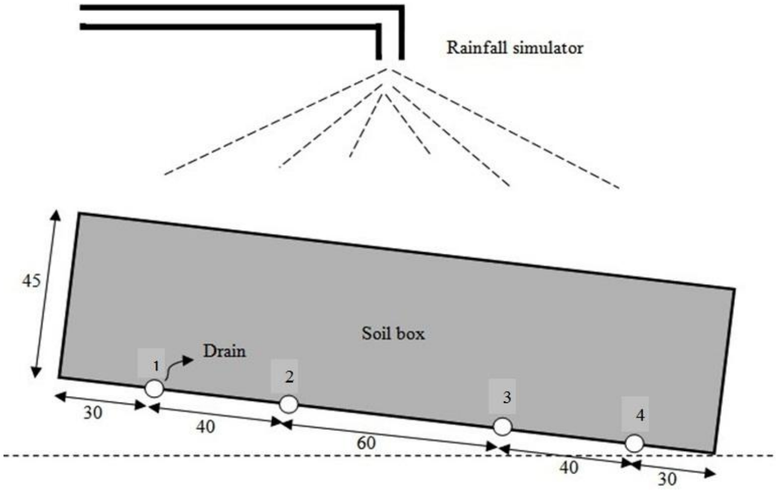

Figure 1: A scheme of the physical model (dimensions are in cm).

Before conducting each of the experiments and after the three days passed from leaching and drainage, a sample of the soil was taken to determine its volumetric water content, bulk density and porosity. The soil saturated hydraulic conductivity was measured using the constant-head method. Table 1 gives the soil physical properties.

Table 1: Soil physical properties

Volumetric water content (%)	Bulk density (g/cm^3)	Porosity (%)	Saturated hydraulic conductivity (cm/min)	Particle size distribution (mm) Clay (<0.002) (%)	Silt (0.002-0.05) (%)	Sand (0.05-2) (%)
16.94	1.34	47.86	0.68	3	4.2	92.8

2.2. Transport experiments

First the soil of the box was leached several times using tap water, so that the concentration of the soil solution approximated to that of tap water. During the experiments, concentrations of water samples taken from the drains were measured using an EC/TDS meter (AZ-86501, Taiwan). This device indicates the solute concentration (c) in grams per liter (g/L) at any temperature, and also converts automatically the concentrations by a correction factor to show them in 25 ^{0}C.

At the end of leaching, after application of the water by rainfall simulator, the saturated soil was allowed to be drained for three days. This promoted further compaction of the soil [20], so that the height of the soil bulk approximately reached to 40 cm.

The experiments were conducted in two distinct scenarios. In each scenario, after applying a slope of 2.5 percent to the soil box, 200 L of solution (NaCl and KH_2PO_4 for the first and second scenarios, respectively) was used to fill the related reservoir. Then the solution was applied by the rainfall simulator with the rate of 400 L/h (i.e., 0.33 cm/min). The application rate was chosen so as to be less than the soil saturated hydraulic conductivity and to prevent runoff. After About 15 min from the beginning of the solute application, outflow was observed in each of the four drains. Sampling from the drains began from this moment and was continued until the end of the experiment with time intervals of 5 min. After 30 min application of the solution, it was finished and the tap water immediately was started to be applied with the same rate and continued up to minute 180; it was the time the breakthrough concentrations reached close to the concentration of tap water.

2.3. Simulation

The Hydrus-2D model was used to simulate the experiments. This model numerically solves the Richards' equation for water flow and the advection-dispersion equation for solute transport using Galerkin-type linear finite element schemes.

Water flow

Combining the Darcy's law and the law of conservation of mass and ignoring the role of air in the water flow process, the governing flow equation in a two-dimensional, isothermal, rigid and variably saturated porous medium is given by the following modified form of the Richards' equation:

$$\frac{\partial \theta}{\partial t}=\frac{\partial}{\partial x_i}\left[K\left(K_{ij}^{A}\frac{\partial h}{\partial x_j}+K_{ij}^{A}\right)\right]-S \tag{1}$$

where θ is the volumetric soil water content [L^3L^{-3}], h is the pressure head [L], S is a sink term [T^{-1}], x_j (j=1,2) are the spatial coordinates [L], t is time [T], K_{ij}^{A} are components of a dimensionless anisotropy tensor K^A, and K is the unsaturated hydraulic conductivity function [LT^{-1}].

The soil hydraulic characteristics are given by the van Genuchten-Mualem model [21]:

$$\theta(h)=\theta_r+\frac{\theta_s-\theta_r}{[1+|\alpha h|^n]^m} \tag{2}$$

$$K(h)=K_sS_e^{0.5}(1-\left(1-S_e^{1/m}\right)^m)^2 \tag{3}$$

where α and n are empirical coefficients affecting the shape of the hydraulic functions, S_e is the effective saturation, m=1-1/n, and θ_r, θ_s and K_s are the residual and saturated water contents and the saturated hydraulic conductivity, respectively. In this study, the parameters of van Genuchten-Mualem model were estimated from the soil texture and bulk density using the Rosetta Lite software [22] implemented in the HYDRUS model. However, the predicted θ_s and K_s values by the Rosetta were replaced by the measured porosity and the hydraulic conductivity (the latter obtained from the constant head method), respectively.

Solute transport

The redistribution of solutes can be described by the following advection-dispersion equation:

$$\frac{\partial \theta c}{\partial t}=\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial c}{\partial x_j}\right)-\frac{\partial q_i c}{\partial x_i} \tag{4}$$

where c represents the solute concentration [ML^{-3}], q_i is the i-th component of the volumetric flux density [LT^{-1}], and D_{ij} is the dispersion coefficient tensor [L^2T^{-1}] defined as [23]:

$$\theta D_{ij}=a_T|q|\delta_{ij}+\left(a_L-a_T\right)\frac{q_iq_j}{|q|}+\theta D_w\tau_w\delta_{ij} \tag{5}$$

where D_w is the molecular diffusion coefficient in free water [L^2T^{-1}], τ_w is a tortuosity factor [-], |q| is the absolute value of the Darcian fluid flux density [LT^{-1}], δ_{ij} is the Kronecker delta function (δ_{ij}=1 if i=j, and δ_{ij} =0 if i≠j), and a_L and a_T are the longitudinal and transverse dispersivities [L], respectively. The dispersivity is a material constant independent of flow rate [24].

Many researchers have adopted the longitudinal dispersivity equal to one-tenth of the length of the flow domain [e.g., 25, 26] and the transverse dispersivity equal to one-tenth of the longitudinal dispersivity [e.g., 27, 28]. In our experiments, the soil bulk depth was the transport length and, therefore, as the initial estimation we considered the longitudinal dispersivity equal to 4 cm (i.e., one-tenth of the soil bulk depth) and the transverse dispersivity equal to 0.4 cm. However, Gelhar *et al.* [1] states that this ratio is of field scale, which due to the heterogeneity found in nature, is several times larger than laboratory scale. By obtaining the observation data, the HYDRUS-2D model, is able to estimate the optimal values of soil hydraulic and solute transport parameters, using Marquardt-Levenberg algorithm and inverse solution method. So, in this study, to enhance the accuracy of the simulation results, having the concentrations of observed outflows, the inverse solution with 10 iterations was used to optimize the dispersivity coefficients, θ_r, α and n (θ_s, K_s and ρ_b being obtained from the experiments, were not optimized). Table 2 presents the van Genuchten-Mualem parameters and the dispersivity coefficients before and after optimization and calibration.

Table 2: Values of van Genuchten-Mualem parameters and dispersivity coefficients

	θ_r	θ_s	α	n	K_s (cm/min)	a_L (cm)	a_T (cm)
Initial estimation	0.0497	0.4786	0.0379	2.8213	0.98	4	0.4
Optimized values	0.0497	-	0.037924	2.8268	-	4.414	1.064

The volumetric soil water content of 0.1694 m^3m^{-3} and the concentration of 0.225 g/L were applied as the initial condition. In the case of water flow, the soil surface was defined as an atmospheric boundary condition and the drains, due to no suction, were set as zero pressure head gradient or free drainage boundary conditions [24]. In the case of solute transport, the third-type or flux-type condition was chosen at the both input (soil surface) and output (drains) boundaries. A zero flux condition was applied at the boundaries between the drains as well as at the two vertical boundaries, assuming the symmetrical flow and therefore no gradient over the boundaries. Figure 2 shows the boundary conditions of the experimental domain.

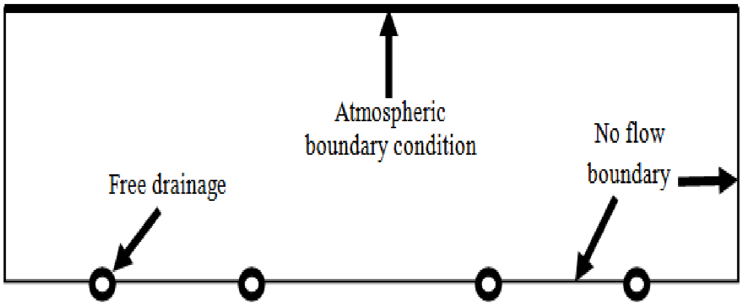

Figure 2: Boundary conditions of the experimental domain

2.4. Adsorption Isotherm

An adsorption isotherm is a function that relates the quantity of a species adsorbed by solid to its quantity in the liquid phase at a fixed temperature, under conditions of chemical equilibrium between the two quantities. The three most common adsorption isotherm models are as follows [29]:

a. linear adsorption: there is a direct, linear relationship between the amount of a solute adsorbed by soil surface (s) and the concentration of the solute (c):

$$s = K_d c \tag{6}$$

where c is concentration of the solute in the solution (ML^{-3}), s is concentration of the solute adsorbed by the particles (MM^{-1}) and K_d is known as the distribution coefficient (L^3M^{-1}).

b. Freundlich: is a more general adsorption isotherm and is defined by the non-linear relationship:

$$s = Kc^N \tag{7}$$

where K and N are constants. The values of N ranges from 2-10 indicating good adsorption capacity,1-2 moderate adsorption capacity and less than one indicates poor adsorption capacity [30].

c. Langmuir: was developed with the concept that a solid surface possesses a finite number of sorption sites. When all these sites are filled, the surface will no longer adsorb solute from solution. The form of this model is:

$$s = \frac{\alpha\beta c}{1+\alpha c} \tag{8}$$

where α is a constant related to the binding energy (L^3M^{-1}) and β is the maximum amount of solute that can be adsorbed by the solid (MM^{-1}).

Determination of adsorption isotherm coefficients

To evaluate the adsorption models in describing the non-conservative solute transport, 5 g of soil samples were put in centrifuge tubes. Then, 20 ml of KH2PO4 with different concentrations (1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 g/L) were added in triplicate. The suspensions were shaken for 30 min using an electric mixer and after being kept for 24 hours at 25 °C, were shaken again for 30 min. After that, the suspensions were centrifuged for 15 min at 3000 rpm. Then, the solutions were passed through a Whatman-42 filter paper and their concentrations (c) were measured. The difference between the initial and final concentrations of the solutions was taken as the amount of adsorption by the soil particles and was determined per mass unit of the soil particles (s). The results obtained for c and s were fitted to the linear, Freundlich and Langmuir equations and the relations of $s = 0.00064c$, $s = 0.0012c^{0.49}$ and $s = \frac{(0.664)(0.003)c}{1+0.664c}$ were obtained, respectively. Table 3 presents the coefficients of the three adsorption isotherms. For simulation, the coefficients of these relations were introduced to the HYDRUS-2D model. In Freundlich model, the values of N between 2 to 10 indicates good adsorption capacity, between 1 to 2 imply moderate adsorption capacity and less than one indicates poor adsorption capacity [30]. In this research, N was obtained equal to 0.49, indicating a law adsorption of KH_2PO_4.

Table 3: Coefficients of the linear, Freundlich and Langmuir models

Adsorption isotherm model	Coefficients	
Linear	K_d=0.00064	-
Freundlich	K=0.0012	N=0.49
Langmuir	$\alpha = 0.664$	$\beta = 0.003$

2.5. *Assumptions*

The major assumptions used in development of water flow and solute transport in this study are:

- Water Flow is two-dimensional.
- Hydrodynamic dispersion and convective transport are two-dimensional.
- Adsorption of solute on soil particles occurs in isothermal condition.

2.6. Model performance criteria

The model performance was evaluated by three frequently used statistical indices:

(i) Coefficient of determination (R^2):

$$R^2 = \frac{[\sum_{i=1}^{n}\left(O_i - \bar{O}\right)(P_i - \bar{P})]^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2 \sum_{i=1}^{n}(P_i - \bar{P})^2} \tag{9}$$

where O_i and P_i are the observed and predicted values and $\bar{O}$ and $\bar{P}$ are their mean values, respectively, and n is the number of data pairs. Values of R^2 indicate if the precision of the model is high or low. If precision is high and there is a strong correlation between the predicted and observed data the value of R^2 will be close to one. It is relevant to discuss the precision in relation to model evaluation when accuracy is high.

(ii) Root mean square error (RMSE):

$$RMSE = \sqrt{\sum_{i=1}^{n} \frac{(O_i - P_i)^2}{n}} \tag{10}$$

The RMSE's closeness to 0 indicates the low average error in the model, however in same unit as variable.

(iii) Nash-Sutcliffe efficiency coefficient (EF):

$$EF = 1 - \frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \tag{11}$$

The efficiency coefficient (EF) can vary from $-\infty$ to 1, but the closer the model efficiency is to 1, the more accurate the model is. A zero value of EF indicates that the model predictions are no better predictors than the mean of the observed data, while a negative efficiency occurs when the observed mean is a better predictor than the model.

3. Results and discussion

3.1. Experiments results

The transport of NaCl (conservative)

The peak concentrations of the effluent from drains 1, 2, 3 and 4 were observed at the times of 95, 90, 90 and 80 min after the start of solution injection and their values were equal to 3.747, 3.823, 3.882 and 3.900 g/L, respectively. From the beginning to the end part of the sloping soil bulk, i.e. from drain 1 to drain 4, the peak concentration increased and the time for achieving to the peak decreased. In the experiment of Yu *et al*. [31] the maximum concentration was observed at the beginning part of the slope, because the solute was injected at one point at the beginning of the slope (the solute supply was at the beginning), and therefore, concentration was higher at that point. In addition, the simultaneous injection of solute-free water and NaCl solution diluted the solution before its arrival to other points; while in this study the solute was evenly injected through the entire soil surface.

The elapsing time of the outflow concentration to reach its minimum value (i.e., concentration of the solute-free water) decreased from the beginning to the end part of the sloping soil bulk. At the last sampling time (the time that the breakthrough concentrations approximately reached to the concentration of tap water), the outflow concentrations of the drains 1, 2, 3 and 4 were equal to 0.228, 0.232, 0.253 and 0.291 g/L, respectively. From the beginning to the end of the experiment (the minute 0 to the minute 240) totally 1069 liters of water exited from the drains which consisted of 242, 263.5, 270 and 293.5 liters, equivalent to 22.64%, 24.65%, 25.26% and 27.46% belonged to the drains 1, 2, 3 and 4, respectively. The average concentrations of outflow from the drains were equal to 0.862, 0.868, 0.874 and 0.902 g/L, respectively. The volume of outflow as well as its concentration increased from the drain 1 to drain 4. The total amount of NaCl was calculated 938.17 g with respect to the volume of the outflow and its concentration. This amount was equivalent to 93.82% of the total injected NaCl. This may be due to remaining some of the solute in the pores of soil or because of measurement errors. Of this amount, the shares of the drains 1, 2, 3 and 4 were equal to 208.59 g (22.23%), 228.79 g (24.39%), 236.01 g (25.16%) and 264.78 g (28.22%), respectively. Therefore, the amount of NaCl exited from the drains increased from the beginning to the end of the sloping soil bulk. However, it was so much compared to the amount of the recovered bromide from the drains in the experiment of Yu *et al*. [31], which was only about 29% of the total bromide. The reason of this difference is that in the experiment of Yu *et al*. [31], the surface runoff process dominated the solute transport and, thus, a large amount of the bromide was carried by the runoff, while the injection intensity was so adjusted that no runoff was created as much as possible in our experiment. Also, splashing a certain amount of bromide out of the soil box due to raindrops (especially in areas close to the edge of the box) in the experiment of Yu *et al*. [31] could be another reason for this difference; because in this study, the walls surrounding the soil box prevented splashing the solute out of it.

The transport of KH_2PO_4 (non-conservative)

The peak concentrations in the drains 1, 2, 3 and 4 were observed at the times of 105, 100, 100 and 95 min after the start of injection. Their values were 3.260, 3.340, 3.469 and 3.470 g/L, respectively. From the drain 1 to drain 4 the peak concentration of the outflow increased and the time for achieving to peak concentration decreased. The relevant lag time of the outflow concentrations to the minimum value decreased from the drain 1 to drain 4. At the last sampling time, the outflow concentrations were 0.277, 0.254, 0.251 and 0.226 g/L for the drains 1, 2, 3 and 4, respectively.

The volume of water exited from all the drains during the experiment was approximately equal to that of NaCl transport experiment. The total concentrations of outflow from the drains 1, 2, 3 and 4 were 0.822, 0.824, 0.855 and 0.857 g/L, respectively. Therefore, the outflow volume and its concentration increased from the beginning to the end of the slope. The total amount of KH_2PO_4 exited was equal to 896.7 g, being 89.67% of the total KH_2PO_4 injected. Of this amount, the shares of the drains 1, 2, 3 and 4 were equal to 198.88 g (22.18%), 217.24

g (24.23%), 230.72 g (25.73%) and 249.86 g (27.86%), respectively. The amount of KH_2PO_4, therefore, increased from the beginning to the end of the slope.

The difference between transport of NaCl and KH_2PO_4

In the transport of the both solutes, the time to reach the peak concentrations decreased from the beginning to the end of the slope, but these concentrations occurred later in the case of KH_2PO_4, so that this time was between minutes 80 and 95 for NaCl and between minutes 90 and 105 for KH_2PO_4. Furthermore, in the case of KH_2PO_4 the value of this concentration in all the drains was less than that of NaCl. In the work of Amin *et al.* [32], estrogen transport in soil, due to its adsorption on soil particles, was much slower than NaCl (as a conservative solute with negligible adsorption) transport.

The time to reach minimum concentration in the both solutes decreased from the beginning to the end of the slope. The outflow volume and the amount of the both solutes increased from the drain 1 to drain 4; although, due to the reactivity and adsorption properties of KH_2PO_4 compared to NaCl, the amount of KH_2PO_4 exited from the drains was less than the corresponding amount of NaCl. Figure 3 presents a better comparison of the both solutes' breakthrough behavior. In this figure, the vertical axis is the relative concentration (ratio of the effluent concentration to the influent concentration).

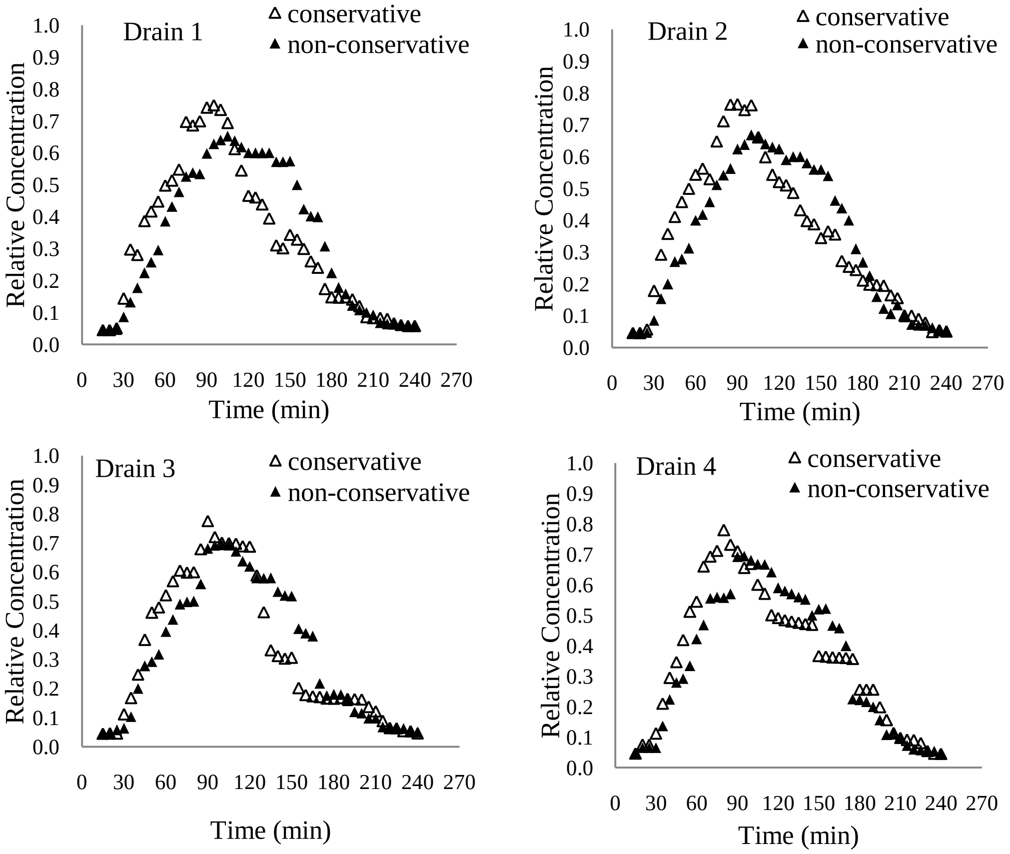

Figure 3: Comparison of NaCl (conservative solute) and KH_2PO_4 (non-conservative solute) breakthrough curves

3.2. Simulation results

Conservative solute (NaCl)

Figure 4 shows the observed and simulated breakthrough curves (BTCs) of NaCl for all the drains. The HYDRSU-2D model estimated the first breakthroughs 10 min later than the observed time (i.e., in the minute 20). However, the values of simulated concentrations showed no significant difference with the corresponding observed values. Although the times to reach peak concentrations were estimated earlier than the observed times, but they decreased from the beginning to the end of the sloping soil bulk, which was consistent with the observations. The values of these concentrations were estimated equal to 3.385, 3.470, 3.445 and 3.495 g/L for the drains 1, 2, 3 and 4, respectively. In the terms of increasing the peak concentration from the beginning to the end of the slope, the model results corresponded with the experimental results. The tails of BTCs were acceptably simulated.

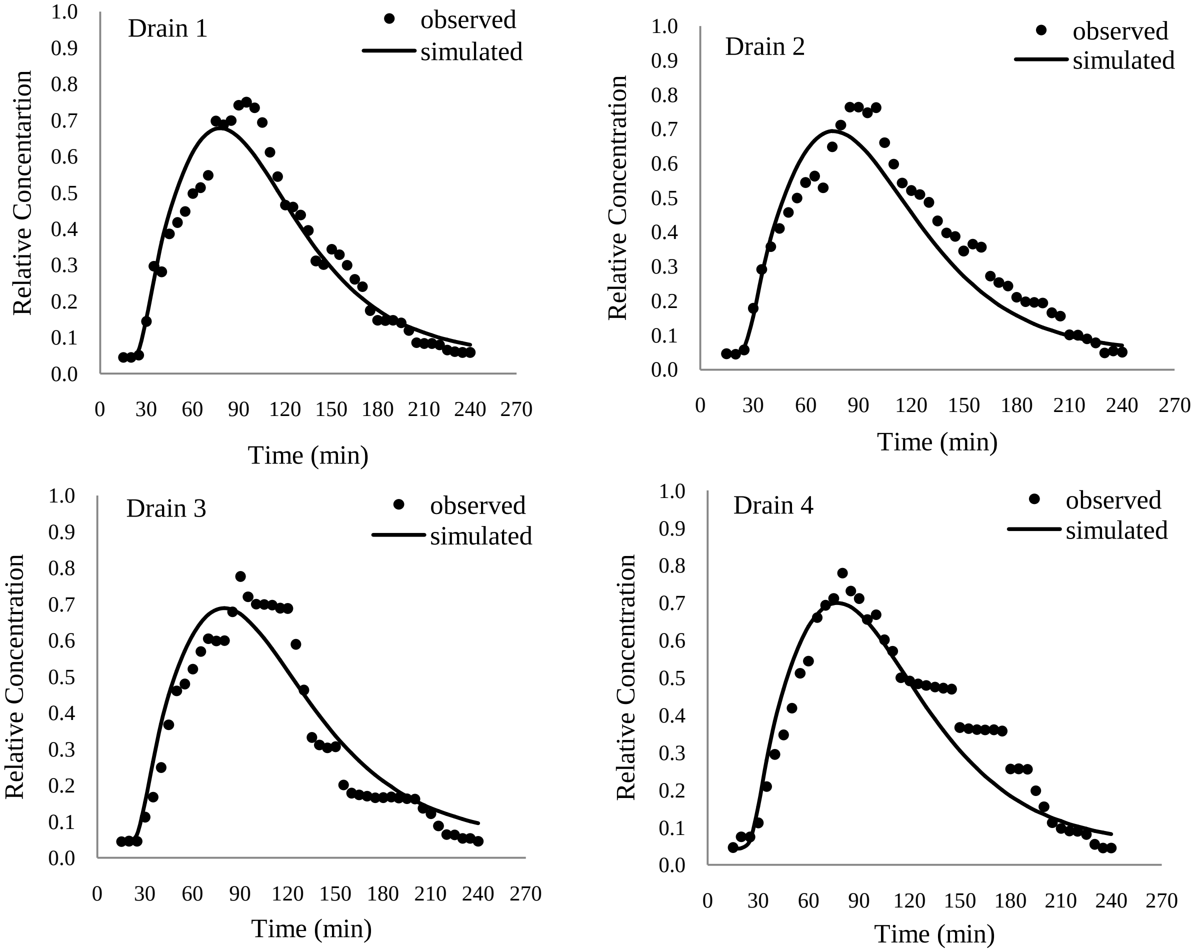

Figure 4: Observed and simulated BTCs of NaCl

Non-conservative solute (KH_2PO_4)

Figure 5 shows the observed and simulated (using linear, Freundlich and Langmuir models) BTCs of KH_2PO_4. All the three models estimated the first breakthroughs about 10 min later than the observed time.

The linear model estimated the peak concentration times 75 to 80 min after the start time of the injection, which were earlier than the observed times. The simulated peak concentration values for the drains 1, 2, 3 and 4 were equal to 3.340, 3.410, 3.400 and 3.400 g/L, respectively. The initial and end parts of the sloping soil bulk had the minimum and maximum peak concentration, respectively. The tails of BTCs were not accurately simulated.

The Freundlich model estimated the peak concentration times between the minutes 100 to 105 and thus had a great compliance with the observed times. The peak concentrations were simulated equal to 3.340, 3.410, 3.400 and 3.400 g/L for the drains 1, 2, 3 and 4, respectively. The results of the Freundlich model in terms of increasing the peak concentration from the initial to end parts of the sloping soil bulk were in accordance with the observations, but the values of these concentrations somewhat disagreed with the corresponding observed values. The tails of BTCs were consistent with the observations.

The Langmuir model estimated the peak concentration times between the minutes 75 to 85, which were earlier than the observed times. The simulated peak concentrations using this model were equal to 3.310, 3.380, 3.360

and 3.420 g/L for the drains 1, 2, 3 and 4, respectively. Thus, the initial and end parts of the sloping soil bulk had the minimum and maximum peak concentration, respectively. The tails of BTCs were not in accordance with the observations.

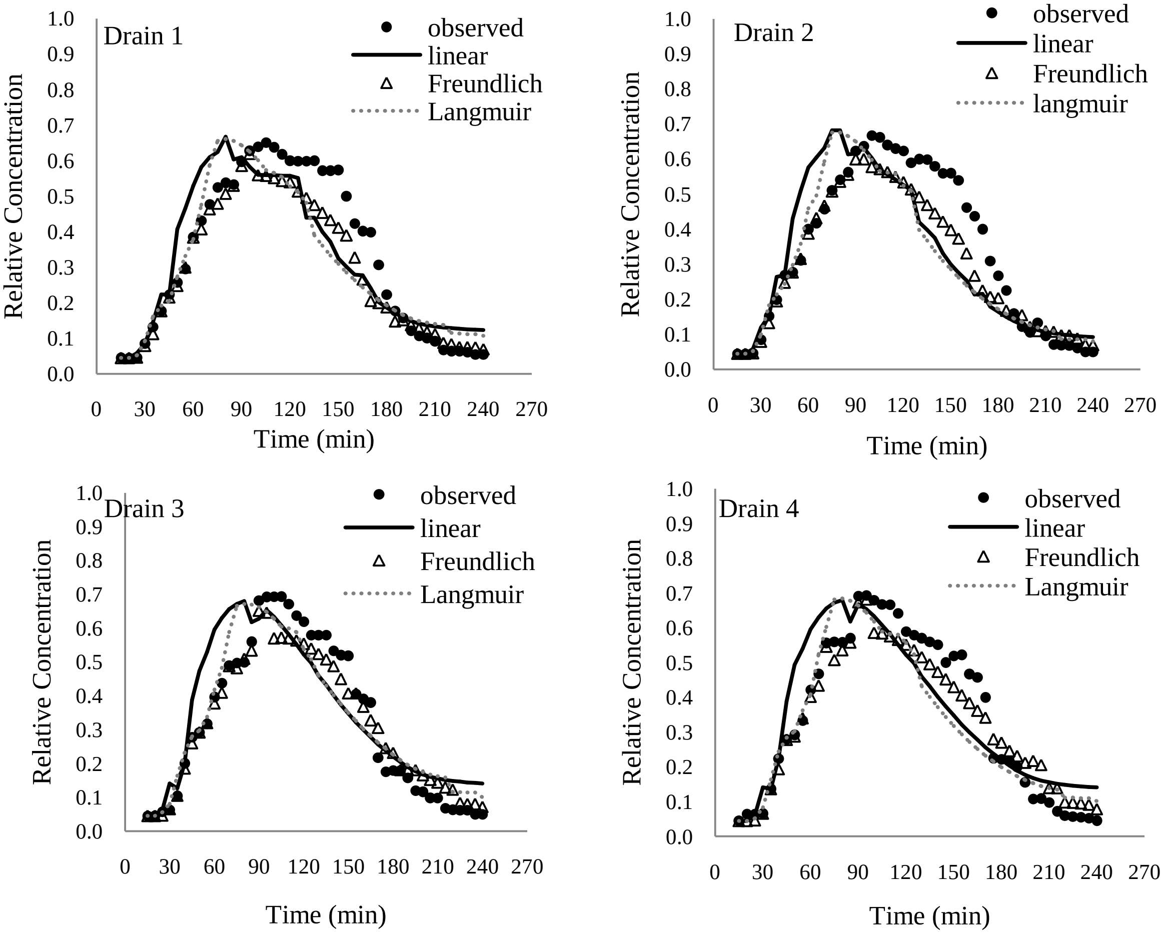

Figure 5: Observed and simulated BTCs of KH_2PO_4

Comparison of the three adsorption isotherm models

As mentioned earlier, all the three models estimated the first breakthroughs about 10 min later than the observed time. However, the concentrations obtained from the Freundlich model compared to the two other models were closer to the observations. The time to reach the peak concentrations was estimated more accurately by the Freundlich model than the linear and the Langmuir models, but the accuracy of the simulated values for concentrations was high by the linear model and the Langmuir. All the three models were, in terms of increasing the peak concentration value from the beginning to end of the sloping soil bulk, in accordance with the observations. The Freundlich model, compared to the two other models, had the best accuracy in simulation of the tails of the BTCs.

3.3. Statistical analysis

The HYDRUS-2D model performance was assessed using the three statistical criteria, namely R^2, RMSE and EF. The computed values of these criteria are presented in Table 4. In the case of the conservative solute, the R^2 and EF values are close to 1 (both equal to 0.907) and the low values of RMSE (0.351 g/L) indicated that HYDRUS-2D had an acceptable accuracy in the simulations. In the case of the non-conservative solute, the Freundlich model with the R^2 and EF values close to 1 (0.951 and .920, respectively) and the low values of

RMSE (0.064 g/L) had a good performance and the accuracy of the Langmuir model with R^2=0.811, EF=0.802 and RMSE=0.101 g/L was acceptable. The linear model with R^2=0.762, EF=0.761 and RMSE=0.111 g/L was less accurate than the two other models. Seuntjens [33] in comparing the two types of linear and non-linear adsorption models for the transport of cadmium in soil, observed that the non-linear model estimated the amounts of cadmium better than the linear model does. Subramanyam and Das [4] in investigating the phenol adsorption by soil found that the non-linear adsorption compared to linear model had a less average error in the prediction of adsorption process. Bache and Williams [34] and Holford *et al*. [35] have stated that the Freundlich and Langmuir models usually show the best fit to the observed data. This result was confirmed in this study as well.

Table 4: Model performance statistics for simulated conservative and non-conservative solutes concentrations

	Adsorption isotherm model	R^2 -	RMSE (g/L)	EF -
KH_2PO_4	-	0.907	0.351	0.907
NaCl	Linear	0.762	0.111	0.761
	Freundlich	0.951	0.064	0.920
	Langmuir	0.811	0.101	0.802

3.4. *Limitations*

Limitations of this study are:

- Presence of cracks and/or macropores is ignored.
- Hysteresis, root water uptake, evaporation and transpiration do not occur.
- There are no internal source/sink terms in the transport medium.

Conclusions

A conservative and a non-conservative solute movement in soil was investigated under laboratory conditions and was simulated using the HYDRUS-2D model. In the simulation of the non-conservative solute transport, three adsorption isotherm models were used to evaluate the adsorption by the soil. Our results showed that the concentration distribution varied in different parts of the slope in a sloping soil bulk. The non-conservative solute, due to its adsorption by soil particles, moved slower than the conservative solute. The non-conservative solute movement was well simulated by the non-linear Freundlich model and the non-linear Langmuir model provided acceptable results, but the results of the linear model were not consistent with the observations. The HYDRUS-2D model satisfactorily simulated the transport of the both solutes.

References

1. Gelhar L. W., Welty C., Rehfeldt K. R., *Water Resour. Res.* 28 (7) (1992) 1955.
2. Hussain A., Ghafoor A., Anwar-Ul-Haq M., Nawaz M., *Int. J. Agric. Biol.* 5 (3) (2003) 349.
3. Shafqat M. N., Pierzynski G. M., *Chemosphere*, 99 (2014) 72.
4. Subramanyam B., Das A., *Int. J. Environ. Sci Tech.* 6 (4) (2009) 633.
5. Aslam M., ZIA M. Sh., Rahmat U., Yasin M., *Int J. Agric. Biol.* 2 (4) (2000) 286.
6. Pang L., Hunt B., *J. Contam. Hydrol.* 53 (1-2) (2001) 21.
7. Charm M., Abdollahi F., *J. Agric.* 28 (2) (2005) 53 (in Farsi).
8. Branger F., Tournebize J., Carluer N., Kao C., Braud H., Vauclin M., *Agric. Water Manage.* 96 (3) (2009) 415.
9. Khan Q. U., Khan M. J., Saif R., Ullah S., *Soil Environ.* 29 (1) (2010) 11.
10. Pang L., Close M. E., Watt J. P. C., Vincen K. W., *J. Contam. Hydrol.* 44 (1) (2000) 19.
11. Rudra R. P., Negi S. C., Gupta N., *Water Qual. Res. J. Can.* 40 (1) (2005) 71.
12. McGrath G., Hinz Ch., Sivapalan M., *J. Contam. Hydrol.* 113 (1-4) (2010) 56.

13. Vanderborght J., Kasteel R., Herbst M., Javaux M., Thiery D., Vanclooster M., Mouvet C., Vereecken H., *Vadose Zone J.* 4 (1) (2005) 206.
14. Zhu Y., Shi L., Yang J., Wu J., Mao D., *J. Hydrol.* 501 (2013) 56.
15. Simunek J., van Genuchten M. Th., Sejna M., The HYDRUS Software Package for Simulating Two- and Three-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media. Technical Manual, Version 1.0, PC Progress, Prague, Czech Republic, (2006).
16. Haws N. W., Das Bh. S., Rao P. S. C., *J. Contam. Hydrol.* 75 (3-4) (2004) 257.
17. Haws N. W., Rao P. S. C., Simunek J., Poyer I.C., *J. Hydrol.* 313 (3-4) (2005) 257.
18. Dos Santos D. Rh., Cambier Ph., Mallmann F. J. K., Labanowski J., Lamy I., Tessier D., van Oort F., *J. Contam. Hydrol.* 145 (2013) 54.
19. Vandenbruwane J., De Neve S., Qualls R. G., Sleutel S., Hofman G., *Geoderma* 139 (1-2) (2007) 144.
20. Huang K., Toride V., van Genuchten M. Th., *Transport Porous Med.* 18 (3) (1995) 283.
21. van Genuchten M. Th., *Soil Sci. Soc. Am. J.* 44 (5) (1980) 892.
22. Schaap M. G., Leij F. J., van Genuchten M. Th., *J. Hydrol.* 251 (3-4) (2001) 163.
23. Bear J., Dynamics of Fluid in Porous Media, Elsevier, (1972).
24. Jacques D., Simunek J., Timmerman A., Feyen J., *J. Hydrol.* 259 (1-4) (2002) 15.
25. Phogat V., Mahadevan M., Skewes M., Cox J. W., *Irrigation Sci.* 30 (4) (2011) 315.
26. Siyal A. A., van Genuchten M. Th., Skaggs T. H., *Agric. Water Manage.* 121 (3) (2013) 73.
27. Abbaspour K. C., Kohler A., Simunek J., Fritsch M., Schulin R., *Eur. J. Soil Scie.* 52 (3) (2001) 433.
28. Gardenas A. I, Simunek J., Jarvis N., van Genuchten M. Th., *J. Hydrol.* 329 (3-4) (2006) 647.
29. Fetter C. W., Contaminant Hydrology, Prentice Hall, (1999).
30. Hamdaouia O., Naffrechoux E., *J. Hazard. Mater.* 147 (1-2) (2007) 381.
31. Yu C., Gao B., Carpena R. M., Tian Y., Wu L., Ovilla O. P., *J. Hydrol.* 402 (1-2) (2011) 159.
32. Amin M. G. M., Simunek J., Lagdsmand M., *Agric. Water Manage.* 131 (3) (2014) 17.
33. Seuntjens P., *Water Air Soil Pollut.* 140 (1) (2002) 401.
34. Bache B. W., Williams E. G., *J. Soil Sci.* 22 (3) (1971) 289.
35. Holford I. C. R., Wedderburn R. W. M., Mattingly G. E. G., *J. Soil Sci.* 25 (2) (1974) 242.

(2016) ; http://www.jmaterenvironsci.com/