The Efficiency of Physical Equilibrium and Non-Equilibrium Models for Simulating Contaminant Transport in Laboratory-Scale

Shahmohammadi Kalalagh, Shahram*+
Department of Water Sciences and Engineering, Tabriz Branch, Islamic Azad University, Tabriz, I.R. IRAN

Taran, Farshid
Department of Water Engineering, University of Tabriz, Tabriz, I.R. IRAN

ABSTRACT: *In order to better management of contaminants in porous media, it is essential to recognize their transport behavior using appropriate models. In this research, Convection-Dispersion Equation (CDE) and Mobile-ImMobile (MIM), as physical equilibrium and non-equilibrium models, respectively, were used to simulate the bromide transport (as a conservative contaminant) through undisturbed and saturated clay loam and sandy loam soil columns (diameter of 10 and height of 40 cm). To simulate the transport, CXTFIT2.1 software, in which the CDE and the MIM models are included, was used. The values of mass transfer coefficient ($\omega<100$) and mobile water fraction ($\beta<1$) as an indicator for determining the equilibrium and non-equilibrium indicated that bromide transport behavior within these columns was anomalous or non-Fickian transport. Hence, non-equilibrium and the MIM model are suitable and more efficient than the Fickian-based CDE. The fitted breakthrough curves (BTCs) and the larger determination coefficient (R^2) and the smaller Root Mean Square Error (RMSE) values of the MIM model compared to those of the CDE confirmed the effectiveness of the MIM model in simulating bromide transport in the clay loam and sandy loam soil columns.*

KEYWORDS: *Anomalous transport, Breakthrough curve, Bromide, CDE model, CXTFIT2.1 software, MIM model.*

INTRODUCTION

The precise and accurate expression of contaminant transport in porous media is very important for assessing and remediation of contaminants in soils and aquifers. An important aspect in understanding the fate of solutes and contaminants in soil is the expression of their transport behavior using appropriate models. The Convection-Dispersion Equation (CDE) is the first model widely used to express the contaminant transport in porous media and has led to satisfactory results in homogeneous soils (in laboratory-scale) [1, 2]. However, research has shown that this model cannot predict all aspects of the behavior and transport of solutes, especially in heterogeneous soils [2, 3]. Natural porous media is often heterogeneous in which the water velocity changes with the medium heterogeneity

* *To whom correspondence should be addressed.*
+ *E-mail: shahmohammadi_sh@yahoo.com*
1021-9986/2021/6/1860-1867 8/$/5.08

and therefore, the solute transport process is complex. In such media, the BreakThrough Curves (BTCs) are stretched (unlike homogeneous soils, in which the BTCs are usually symmetrical). This phenomenon is referred to as anomalous or non-Fickian transport [4; 3]. Hence, it is difficult to simulate the solute transport in natural porous media using the CDE model and it should be replaced by a higher-performance model with more accuracy. One of the limitations of the CDE model is the assumption that the solute transport in the soil is equilibrium. However, this assumption is correct only if the transport occurs in a homogeneous porous medium, there is sufficient time for adsorption and the adsorption is linear and reversible [5]. However, an aquifer has a different condition which is called a non-equilibrium state. In a non-equilibrium state, the solute transport in the soil can be subject to the physical conditions of the soil layers (due to the heterogeneity characteristics, preferential flow, and kinetic dispersion), or their chemical conditions. Also, unlike the equilibrium condition, the effect of water velocity in porous media should not be ignored [5].

Various models such as the Convective Lognormal Transfer (CLT) [1; 6], Continuous Time Random Walk (CTRW) model [7], and the Fractional Advection Dispersion Equation (FADE) [8; 9] have been proposed to express the anomalous transport of solute in soil. Also, the Mobile-Immobile Model (MIM) [5; 10] (referred to as a physical non-equilibrium model or two-region model) has been presented. This model can be used to describe the solute transport in a variety of porous media (homogeneous and heterogeneous). In the MIM, unlike the CDE assumes that all the water in the soil plays a role in the solute transport, only the effect of a portion of the water in the soil is considered in the solute transport. In other words, water in the soil can be divided into two parts: a) mobile water: part of the water that plays a role in the convective movement of solute, and b) immobile water: the stagnant part of the water that is only effective through other processes, such as the diffusion, on the solute transport. In the mobile part, the convective flow is the dominant process, and therefore, the water movement and solute transport is rapid. However, the solute transport from the mobile part to the immobile part or vice versa occurs through diffusion and is very slow. Thus, the anomalous transport of solute arises from the stagnant and immobile water in the soil system [5; 10].

The transport of a solute in porous media depends on several factors, including the solute properties, the fluid velocity field within the porous medium, and the microgeometry, i.e., shape, size, and location of the solid part of the medium and the voids [11]. Solutes in aqueous solutions can be classified according to their chemical reactivity such as radioactive decay, production, adsorption, ion exchange, etc. Conservative solutes are those that do not react chemically, and thus their concentration is not changed by transport processes. Examples of conservative solutes include chloride and bromide. On the other hand, solutes whose concentration is changed by chemical and/or biological transformations are referred to as nonconservative or reactive solutes. Nutrients such as nitrate and phosphate are examples of reactive solutes [12].

The efficiency of the physical equilibrium model (CDE) and non-equilibrium model (MIM) in the simulation of conservative solute transport in a variety of homogeneous and heterogeneous soils [13-14; 16-22], saturated and unsaturated soils [15-16; 23], compacted soils [13; 15] and disturbed and undisturbed soils [24-27] have been evaluated and confirmed. Despite the numerous studies, the efficiency of these models in loamy soils, especially undisturbed soils, has not yet been investigated. Hence, the main aim of this study is to evaluate the efficiency of CDE and MIM models for simulating bromide transport in undisturbed clay loam and sandy loam soil columns on a laboratory scale.

EXPERIMENTAL SECTION

Soil columns preparation and experiment

The undisturbed soil samples were collected from the research site of the Islamic Azad University of Tabriz, with a longitude of 38° 02' 77.88" N and latitude of 46° 43' 97.07" E from the root zone (depths of 0 to 40 cm). Some physical properties of the two used soil types are given in Table 1. The prepared soil columns (made of PVC, with diameter and height of 10 and 40 cm, respectively) were connected to a Mariotte bottle for being washed with a 0.01 molar $CaCl_2$ solution as a background solution. The Mariotte bottle was used to maintain a constant flow rate of the solution on the soil columns. The bottom of these columns was fixed inside a plastic funnel on the wired plate. To overflow the solution, an outlet was installed at 10 cm above the columns to keep the water head constant on each column. The outlet height was adjustable according

Table 1: The physical properties of the soils examined.

Soil properties	Sandy loam	Clay loam
Sand (%)	62.1	26
Silt (%)	25.3	38.5
Clay (%)	12.6	35.5
Bulk density (g cm^{-3})	1.40	1.30
Mean weight diameter (mm)	0.18	1.25

to the required flow rate. The soil columns were saturated from the bottom with $CaCl_2$ solution. The saturation was carried out without making any hydrostatic pressure in the wetting front to prevent air entrapment. This was performed by putting the bottom of the soil columns at an equivalent height to the surface of the background solution. The background solution rose due to capillarity and saturated the column from the bottom. By stopping the capillary rise, the solution level was raised 1 cm to complete the saturation process and reach the level of the background solution to the soil surface. To ensure full saturation, in the end, a 1 cm height of solution was allowed to be on the soil surface. By disconnecting the background solution, 1 liter of 0.01 molar $CaBr_2$ solution (C_0) was injected into the columns by pulse technique. Then, the background solution flow was established again with the 1 cm constant head. After injection of $CaBr_2$ solution, the columns effluent were collected at different times immediately and bromide concentration was determined using a pH meter equipped with a bromide selective electrode (from the Spain Crison Co.) This continued until the concentration of bromide in the output flow reached a constant value. The experiment duration for the clay loam and sandy loam soil columns was 90 and 30 min, respectively.

Model Theory

Equilibrium model

The parabolic convection-dispersion equation for the one-dimensional transport of a conservative solute under steady state flow is expressed as follows [28]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} \tag{1}$$

Where, C is the solute concentration (ML^{-3}), D is the hydrodynamic dispersion coefficient (L^2T^{-1}), V is the average pore water velocity (L^2T^{-1}), x is the distance (L) and t is time (T).

Non-equilibrium model

The Mobile-Immobile Model (MIM), also known as the two-region model, divides soil water into two mobile and stagnant parts. The mobile part contains the water located in macropores in which the solute transport occurs by convection and hydrodynamic dispersion. In this part, water has a dynamic state. The stagnant part is the water is located in the soil matrix in which the solute transport is only due to molecular diffusion. In general, the MIM model includes a CDE for expressing the solute transport in the macropore and an equation to describe the solute transport between the mobile (macropore) and stagnant (matrix) regions. The second equation expresses the transport rate proportional to the difference in concentration between the two regions. The one-dimensional MIM model for transport of a conservative solute under steady-state flow is as follows [14]:

$$\theta_m\frac{\partial C_m}{\partial t} + \theta_{im}\frac{\partial C_{im}}{\partial t} = \theta_m D_m\frac{\partial^2 C_m}{\partial x^2} - \theta_m V_m\frac{\partial C_m}{\partial x} \tag{2a}$$

$$\theta_{im}\frac{\partial C_{im}}{\partial t} = \omega\left(C_m - C_{im}\right) \tag{2b}$$

Where, θ_m and θ_{im} are the volumetric water content of the mobile and immobile region, respectively. $\theta_m + \theta_{im} = \theta$ in which θ is the soil total water and is equal to the porosity in saturated soils (-). C_m and C_{im} are the solute concentration (ML^{-3}) in the mobile and immobile regions, respectively. D_m is the hydrodynamic dispersion coefficient of the mobile region (L^2T^{-1}), V_m is the pore water velocity of the mobile region (LT^{-1}) and $V_m\theta_m$ is the flow rate in the mobile region or the Darcy velocity (LT^{-1}). ω is the mass transfer coefficient between the mobile and immobile regions (T^{-1}).

Estimation of the Transport Parameters

In this research, an inverse solution method, as an optimization method, was used to estimate the transport

Table 2: The bromide transport parameters obtained by CDE and MIM.

Soil type	CDE model					MIM model					
	V (cm min^{-1})	*D* (cm^2 min^{-1})	*λ* (cm)	RMSE	R^2	V_m (cm min^{-1})	D_m (cm^2 min^{-1})	*β* (-)	*ω* (min^{-1})	RMSE	R^2
Clay loam	0.83	6.15	7.41	0.028	0.992	0.73	2.34	0.0001	14.73	0.024	0.995
Sandy loam	2.23	1.75	0.78	0.034	0.986	1.98	0.57	0.0001	6.97	0.025	0.995

In this Table, the parameters V, D, λ, β and ω are flow velocity, dispersion coefficient, dispersivity, mobile water fraction, mass transfer coefficient. The subscript m is related to the MIM model.

parameters. In inverse modeling, in addition to the measured data, an appropriate mathematical model is needed to express the equations governing the phenomenon and an optimization algorithm is needed to minimize an objective function. CXTFIT2.1 is software with the ability of inverse solution. This software is based on the analytical solution of the CDE and the MIM model by using the Levenberg-Marquardt optimization algorithm. The CXTFIT2.1 was used to estimate the parameters of the CDE (V and D) and the MIM model (V_m, D_m, $\beta=\theta_m/\theta$, and ω). The objective function for the CDE and MIM is in Eq.3 and Eq.4, respectively:

$$\chi^2(V,D)=\sum_{i=1}^{n}\left[C_i-C(x,t_i;V,D)\right]^2 \quad (3)$$

$$\chi^2(V_m,D_m,\beta,\omega)=\sum_{i=1}^{n}\left[C_i-C(x,t_i;V_m,D_m,\beta,\omega)\right]^2 \quad (4)$$

Where C_i is the observed concentration. $C(x, t_i; V, D)$ and $C(x, t_i; V_m, D_m, \beta, \omega)$ are the estimated concentration in location x and time t in the CDE and MIM, respectively. n is the total number of observations.

Models Performance Criteria

The performance of the models was evaluated by two frequently used statistical indices of determination coefficient (R^2) and root mean square error (*RMSE*) [14; 29]:

$$R^2=1-\frac{\sum_{i=1}^{n}\left(C_{io}-C_{ie}\right)^2}{\sum_{i=1}^{n}\left(C_{io}-\bar{C}_{io}\right)^2} \quad (5)$$

$$RMSE=\sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(C_{io}-C_{ie}\right)^2} \quad (6)$$

Where Cie is the estimated concentration, Cio is the observed concentration, $\bar{C}_{io}$ represent the mean values of Cio, and n is the number of data pairs.

RESULTS AND DISCUSSION

Estimated parameters

The estimated parameters from the simulation of bromide transport in the saturated clay loam and sandy loam soil columns by CDE and MIM are presented in Table 2. According to Table 2, the dispersion coefficient (*D*) of clay loam soil is higher than that of sandy loam soil. This shows that bromide transport in the clay loam soil, compared to the sandy loam soil, is more affected by the hydrodynamic dispersion than the convection phenomenon. As a result, its BTC is more stretched and less symmetrical (Fig.1). This can also indicate a greater possibility of occurrence of preferential flow in these types of soil [30]. Similarly, *Lee et al.* [31] obtained a larger dispersion coefficient in undisturbed soils (silty loam texture, non-angular block structure) for columns with preferential paths, compared to those without preferential paths. In contrast, the higher flow velocity (*V*) and lower dispersion coefficient (*D*) in the sandy loamy soil show that bromide transport in this soil type is more influenced by the convective flow than the hydrodynamic dispersion. As a result, bromide displacement and movement rates are higher through the sandy loam soil compared to the clay loam soil. In other words, bromide breakthrough time (the time duration of bromide movement along the soil column) is less in the sandy loam soil than the clay loam soil. For example, the peak relative concentration in the clay loam soil is observed after about 100 minutes, while this time in the sandy loam soil is approximately 38 minutes (Fig.1).

The R^2 values greater than 0.98 for both CDE and MIM indicate the high ability of these models to simulate bromide transport in the columns. However, the larger R^2 values and the smaller RMSE values of the MIM model compared to those of the CDE state that the accuracy and efficiency of the MIM model is higher. The BTCs in Fig.1 also confirm this.

The dispersivity (λ=D/V) in the CDE is an empirical parameter and depends on various factors such as soil texture, soil heterogeneity, the water flow rate in soil, soil water content, experiment scale, etc. [32]. The amount of λ in coarse texture soils is often less than in fine texture soils and in homogeneous soils is less than in heterogeneous soils [33]. In the present study, the same results were obtained (Table 2).

The parameter ω (Table 2) shows the amount of solute exchange between the two mobile and stagnant regions in the MIM model. Based on the assumption of the MIM model, the solute exchange between these two regions is only due to the molecular diffusion and the exchange rate depends on the contact surface of the two regions, the flow velocity, the volume, and geometric properties of the stagnant region pores [32]. The decrease in the water and solute velocity in the inter-aggregate pores (macropores) results in the increase of the solute exchange between the two mobile regions due to the longer residence time of bromide in the soil and consequently, leads to the increase of ω [30]. In clay loam soils, due to having a strong structure (with a mean weighted diameter of soil aggregates of 1.25 mm), the large size of aggregates means an increase in the length of the bromide molecular diffusion pathway, which causes the BTC to be more stretched; so that with increasing ω, the BTC of the clay loam soil is completely out of symmetry mode (Fig. 1).

The parameters ω and β are indicators for determining the equilibrium and non-equilibrium transport in porous media, so that $\omega \geq 100$ and $\beta = 1$ indicate an equilibrium condition, and $\omega < 100$ and $\beta < 1$ represent the non-equilibrium transport [34]. Therefore, the values of these parameters in this study (Table 2) represent the physical non-equilibrium transport of bromide in the undisturbed clay loam and sandy loam soil columns. Accordingly, it is expected that the MIM model, which is based on the assumption of the non-equilibrium transport is more efficient than the CDE model (equilibrium transport). Fig. 1 and Table 3 show this issue.

Br_2 transport simulation

The bromide experimental and estimated BTCs (obtained by CDE and MIM models) in the clay loam and sandy loam soil columns in two normal and semi-logarithmic modes are shown in Fig. 1. The BTCs of both soil types have been obtained from an average of three replicates. According to Fig.1, the concentrations estimated by the CDE are less than the measured values in the initial parts of the BTC, but are more than the measured concentrations at the tail parts. Similar results have been reported by *Berkowitz and Scher* [4] and *Berkowitz et al.* [3], which have referred to this phenomenon as anomalous or non-Fickian transport. In Fig. 1, MIM model, in comparison with the CDE, shows a better fit with the measured data in the two soil types. This means that bromide transport in clay loam and sandy loam columns is more anomalous or non-Fickian and therefore, the MIM model is more suitable than the CDE (Fickian-based) for simulating the bromine transport. Similar results have been reported by *Gao et al.* [14], *Asghari et al.* [25], and *Safadoust et al.* [27]. The results of the statistical analysis in Table 3 also confirm this.

The initial breakthrough of bromide and the peak arrival time in the sandy loam column occurred much earlier than in the clay loam column. This can be due to the presence of macropores, less pore tortuosity, soil structure destruction, and increased flow velocity in the sandy loam soil [17, 25, 27]. As previously mentioned, this indicates that the convection flow is dominant over the dispersion phenomenon in solute transport in sandy loam soils.

CONCLUSIONS

In this research, simulation of bromide transport through undisturbed and saturated clay loam and sandy loam soil columns using physical equilibrium (CDE) and non-equilibrium (MIM) models was investigated. The dispersion coefficient (*D*) of clay loam soil was obtained higher than the sandy loam soil. This showed that bromide transport in the clay loam soil, compared to the sandy loam soil, has been more affected by the hydrodynamic phenomenon. As a result, its BTC was more stretched and less symmetrical. In contrast, the higher flow velocity (*V*) and lower dispersion coefficient (*D*) in the sandy loamy soil showed that bromide transport in this soil type has been more influenced by the convective phenomenon. As a result, bromide displacement and movement rates are higher in the sandy loam soil compared to the clay loam soil.

The values of $\omega < 100$ and $\beta < 1$, represent the physical non-equilibrium transport of bromide in the undisturbed clay loam and sandy loam soil columns. Accordingly, it is expected that the MIM model, which is based on the assumption

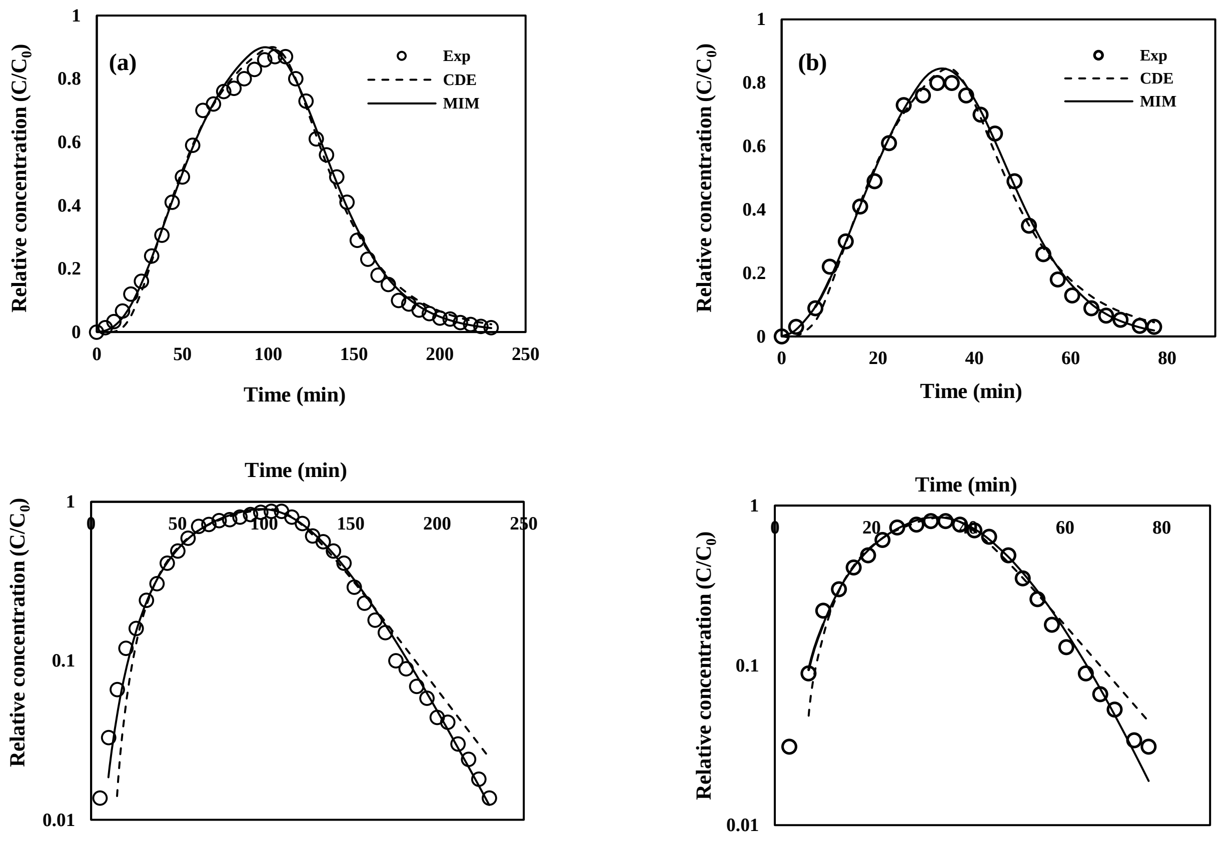

***Fig. 1:** Comparison of Br_2 concentration calculated with CDE and MIM and the measured data in linear axes and semi-log axes: (a) clay loam column and (b) sandy loam column.*

of the non-equilibrium transport, is more efficient than the CDE model (equilibrium transport). Also, the R^2 values greater than 0.98 for both CDE and MIM indicate the ability of these models to simulate bromide transport in the columns. However, the larger R^2 values and the smaller RMSE values of the MIM model compared to those of the CDE state that the accuracy and efficiency of the MIM model are higher.

The higher and better efficiency of the MIM model compared to the CDE model in this study, which was performed under controlled laboratory conditions, could not be a strong and reliable judgment in evaluating these models. Because the precision and accuracy of the models in the solute transport simulating depends on several factors such as solute characteristics (concentration, reactivity, conservative), physical and chemical properties of the soil, and the initial and boundary conditions governing the flow. Therefore, a more accurate assessment depends on conducting research and experiments in real and field conditions, taking into account most of the mentioned effective factors.

Received : May. 17, 2020 ; Accepted : Aug. 3, 2020

REFERENCES

[1] Jury W.A., Simulation of Solute Transport Using a Transfer Function Model, *Water Resour. Res.*, **18**: 363-368 (1982).

[2] Huang G., Huang Q., Zhan H., Chen J., Xiong Y., Feng S., Modeling Contaminant Transport in Homogeneous Porous Media with Fractional Advection Dispersion Equation, *Sci. China Ser. D Earth Sci.*, **48**: 295-302 (2005).

[3] Berkowitz B., Emmanuel S., Scher H., Non-Fickian Transport and Multiple-Rate Mass Transfer in Porous Media, *Water Resour. Res.*, **44**: 1-16 (2008).

[4] Berkowitz B., Scher H., On Characterization of Anomalous Dispersion in Porous Media, *Water Resour. Res.*, **31**: 1461–1466 (1995).

[5] Pang L., Close M., Schneider D., Stanton G., Effect of Pore-water Velocity on Chemical Non-Equilibrium Transport of Cd, Zn, and Pb in Alluvial Gravel Columns, *Contam. Hydrol.*, **57**: 241-258 (2002).

[6] Jury W.A., Roth K., "Transfer Function and Solute Movement through Soil: Theory and Applications", Birkhauser Boston, Cambrige, Mass, (1990).

[7] Berkowitz B., Scher H., Exploring the Nature of Non-Fickian Transport in Laboratory Experiments, *Adv. Water Res.*, **32**: 750-755 (2008).

[8] Benson D.A., Wheatcraft S.W., Meerschaert M.M., Application of a Fractional Advection-Dispersion Equation. *Water Resour Res.*, **36**: 1403-1412 (2000a).

[9] Benson D.A., Wheatcraft S.W., Meerschaert M.M., The Fractional-Order Governing Equation of Levy Motion, *Water Resour. Res.*, **36**: 1413-1423 (2000b).

[10] Bond W.J., Wierenga P.J., Immobile Water During Solute Transport in Unsaturated Sand Columns, *Water Resour. Res.*, **26**: 2475-2481 (1990).

[11] Goldsztein G.H., Solute Transport in Porous Media. Media with Capillaries as Voids. *SIAM J. Appl. Math.*, **68**: 1203-1222 (2008).

[12] Lamberti G., Hauer F.R., "Methods in Stream Ecology: Vol. 2: Ecosystem Function". Academic Press (2017).

[13] Toride N., Inoue M., Leij F., Hydrodynamic Dispersion in an Unsaturated Dune Sand, *Soil Sci. Soc. Am. J.*, **67**: 703-712 (2003).

[14] Gao G., Zhan H., Feng S., Huang G., Mao X., Comparison of Alternative Models for Simulating Anomalous Solute Transport in a Large Heterogeneous Soil Column, *J. Hydrol.*, **377**: 391-404 (2009).

[15] Arora B., Mohanty B.P., McGuire J.T., Inverse Estimation of Parameters for Multidomain Flow Models in Soil Columns with Different Macropore Densities, *Water Resour. Res.*, **47**: 4 (2011).

[16] Padilla I.Y., Yeh T.C.J., Conklin M.H., The Effect of Water Content on Solute Transport in Unsaturated Porous Media. *Water Resour. Res.*, **35**: 3303-3313 (1999).

[17] Shahmohammadi-Kalalagh S., Beyrami H., Modeling Bromide Transport in Undisturbed Soil Columns with the Continuous Time Random Walk. *Geotech. Geol. Eng.*, **33**: 1511-1518 (2015).

[18] Mehdinejadiani B., Estimating the Solute Transport Parameters of the Spatial Fractional Advection-Dispersion Equation Using Bees Algorithm, *J. Contam. Hydrol.*, **203**: 51-61 (2017).

[19] Ghazal M., Behrouz M., Modelling Solute Transport in Homogeneous and Heterogeneous Porous Media Using Spatial Fractional Advection-Dispersion Equation. *Soil Water Res.*, **13**: 18-28 (2018).

[20] Moradi G., Mehdinejadiani B., An Experimental Study on Scale Dependency of Fractional Dispersion Coefficient. *Arab. J. Geosci.*, **13**: 409 (2020).

[21] Bouredji H., Bendjaballah-Lalaoui N., Rennane S., Merzougui A., Predicting Solute Transport Parameters in Saturated Porous Media Using Hybrid Algorithm. *Iran. J. Chem. Chem. Eng., (IJCCE)* **40(3):** 945-954 (2021).

[22] Sharma P.K., Agarwal P., Mehdinejadiani B., Study on Non-Fickian Behavior for Solute Transport Through Porous Media. *ISH J. Hydraul. Eng.*, 1-9 (2020).

[23] Shahmohammadi-Kalalagh S., Modeling Contaminant Transport in Saturated Soil Column with the Continuous Time Random Walk. *J. Porous Media*, **18**: 1-6 (2015).

[24] Poulsen T.G., Moldrup P., de Jonge L.W., Komatsu T., Colloid and Bromide Transport in Undisturbed Soil Columns. *Vadose Zone J.*, **5**: 649-656 (2006).

[25] Asghari S., Abbasi F., Neyshabouri M.R., Effects of Soil Conditioners on Physical Quality and Bromide Transport Properties in a Sandy Loam Soil. *Biosyst. Eng.*, **109**: 90-97 (2011).

[26] Safadoust A., Mahboubi A., Mosaddeghi M.R., Gharabaghi B., Unc A., Voroney P., Heydari A., Effect of Regenerated Soil Structure on Unsaturated Transport of *Escherichia Coli* and Bromide, *J. Hydrol.*, **430–431**: 80–90 (2012).

[27] Safadoust A., Amiri Khaboushan E., Mahboubi A.A., Gharabaghi B., Mosaddeghi M.R., Ahrens B., Hassanpour Y., Comparison of Three Models Describing Bromide Transport Affected by Different Soil Structure Types, *Arch. Agron. Soil Sci.*, **62**: 674-687 (2016).

[28] Bear J., "Dynamics of Fluids in Porous Media", Dover Publications, New York, (2013).

[29] Toride N., Leij F.J., van Genuchten M.Th., "The CXTFIT Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments". Version 2.1, Research Rep. 137. U.S. Salinity Lab, Riverside, CA, USA, (1999).

[30] Ersahin S., Papendick R.I., Smith J.L., Keller C.K., Manoranjan v.s., Macropore Transport of Bromide as Influenced by Soil Structure Differences, *Geoderma*, **108**: 207-223 (2002).

[31] Lee J., Horton R., Noborio K., Jaynes D.B., Characterization of Preferential Flow in Undisturbed Structured Soil Columns Using a Vertical TDR probe, *J. Contam. Hydrol.*, **51**: 131-14 (2001).

[32] Hillel D., "Introduction to Soil Physics". Elsevier, (2013).

[33] Perfect E., Sukop M.C., Haszler E.R., Prediction of Dispersivity for Undisturbed Soil Columns from Water Retention Parameters, *Soil Sci. Soc. Am. J.*, **66**: 696-701 (2002).

[34] Pang L., Close M.E., Non-Equilibrium Transport of Cd in Alluvial Gravels, *J. Contam. Hydrol.*, **36**: 185-206 (1999).