Non-reactive solute transport modelling with time-dependent dispersion through stratified porous media

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Abstract. We present a numerical solution of the mobile-immobile model (MIM) with time-dependent dispersion coefficient to simulate solute transport through heterogeneous porous media. Observed experimental data of non-reactive solute transport through hydraulically coupled stratified porous media have been simulated using asymptotic and linear time-dependent dispersion functions. Non-Gaussian breakthrough curves comprising long tails are simulated well with the MIM incorporating asymptotic time-dependent dispersion model. The system is under the strong influence of physical nonequilibrium, which is evident by variable mass transfer coefficient estimated at different down-gradient distances. Asymptotic time-dependent functions are capable of capturing the rising limb of the solution phase breakthrough curves with improved accuracy, whereas tailing part simulation capabilities are similar for both asymptotic and linear time-dependent dispersion functions. Further, the temporal moment analysis demonstrated increased spreading, variance for linear dispersion model as compared with asymptotic dispersion model. It is also observed that the first-order mass transfer coefficient varies inversely with travel distance from the input source. It can be concluded from the study that MIM with time-dependent dispersion function is simpler yet sensitive to account for medium's heterogeneity in a better manner even for small observation distances from the source.

Keywords. Nonreactive solute; mobile-immobile model; time-dependent dispersion; temporal moment of solute concentration; stratified porous media.

1. Introduction

Contaminant transport through soil has been an important research problem in the field of geo-environmental engineering. The area is still evolving with complex modelling approach and inclusion of (distance) scale- and time-dependent transport parameters. Classical advection-dispersion equation (ADE) is commonly used for describing solute transport through porous media due to its simplicity and lumped parameter estimation [1, 2]. When the porous medium is heterogeneous, early arrival and long tailing of solute particles in the time-concentration plots (breakthrough curves—BTCs) have been observed, which are attributed to anomalous transport behaviour [3, 4]. It has been reported in literature that ADE is less adequate for simulating anomalous transport through heterogeneous porous media [3, 5–9]. Therefore, higher-order modelling approaches have been proposed that can capture anomalous transport behaviour of solute, considering physical and chemical partitioning in saturated porous media [8, 10–15]. Physical partitioning results from the hydraulic

coupling of mobile (advective) and immobile (nonadvective) regions such as stratified porous media, in which the former behaves as sink/source component. Chemical partitioning results from site-specific interaction between solute and grains of porous material [10]. For the transport of nonreactive solute, mobile-immobile model (MIM) is a powerful tool. MIM divides the porous medium into flowing (mobile) and stagnant (immobile) regions. Diffusive mass transfer between mobile and immobile partitioning is mathematically accounted by mass transfer coefficient. It has been observed that the mass transfer coefficient contributes in early arrival and long tailing of BTC apart from retardation factor and dispersion coefficient [16]. In addition to this, the most challenging aspect of studying solute transport through heterogeneous porous media is ever-growing scale effect with space or time on the estimation of dispersion coefficient [17–19] since constant dispersion coefficient is a lumped parameter and unable to capture the broad spectrum of time scale BTCs through a heterogeneous porous medium [20–24]. To incorporate the scale effects, time-dependent and scale (distance)-dependent dispersion models in pre-asymptotic regime have been developed over the past decade [8, 25–28]. Fractal concept and stochastic studies have

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established that apart from heterogeneity, travel time or distance influences the dispersion parameter until it reaches an asymptotic value [17, 18, 20, 22, 29–34]. Sharma and Srivastava [26] compared distance- and time-dependent dispersion coefficients incorporated into a general transport model for physically and chemically heterogeneous porous medium. It was concluded that the distance-dependent dispersion resulted in a steeper concentration profile compared with time-dependent dispersion coefficient. Another major limitation of space-dependent dispersion coefficient is ever-growing behaviour with space [8, 20, 35]. Since the solution phase concentration rather changes with each time step, for a heterogeneous medium, time-dependent dispersion captures spreading in a better manner [9, 26, 36]. ADE incorporating time-dependent dispersion coefficient has been presented for homogeneous porous media [23, 37–40]. Basha and El-Habel [41] presented analytical solutions of ADE with arbitrary time-dependent dispersion model using variable transformation technique. There have been very few studies incorporating time-dependent dispersivity with MIM model, considering a function of mean travel distance ($\bar{x}$) [26]. In the present study, time-dependent dispersion coefficient is demonstrated as a function of mean travel distance ($\bar{x}$) while in the previous studies, time-dependent dispersivity is represented by space coordinate (x) [26, 33, 42, 43]. These two are not interchangeable as mean travel distance ($\bar{x}$) represents the distance of solute front at any time instance, whereas space coordinate (x) is the fixed distance of the observation point from the source [27]. Hence it has been proposed that a time-dependent dispersivity should be an arbitrary function of time only [37, 41].

From literature review it is concluded that there is a need to present a novel hybrid numerical approach to solve MIM model with arbitrary time-dependent dispersion function. It is expected that MIM with time-dependent dispersion will capture the spreading in heterogeneous media, with enhanced accuracy, which increases with transport time. Moreover, it will also be interesting to see the effect of arbitrary time-dependent dispersion parameters on the plume spreading in mobile and immobile regions.

Therefore, in this study, firstly an attempt is made to extend MIM to embrace the concept of arbitrary time-dependent dispersion and subsequently to solve it numerically using a hybrid implicit finite difference method. Secondly, the numerical solution developed is then used to simulate the experimental data of Swami *et al* [44]. Log–log plots of BTCs have been used to demonstrate the capabilities of presented solution, particularly in the rising and tailing portion. Thirdly, temporal moment analysis for linear and asymptotic time-dependent dispersion models is performed to study the plume behaviour. This study is expected to reveal the capabilities and limitations of MIM model with arbitrary time-dependent dispersion function.

2. Governing equations

The MIM model developed by van Genuchten and Wierenga [5, 45] is based on partitioning the heterogeneous porous media into mobile and immobile regions. Mobile region accounts for transport processes, i.e., advection and dispersion process, and stagnant or immobile region accounts for first-order diffusive mass transfer between mobile and immobile regions. Both regions include the first-order transformation reaction on specific sites in porous media. Considering linear sorption isotherm, governing equations are expressed as follows:

$$(\theta_m + f\rho_b K_d) \frac{\partial C_m}{\partial t} = \theta_m D(t) \frac{\partial^2 C_m}{\partial x^2} - v_m \theta_m \frac{\partial C_m}{\partial x} - \omega(C_m - C_{im}) - (\theta_m \mu_{lm} + f\rho_b K_d \mu_{sm}) C_m \quad (1)$$

$$(\theta_{im} + (1-f)\rho_b K_d) \frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im}) - (\theta_{im} \mu_{lim} + (1-f)\rho_b K_d \mu_{sim}) C_{im} \quad (2)$$

where C_m and C_{im} are the solute concentrations, respectively, in the mobile and immobile regions (M/L^3) at any time t ; x is the spatial coordinate (L) taken in the direction of the fluid flow; $D(t)$ (L^2/T) represents time-dependent hydrodynamic dispersion coefficient along the flow velocity; θ_m and θ_{im} are volumetric water contents of the mobile and immobile regions, respectively, and $\theta = \theta_m + \theta_{im}$; θ is the total volumetric water content of the porous media; v_m is the mobile pore water velocity (L/T); $v_m \theta_m$ is equal to q (flow rate (L/T)); ω is the first-order mass transfer coefficient (T^{-1}); f and $(1-f)$ represent the fractions of sorption sites that equilibrate instantly with the mobile and immobile regions, respectively; μ_{lm} and μ_{lim} are the first-order decay coefficients for degradation of solutes in the mobile and immobile solution phases, respectively; μ_{sm} and μ_{sim} are the first-order decay coefficients for degradation of solutes in the mobile and immobile region for adsorbed solid phases, respectively; K_d is the distribution coefficient of the linear sorption process (L^3/M) and ρ_b is the bulk density of the porous media (M/L^3).

In this study, linear and asymptotic time-dependent dispersion functions with MIM model have been used to extend the capabilities of numerical simulation. Linear time-dependent dispersion increases with time, until the end of the simulation time grid point, while asymptotic time-dependent dispersion gradually increases with time and ultimately at final time step settles with an asymptotic value. We define following abbreviations to represent our results: MIML is the MIM with linear time-dependent dispersion (LTDD); MIMA is the MIM with asymptotic time-dependent dispersion (ATDD).

Linear dispersion:

$$D(t) = D_0 \frac{t}{K_L} + D_m, \quad (3a)$$

Asymptotic dispersion:

$$D_{(t)} = D_0 \frac{t}{t + K_A} + D_m, \quad (3b)$$

where D_0 is the maximum dispersion coefficient (L^2/T); D_m is the effective diffusion coefficient (L^2/T); K_A (T) is the ATDD coefficient, which is equivalent to mean travel time and K_L (T) is the LTDD coefficient. It is to be noted here that in case of linear dispersion function when $K_L = t$, maximum dispersion coefficient is equal to total dispersion, and is 0.5 times total dispersion in case of asymptotic relation. The slope of dispersion distribution curve at any time is D_0/K_L for linear function and $\frac{D_0 K_A}{(t + K_A)^2}$ for asymptotic function. It shows that the gradient is constant for linear dispersion; however, in case of asymptotic function, the slope is negative. It is interesting to note that the slope of asymptotic function is equal to LTDD function at initial time and is equal to zero at infinite time. Hence, it is expected that during the initial phase of solute transport, dispersion spreading will be similar for both cases; however, later stage linear dispersion function increases with constant slope and asymptotic function reaches a constant flat line with zero slope.

2.1 Initial and boundary conditions

The initial condition assumes that the porous media is not contaminated and is given as follows:

$$C_m(x, 0) = C_{im}(x, 0) = 0. \quad (4)$$

Following inlet and outlet boundary conditions have been used:

$$C_m(0, t) = \begin{cases} C_0, & 0 < t \leq t_p \\ 0, & t > t_p \end{cases} \quad (5)$$

$$\left. \frac{\partial C_m(x, t)}{\partial x} \right|_{x=L} = 0 \quad (6)$$

where C_0 is concentration (M/L^3) of injected solute source at the inlet of the porous media.

3. Development of numerical model and its validation

In the present model, transport of non-reactive solute through saturated porous media is described using coupled partial differential equations. An implicit finite-difference formulation is used to obtain the numerical solution of MIM transport equation with time-dependent dispersion. The advection term in the mobile transport equation has been discretized using fully implicit first-order upwind scheme and dispersive term in the mobile transport

equation has been discretized using second-order central difference scheme. The temporal terms of both Eqs. (1) and (2) have been discretized using a first-order forward difference scheme. Discretization of partial differential equations for non-reactive solute transport in the MIM domain is presented as follows:

$$R_m \left(\frac{C_{m_i}^{t+1} - C_{m_i}^t}{\Delta t} \right) = \theta_m D_{(t)} \left(\frac{C_{m_{i+1}}^{t+1} - 2C_{m_i}^{t+1} + C_{m_{i-1}}^{t+1}}{\Delta x^2} \right) - v_m \theta_m \left(\frac{C_{m_i}^{t+1} - C_{m_{i-1}}^{t+1}}{\Delta x} \right) - \omega \left(C_{m_i}^{t+1} - C_{im_i}^{t+1} \right) - A_1 C_{m_i}^{t+1} \quad (7)$$

$$R_{im} \left(\frac{C_{im_i}^{t+1} - C_{im_i}^t}{\Delta t} \right) = \omega \left(C_{m_i}^{t+1} - C_{im_i}^{t+1} \right) - A_2 C_{im_i}^{t+1} \quad (8)$$

where

$$R_m = (\theta_m + f \rho_b K_d) \quad (9a)$$

$$R_{im} = (\theta_{im} + (1 - f) \rho_b K_d) \quad (9b)$$

$$A_1 = (\theta_m \mu_{im} + f \rho_b K_d \mu_{sm}) \quad (9c)$$

$$A_2 = (\theta_{im} \mu_{im} + (1 - f) \rho_b K_d \mu_{sim}) \quad (9d)$$

where Δt represents the time step; Δx represents the grid size; t represents the known time and $(t + 1)$ represents the unknown time level.

$$(A_7) C_{m_i}^{t+1} - (A_3 D_{(t)}) C_{m_{i+1}}^{t+1} - (A_3 D_{(t)} + A_4) C_{m_{i-1}}^{t+1} - (A_5) C_{im_i}^{t+1} = C_{m_i}^t \quad (10)$$

$$(A_8) C_{im_i}^{t+1} - (A_9) C_{m_i}^{t+1} = C_{im_i}^t \quad (11)$$

where coefficients are defined as follows:

$$A_3 = \frac{\theta_m}{(\Delta x)^2} \left(\frac{\Delta t}{R_m} \right); \quad A_4 = \frac{v_m \theta_m}{\Delta x} \left(\frac{\Delta t}{R_m} \right);$$

$$A_5 = \frac{\omega \Delta t}{R_m}; \quad A_6 = \frac{A_1 \Delta t}{R_m};$$

$$A_7 = 1 + (2A_3 D_{(t)}) + A_4 + A_5 + A_6;$$

$$A_8 = 1 + \left(\frac{\omega \Delta t}{R_{im}} \right) + \left(\frac{A_2 \Delta t}{R_{im}} \right); \quad A_9 = \left(\frac{\omega \Delta t}{R_{im}} \right)$$

$D_{(t)}$ is the time-dependent dispersion coefficient, which is updated after each time step in the numerical simulation. The discretized partial differential equations for solute transport through MIM domain have been solved using Thomas algorithm. The procedure used for simulation is shown in figure 1.

The presented numerical solution is validated with the solutions of Basha and El-Habel [41] by scaling down MIM into ADE. It is assumed that there is vanishing solute concentration in the porous media initially and a continuous

Figure 1. Flowchart of the computational algorithm to solve solute transport equations of MIM model with time-dependent dispersion.

solute source is present at the input end. For validation, input model parameters used are as follows: $L = 100$ m, saturated porosity = 0.35, pore-water velocity = 0.25 m/day, total time = 200 days, retardation factor (R) = 1, saturated porous media bulk density (ρ_b) = 2.11 g/cm³, maximum dispersion coefficient (D_0) = 1 m²/day, ATDD coefficient (K_A) = 50, effective molecular diffusion coefficient (D_m) = 0 m²/day and first-order decay constant = 0 day⁻¹.

Figure 2 presents the variation of relative concentration for continuous injection at $T = 200$ days. Relative concentration decreases gradually with distance, which is due to the dispersion processes. The numerical model shows good agreement with results obtained by Basha and El-Habel [41].

4. Model application and evaluation

4.1 Simulation of experimental data of chloride transport through stratified porous media

Mobile-immobile models with linear (MIM-LTDD) and asymptotic time-dependent dispersion (MIM-ATDD) are

used to simulate observed BTCs. The experimental data of chloride transport through stratified porous media from Swami *et al* [44] are considered for simulation. The transport parameters such as time-dependent dispersion coefficient (K_A or K_L), maximum dispersion coefficient (D_0) and mass-transfer coefficient (ω) have been optimized for different down-gradient distances using simulation. Experimental BTCs have been simulated at various down-gradient distances (50, 100, 150, 200, 300 and 400 cm) for pore-water velocity (v_m) = 0.121 cm/min.

The experimental process on the stratified porous media has been defined in Swami *et al* [44]. Values of physical input parameters are kept the same, i.e., mass fraction of sorbed phase that equilibrates instantly with the mobile region (f) and dry bulk density (ρ_b) of the porous media have been obtained by empirical relations given by Brusseau *et al* [10]:

$$\theta = \theta_m + \theta_{im} \quad (12a)$$

$$f = (\theta_m / \theta) \quad (12b)$$

Figure 2. Concentration profile for non-reactive solute at time $T = 200$ for $K_A = 50$.

$$\rho_b = f\rho_m + (1-f)\rho_{im} \quad (12c)$$

where ρ_m and ρ_{im} are the density of mobile and immobile regions, respectively. Using these relations, the value of $f = 0.44$ has been used in the simulation of all experiments; $\rho_m = 1.65 \text{ g/cm}^3$ and $\rho_{im} = 1.42 \text{ g/cm}^3$ are the values of density for mobile and immobile regions, respectively. Bulk density (ρ_b) = 1.5212 g/cm^3 has been calculated using Eq. (12c). The values of porosities in mobile and immobile zones obtained, respectively, are $\theta_m = 0.33$ and $\theta_{im} = 0.42$. $L = 400 \text{ cm}$, total simulation time (t) = 10080 min and a pulse duration (t_p) of 2880 min at inlet have been considered.

BTCs at different down-gradient distances are simulated separately for all the dispersion models to observe the influence of travel distance on time-dependent dispersion parameters (D_0 and K_L or K_A). Estimated model parameters at all down-gradient distances for MIML and MIMA models are listed in table 1. Figures 3, 4, 5, 6, 7 and 8 show the simulation of experimental data of chloride obtained at 50, 100, 150, 200, 300 and 400 cm down-gradient

Table 1. Estimated values of parameters at different down-gradient distances.

Distance (cm)	Mass transfer coefficient ω (min^{-1})	MIMA		MIML	
		D_0 (cm^2/min)	K_A (min)	D_0 (cm^2/min)	K_L (min)
50	$2.8\text{E}-04$	1.20	550	1.32	5000
100	$1.7\text{E}-04$	1.40	500	2.00	5000
150	$7.2\text{E}-05$	1.50	450	2.77	4500
200	$4.75\text{E}-05$	3.20	400	4.97	3800
300	$2.95\text{E}-05$	3.20	220	5.04	4400
400	$2.12\text{E}-05$	4.51	200	5.89	4500

Figure 3. Simulation of experimental breakthrough curve of chloride at 50 cm down-gradient distance for $v_m = 0.121 \text{ cm/min}$.

Figure 4. Simulation of experimental breakthrough curve of chloride at 100 cm down-gradient distance for $v_m = 0.121 \text{ cm/min}$.

Figure 5. Simulation of experimental breakthrough curve of chloride at 150 cm down-gradient distance for $v_m = 0.121 \text{ cm/min}$.

Figure 6. Simulation of experimental breakthrough curve of chloride at 200 cm down-gradient distance for $v_m = 0.121$ cm/min.

Figure 7. Simulation of experimental breakthrough curve of chloride at 300 cm down-gradient distance for $v_m = 0.121$ cm/min.

Figure 8. Simulation of experimental breakthrough curve of chloride at 400 cm down-gradient distance for $v_m = 0.121$ cm/min.

Table 2. The goodness of fit obtained from simulation of chloride data.

Model	Fitting criterion	Down-gradient distance (cm)					
		400	300	200	150	100	50
MIMA	r^2	0.98	0.97	0.98	0.98	0.98	0.98
	RMSE	0.034	0.048	0.063	0.060	0.061	0.069
	NSE	0.97	0.96	0.95	0.97	0.96	0.97
MIML	r^2	0.96	0.95	0.95	0.96	0.96	0.96
	RMSE	0.055	0.071	0.094	0.078	0.076	0.089
	NSE	0.93	0.91	0.90	0.94	0.95	0.95

distances. Since early breakthrough and long tails contribute to the skewness of BTCs, log-log plots have been used to demonstrate the model capabilities to simulate at different down-gradient distances. Further, to compare the performance of MIMA and MIML models, root-mean-square-error (RMSE), coefficient of correlation (r^2) and Nash–Sutcliffe efficiency (NSE) coefficient are used as criteria to reflect the goodness of simulation. Table 2 shows the goodness of fitting criterion values for all down-gradient distances.

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (C_{iobs} - C_{isim})^2} \quad (13a)$$

$$r^2 = \left(\frac{\sum_{i=1}^n (C_{iobs} - \bar{C}_{iobs})(C_{isim} - \bar{C}_{isim})}{\sqrt{\sum_{i=1}^n (C_{iobs} - \bar{C}_{iobs})^2} \sqrt{\sum_{i=1}^n (C_{isim} - \bar{C}_{isim})^2}} \right)^2 \quad (13b)$$

$$NSE = 1 - \left(\frac{\sum_{i=1}^n (C_{iobs} - C_{isim})^2}{\sum_{i=1}^n (C_{iobs} - \bar{C}_{iobs})^2} \right) \quad (13c)$$

where C_{iobs} and C_{isim} are the i th observed and simulated concentration, respectively; $\bar{C}_{iobs}$ and $\bar{C}_{isim}$ are the mean of observed and simulated concentration, respectively, and n represents the total number of observations taken at any particular observational point.

A skewed shape of experimental and simulated results has been obtained as shown in figures 3, 4, 5, 6, 7 and 8, which is a clear demonstration that the system is under the strong influence of physical nonequilibrium. In the experimental set-up of Swami *et al* [24], the width of the immobile region is large and that is the reason behind the long tails with a high concentration at the concluding part of the experiments. MIM with time-dependent dispersion has demonstrated capabilities to simulate such complex scenario in pre-asymptotic regime. Figures 3, 4, 5, 6, 7 and 8 show the log-log plot clearly accentuating the minuscule

temporal concentration, which linear plots fail to display, particularly in breakthrough and tailing portions in such cases.

Figure 3 shows the BTC at 50 cm down-gradient distance; the broad peak shows the longer availability of concentration source due to proximity to the source. Hence, initial breakthrough concentration is higher and tailing portion concentration is low compared with other distances, since most of the solute particles tend to elude due to maximum exposure to fresh water source. Both MIML and MIMA demonstrated similar simulation capabilities at 50 and 100 cm; however, MIMA model simulates initial breakthrough and tailing concentrations with slightly higher accuracy compared with MIML.

Figures 5, 6, 7 and 8 show the BTCs at 150–400 cm down-gradient distances; in all the curves a substantial difference between breakthrough time prediction by MIMA and MIML can be observed, where lagging of the latter increases with distance. Observation points of figures 5 and 6 placed at the centre displayed a considerable difference in prediction by MIML and MIMA in tailing portion. Also, it should be noted that the concentration in the tailing portion of the BTCs is higher towards the outlet. These effects are obviously concealed in linear–linear plots representation of BTCs many times. Hence, due to log–log representation, the limitation of MIM model with time- or scale-dependent dispersion model is truly highlighted here; it fails to capture the tailing portion of the BTCs at latter distances. A possible explanation can be that since MIM contains first-order value of mass transfer coefficient, it can be optimized to target only a specific portion of the BTC. As in many of the cases the target concentration is the peak value; hence MIM with first-order mass transfer value will fail to capture the tail portion; however, in this case, it is clear that due to inclusion of time-dependent dispersion, overall capabilities of MIM model can be enhanced to a greater extent.

It is clear from the analysis that high time-dependent dispersion coefficient (K_A) of MIMA model is obtained for the shorter distance from input source, which is attributed to lower overall dispersion coefficient. Value of dispersion coefficient should be higher at large travel distance, which is further attributed to smaller value of time-dependent dispersion coefficient (K_A) at large travel distance. It is evident from table 1 that the MIM with time-dependent dispersion is a powerful tool to capture observed BTCs with a highly complex experimental model with sufficiently large immobile matrix. It is also observed that due to the presence of large immobile matrix, a significant amount of concentration source is stored in an immobile matrix and it keeps on eluding till the infinite time, reaching an asymptotic state. From the BTCs and table 1 it can be concluded that the first-order diffusive mass transfer cannot be a unique value; rather it depends on the distance from the source and the time of experimentation. In the next section, temporal moment analysis is presented to provide insight of the plume behaviour within the media.

5. Temporal moment analysis

In the problem of contaminant transport through heterogeneous porous media, method of moments is often useful to describe the skewed BTCs at a given location. Moment analysis is even found to be a powerful tool for inverse modelling in estimating the transport parameters such as pore-water velocities and dispersion coefficients [46–49]. The difference in hydraulic conductivity causes non-ideal solute transport behaviour through heterogeneous porous media and results in a skewed BTC and higher order of first normalized temporal [50]. The zeroth moment of solute concentration represent the total mass in the system at any time instant. The first and second normalized moment of solute concentration identifies, respectively, the mean breakthrough time and the degree of spreading at any assumed location. For a condition during the experiment when a singular pulse is replaced with a clean source, the zeroth absolute temporal moment of solute concentration will start decreasing with the increase in travel distance [51, 52]. From the moment analysis, it is identified that the total solute mass recovery is less for a larger value of mass-transfer coefficient. Therefore, the performance of MIMA and MIML dispersion models has been evaluated using temporal moment analysis in this study. Also, sensitivity analysis of time-dependent dispersion coefficients (MIMA and MIML) is performed using zeroth, first and second temporal moment of solute concentration.

5.1 Calculation of temporal moments

Temporal moment of solute concentration provides time-averaged response of solute behaviour in the soil [53]. The n th-order absolute temporal moment of a BTC at a location x is defined as

$$M_n = \int_0^T t^n C(x, t) dt \quad (14)$$

where for $n = 0, 1, 2$, obtained moments M_0 , M_1 and M_2 , respectively represent zeroth, first and second absolute temporal moments and T is the total residence time; n th-order normalized temporal moment of solute concentration is given by following equations:

$$\mu_n = \frac{M_n}{M_0} = \frac{\int_0^T t^n C(x, t) dt}{\int_0^T C(x, t) dt} \quad (15)$$

$$T_1(x) = \mu_1 \quad (16)$$

$$T_2(x) = \mu_2 - (\mu_1)^2 \quad (17)$$

where μ_1 and μ_2 are the normalized first and second temporal moments, respectively. $T_1(x)$ and $T_2(x)$ are the first normalized temporal moment and second central temporal moments, respectively. The first normalized temporal moment is descriptor of mean breakthrough time, which is the average time spent by solute molecules inside the porous media. The second central temporal moment represents the variance of the BTC, which provides a measure of solute spreading.

5.2 Comparison of MIMA and MIML using temporal moment analysis

In this section, temporal moment of solute concentration has been compared for different time-dependent functions used with MIM model. The temporal moment analysis technique reveals the behaviour of solute plume through the porous media. Input parameters used for the temporal moment techniques are pore-water velocity (v_m) = 0.121 cm/min, mass transfer coefficient (ω) = $2.12 \times 10^{-5} \text{ min}^{-1}$, $L = 400 \text{ cm}$, total simulation time (t) = 10080 min, a pulse duration (t_p) of 2880 min, $K_A = 200$ and $K_L = 4500$ for MIMA and MIML model, respectively, and $D_0 = 4.51 \text{ cm}^2/\text{min}$ and $D_0 = 5.89 \text{ cm}^2/\text{min}$ for MIMA and MIML model, respectively; figure 9a, b and c presents the zeroth, first and second temporal moments.

Figure 9a shows comparison of the zeroth normalized temporal moment of solute concentration for linear and ATDD functions. It is evident from figure 9a that the zeroth temporal moment of solute concentration decreases linearly with travel distance for both the MIML and MIMA models. However, at large travel distances, zeroth temporal moment of solute concentration for MIMA model attains an asymptotic value while for MIML it keeps on decreasing. Since the system is under the influence of strong physical nonequilibrium and experimental BTC having a long tail at the concluding part of the experiments, it is observed that the total mass recovery at the outlet can be better represented by MIMA compared to MIML. This is due to linear variation of dispersion with time for MIML model in comparison to MIMA model. In MIMA model, dispersion varies non-uniformly with time and reaches to an asymptotic value at higher transport time. The first temporal moment analysis in next figure is carried out to identify the average time spent by solute particles in the system for each distance.

Figure 9b shows the spatial variation of first temporal moment of solute concentration and it is clear that at small travel distance, temporal moment is linear for both the models. At large travel distances, first temporal moment of solute concentration varies non-linearly for both the models, higher in the case of MIML dispersion model. The pattern of the first moment reveals the physical ever-growing nature of the MIML model with time. This shows

Figure 9. (a) Spatial distribution of zeroth temporal moment for MIMA and MIML. (b) Spatial distribution of first normalized temporal moment for MIMA and MIML. (c) Spatial distribution of second temporal moment for MIMA and MIML.

that the applicability of the time-dependent dispersion is appropriate for smaller distances or experimental duration, but for the field scale, it tends to demonstrate nonrealistic representation of the plume behaviour without any upper bound. In the next figure, spatial variation of second temporal moment of solute concentration is analysed for both MIML and MIMA dispersion models.

It is evident from figure 9c that the second temporal moment of solute concentration for MIMA and MIML models increases non-linearly with travel distance. The variance of BTC attains an asymptotic peak value for MIMA at large travel distance; however, it decreases for MIML model. MIML tends to depart from the mean, which is due to its linear dependence on time of experimentation, which affects the plume without any upper bound. The moment analysis provides a useful insight into the plume behavior, which BTCs fall short in describing. From the moment analysis, it can be concluded that the MIML is not useful for higher experimentation time as it shows less mass recovery, higher residence time and a significant departure from the average plume moment.

6. Conclusions

This study presented numerical solution of MIM model with arbitrary LTDD and ATDD functions. In the case of time-dependent dispersion function, it is emphasized that the mean travel distance and space coordinate are not interchangeable. MIM model with time-dependent dispersion function showed enhanced accuracy for simulating experimental BTCs of non-reactive solute transport through stratified porous media. However, it is revealed in the log–log plot that the MIM incorporating time-dependent dispersion function fails to capture the tailing portion of BTCs. MIM embraced with time-dependent dispersion is a powerful tool, but one must prioritize the target concentration and optimize the model parameters accordingly. In this study, capturing peak concentration has been the objective function while simulating experimental BTCs. MIM model with ATDD demonstrated enhanced accuracy compared with linear dispersion (LTDD) model. Temporal moment analysis revealed the limitation of MIML at higher travel distances and endorsed the use of MIMA due to its realistic representation of spreading, skewness and mean travel time of solute plume. In future, such skewed BTCs can be analysed for rising and falling limb separately to get an insight about the first-order mass transfer coefficient in MIM incorporating time-dependent dispersion function. Additionally, in future the transport of reactive solutes through heterogeneous porous media can also be included for a realistic scenario.

List of symbols

C_0 injected concentration of solute source (M/L^3)

C_m	solute concentration in the mobile region at any time t (M/L^3)
C_{im}	solute concentration in the immobile region at any time t (M/L^3)
$D_{(t)}$	time-dependent hydrodynamic dispersion coefficient along the flow velocity (L^2/T)
D_0	maximum dispersion coefficient (L^2/T)
D_m	effective diffusion coefficient (L^2/T)
K_A	asymptotic time-dependent dispersion coefficient (T)
K_L	linear time-dependent dispersion coefficient (T)
M_0	zeroth absolute temporal moment of solute concentration
M_1	first absolute temporal moment of solute concentration
M_2	second absolute temporal moment of solute concentration
$T_1(x)$	first normalized temporal moment of solute concentration
$T_2(x)$	second central temporal moment of solute concentration
θ_m	volumetric water content of the mobile region
θ_{im}	volumetric water content of the immobile region
θ	total volumetric water content of the porous media
v_m	mobile pore water velocity (L/T)
q	flow rate (L/T)
ω	first-order mass transfer coefficient (T^{-1})
f	fraction of adsorption sites that equilibrate instantly with the mobile regions
μ_{lm}	first-order decay coefficient for degradation of solute in the mobile solution phase (T^{-1})
μ_{lim}	first-order decay coefficient for degradation of solute in the immobile solution phase (T^{-1})
μ_{sm}	first-order decay coefficient for degradation of solute in the mobile region adsorbed solid phase (T^{-1})
μ_{sim}	first-order decay coefficient for degradation of solute in the immobile region adsorbed solid phase (T^{-1})
μ_1	first normalized temporal moment of solute concentration
μ_2	second normalized temporal moment of solute concentration
K_d	distribution coefficient of the linear sorption proc (L^3/M)
ρ_b	bulk density of the porous medium (M/L^3)
x	spatial coordinate taken in the direction of the fluid flow (L)
ADE	advection–dispersion equation
ATDD	asymptotic time-dependent dispersion function
LTDD	linear time-dependent dispersion function
MIM	mobile–immobile model
MIMA	mobile–immobile model with asymptotic time-dependent dispersion function

MIML mobile-immobile model with linear time-dependent dispersion function

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