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Change in macroscopic concentration at the interface between different materials: Continuous or discontinuous

Xiaoxian Zhang,¹ Xuebin Qi,² and Dongmei Qiao²

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[1] There have been conjectures that a spatial average could result in a volume-average concentration which is no longer continuous at sharp interfaces between different materials. However, convincing experimental evidence showing the existence of such a discontinuity is not available because of the difficulty associated with measuring solute concentration in the void space within a porous medium. In this paper we used pore-scale simulations to explore the change in macroscopic concentration when solute moves from one material into another. Water flow through the void space was assumed to be laminar, and solute transport consisted of molecular diffusion and advection; both were simulated using the lattice Boltzmann equation methods. To accurately represent the fluid-solid interface, the multiple-relaxation-time lattice Boltzmann equation method was used to simulate fluid flow. We first simulated solute transport in a 3D column with one half packed with fine glass beads and the other half with coarse glass beads. The simulated solute concentration and solute flux at pore scale were then spatially averaged to produce volume-average and flux-average concentration profiles, respectively, in attempts to understand if solute accumulates at the media interface when moving from one medium into another. The results revealed that, when solute migrated from the coarse medium into the fine medium, it did accumulate at the media interface; we also found mass accumulation at the reservoir-column interface. Such accumulations made solute take more time to break through the column when flowing from the coarse medium to the fine medium than from the fine medium to the coarse medium. We also simulated solute movement in an idealized 2D column packed with different rectangular solids and with high porosity; the results indicated that, although the dispersive properties of the two media differed considerably, there was no mass accumulation and the macroscopic concentration was found to be continuous at the media interface. These simulated results suggest that a sharp change in material properties with moderate porosity will likely lead to a mass accumulation, but knowing the transport properties of the two materials alone is not sufficient to determine if a mass accumulation could develop. What causes mass accumulations appears to be some microstructures in the vicinity of the interface, which cannot be accounted for by the macroscopic transport parameters of each of the two media.

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1. Introduction

[2] Natural porous materials are hierarchically heterogeneous, and how to deal with such heterogeneities in modeling chemical transport has been studied extensively. The continuous time random walk models and stochastic hydrology developed over the past three decades are attempts to account for the heterogeneities that are not explicitly resolved in a model [Berkowitz *et al.*, 2006; Dagan, 1982; Gelhar and Axness, 1983; Neuman and Tartakovsky, 2009]. In heterogeneous media, the transport parameters could endure an abrupt change at an interface

between two different materials, while in most stochastic analysis the solute concentration across such interfaces is often assumed to be continuous. It has been reasoned that although solute concentration is continuous in the void space at pore scale, a spatial average could result in a volume-average concentration which is no longer continuous at the sharp interfaces due to possible mass accumulations when solute moves from one medium into another [Berkowitz *et al.*, 2009; Hornung *et al.*, 2005; Marseguerra and Zoia, 2006]. Such mass accumulations could have a significant effect on chemical migration, rendering its movement into an anomalous dispersion. However, experimental evidence showing the existence of mass accumulations at media interfaces is not available.

[3] The earlier concern over a possible development of mass accumulation (and hence discontinuous concentration) was in analyzing the column displacement experiments where the contact between the column and the inlet and

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outlet reservoirs gives rise to two abrupt interfaces. It was argued that the concentration could become discontinuous due to a mass accumulation at these two interfaces [van Genuchten and Parker, 1984]. Since then, considerable efforts have been made, both experimentally and theoretically, to understand solute behavior at sharp interfaces between different materials [Ahrenholz et al., 2008; Berkowitz et al., 2009; Leij et al., 1991; Marseguerra and Zoia, 2006; Novakowski, 1992a; Sternberg, 2004]. However, because it is difficult to noninvasively measure solute concentration in the void space, the available results are not conclusive as the verification of a possible mass accumulation was to test if the measured breakthrough curves could be described by the classical advection-dispersion equation (ADE). For example, the column experiments of Zhou and Selim [2001] indicated that the ADE can describe the movement of both reactive and nonreactive chemicals through a two-layer system by assuming a continuous concentration. In contrast, the work of Sternberg [2004] revealed that the measured behavior of the concentration profiles along the column differed from that predicted by the ADE, indicating a mass accumulation at the media interface. However, it must be pointed out that, even though a breakthrough curve cannot be described by ADE, it does not necessarily mean a development of discontinuous concentration, as the recent work of Cortis et al. [2004] showed that even in homogeneous media the solute movement could become anomalous.

[4] A number of random walk models based on numerical particle-track methods have been developed to simulate solute transport in layered systems by assuming the particle movement to be either Fickian [LaBolle and Zhang, 2006; LaBolle et al., 1996, 2000; Lim, 2006] or anomalous [Hornung et al., 2005; Marseguerra and Zoia, 2007]. However, most of these models simulated the particle movement above the representative elementary volume (REV) scales, and the layered system was solely characterized by differentiating the dispersive and hydraulic properties of the two adjacent media. Although these random walk models found evidence of mass accumulation at media interfaces, it still remains unclear if a difference in the dispersive properties of two materials alone would necessarily give rise to a mass accumulation and hence discontinuous concentration.

[5] A recent column displacement experiment reported by Berkowitz et al. [2009] renewed the interest in a possible development of discontinuous resident concentration at sharp interfaces. The results of Berkowitz et al. [2009] revealed that the time it took solute to move from one end to another of a layered column was not constant but was dependent on flow direction and that the difference in solute arrival time increased as water velocity decreased. Such a phenomenon cannot be explained by assuming that the solute movement in each medium is Fickian and that the resident concentration at the interface of the two media is continuous. Berkowitz et al. [2009] then conjectured that there might be a mass accumulation at the interface, rendering solute transport into an anomalous dispersion. Cortis and Zoia [2009] derived a continuous time random walk model to explain the dependence of solute arrival time on flow direction by assuming that the jump length of solute particles is asymmetrically distributed in the vicinity of the sharp interface and that the skewness of the distribution

shifts as flow direction changes. The model of Cortis and Zoia [2009] can reproduce the breakthrough curves observed by Berkowitz et al. [2009], but it appears that it still cannot answer the above question of whether a difference in the macroscopic transport properties of two adjacent media alone can quantify the mass accumulation.

[6] Solute movement in heterogeneous media is a complicated process, driven by pore geometry and the connectedness of pores of different sizes. Since directly measuring solute concentration in the void space is infeasible, pore-scale modeling has been used increasingly as a complement to help in understanding some transport processes which remained unknown otherwise [Bijeljic and Blunt, 2006; Kang et al., 2006; Li et al., 2006]. The purpose of this paper is to use pore-scale simulations to investigate if mass accumulations occur when solute moves from one medium into another. Both a 3D column packed with glass beads of different diameters and a 2D column packed with different rectangular solids were simulated. Water flow through the void space was simulated by the multiple-relaxation-time lattice Boltzmann equation (LBE) method in order to correctly recover the water-solid boundary. The simulated concentration and solute flux at pore scale were then averaged spatially to produce volume-average and flux-average concentration profiles along the column to investigate if the solute accumulates at the media interface. In particular, we examined if an abrupt change in material properties will necessarily lead to mass accumulations and if such mass accumulations will make solute arrival time dependent on flow direction.

2. Model Description

2.1. Model for Fluid Flow

[7] The earlier LBE models for simulating pore-scale fluid flow in porous media were based on the single-relaxation-time (SRT) model [Knutson et al., 2001; Pan et al., 2004]. Recent study has found that the SRT model cannot correctly represent the location of the water-solid boundary [d'Humieres and Ginzburg, 2009]. As a result, the permeability estimated from SRT simulations of fluid flow at pore scale is not a constant but increases, unrealistically, with fluid viscosity. To accurately recover the fluid-solid boundary, the multiple-relaxation-time (MRT) model has been developed [Lallemand and Luo, 2000]. In the MRT model, the fluid particle distribution functions are transformed into a space of moments. Since each moment represents a physical quantity, the MRT model offers a more convenient way to calculate the collision as it can use different relaxation times for different physical quantities, and is therefore more robust. The MRT model can be derived by applying a transform matrix to the original LBE model proposed by Qian et al. [1992] as follows [d'Humieres et al., 2002]:

$$f_i(\mathbf{x} + \delta t \xi_i, t + \delta t) = f_i(\mathbf{x}, t) + \mathbf{M}^{-1} \mathbf{S} \mathbf{M} [f_i^{eq}(\mathbf{x}, t) - f_i(\mathbf{x}, t)], \quad (1)$$

where $f_i(\mathbf{x}, t)$ is the particle distribution function at location $\mathbf{x}$ and time t , moving with velocity ξ_i ; $f_i^{eq}(\mathbf{x}, t)$ is the equilibrium distribution function, the value of $f_i(\mathbf{x}, t)$ at the equilibrium state; $\mathbf{M}$ is the transform matrix, which is given by d'Humieres et al. [2002] for the D3Q19 LBE model used

in this work; and $\mathbf{S}$ is a collision matrix. The transformation $\mathbf{m} = \mathbf{M}\mathbf{f}$ transforms the particle distribution functions $\mathbf{f} = (f_0, f_1, f_2, f_3, f_4, f_5, f_6, f_7, f_8, f_9, f_{10}, f_{11}, f_{12}, f_{13}, f_{14}, f_{15}, f_{16}, f_{17}, f_{18})$ into moments; the collision matrix $\mathbf{S}$ is diagonal and its diagonal terms are given by

$$\mathbf{S} = (s_0, s_1, s_2, s_3, s_4, s_5, s_6, s_7, s_8, s_9, s_{10}, s_{11}, s_{12}, s_{13}, s_{14}, s_{15}, s_{16}, s_{17}, s_{18})^T, \quad (2)$$

where

$$\begin{aligned} s_0 &= s_3 = s_5 = s_7 = 0, \\ s_1 &= s_2 = s_9 = s_{15} = 1/\tau, \\ s_4 &= s_6 = s_8 = s_{16} = s_{18} = 8(2 - 1/\tau)/(8 - 1/\tau). \end{aligned} \quad (3)$$

[8] The kinematic viscosity of the fluid in the above MRT model is determined by $\nu = \delta x^2(\tau - 0.5)/6\delta t$, where δx is the size of the cubic volumetric pixel (voxel) and δt is a time step during which the particle moves from one voxel into another.

[9] Like the SRT model, the MRT model also involves a collision step and a streaming step to advance one time step. The collision is performed in the moment space as $\mathbf{m}^* = \mathbf{S}(\mathbf{m}^{eq} - \mathbf{m})$, in which $\mathbf{m}^{eq} = \mathbf{M}\mathbf{f}^{eq}$ is given by

$$\begin{aligned} m_0^{eq} &= \rho, \\ m_1^{eq} &= -11\rho + 19(j_x^2 + j_y^2 + j_z^2)/\rho_0, \\ m_2^{eq} &= 3\rho - 5.5(j_x^2 + j_y^2 + j_z^2)/\rho_0, \\ m_3^{eq} &= j_x, \quad m_5^{eq} = j_y, \quad m_7^{eq} = j_z, \\ m_4^{eq} &= -2j_x/3, \quad m_6^{eq} = -2j_y/3, \quad m_8^{eq} = -2j_z/3, \\ m_9^{eq} &= (2j_z^2 - j_y^2 - j_x^2)/\rho_0, \quad m_{10}^{eq} = (2j_z^2 - j_y^2 - j_x^2)/2\rho_0, \\ m_{11}^{eq} &= (j_y^2 - j_z^2)/\rho_0, \quad m_{12}^{eq} = (j_y^2 - j_z^2)/2\rho_0, \\ m_{13}^{eq} &= j_x j_y / \rho_0, \quad m_{14}^{eq} = j_y j_z / \rho_0, \quad m_{15}^{eq} = j_x j_z / \rho_0, \\ m_{16}^{eq} &= m_{17}^{eq} = m_{18}^{eq} = 0. \end{aligned} \quad (4)$$

[10] The fluid density ρ and fluid momentum $\mathbf{j}$ in (4) are calculated from

$$\begin{aligned} \rho &= \sum_{i=0}^{18} f_i, \\ \mathbf{j} &= \rho_0 \mathbf{u} = \sum_{i=1}^{18} f_i \xi_i, \end{aligned} \quad (5)$$

where ρ_0 is a mean density to ensure that the above LBE model recovers an incompressible fluid when flow reaches steady state in which the pressure is given by $p = \rho \delta x^2 / 3 \delta t^2$. After the collision, the collision result $\mathbf{m}^* = \mathbf{S}(\mathbf{m}^{eq} - \mathbf{m})$ is transformed back to the particle distribution functions as $\mathbf{f}^* = \mathbf{M}^{-1} \mathbf{m}^*$, and $\mathbf{f} + \mathbf{f}^*$ is then streamed from one voxel into another based on (1). Therefore, the ways to treat the

fluid-solid boundaries in MRT are the same as those in the SMT, which were solved by the bounce-back method as explained in our previous work [Zhang *et al.*, 2005]. The particle distribution functions and the associated moments were located at the center of each voxel to ensure that the bounce-back method is second-order accurate.

2.2. Model for Solute Transport

[11] Solute transport through the void space was also simulated using the LBE model. Similar to water flow, the LBE model for solute transport is also to track the movement and collision of a number of solute particles. The movement of each particle is described by the following equation:

$$g_i(\mathbf{x} + \delta t \xi_i, t + \delta t) = g_i(\mathbf{x}, t) + \frac{1}{\tau_c} [g_i^{eq}(\mathbf{x}, t) - g_i(\mathbf{x}, t)], \quad (6)$$

where $g_i(\mathbf{x}, t)$ is the mass of the solute particle at location $\mathbf{x}$ and time t , which moves with velocity ξ_i ; $g_i^{eq}(\mathbf{x}, t)$ is the value of $g_i(\mathbf{x}, t)$ at equilibrium; and τ_c is a dimensionless parameter that controls the rate of $g_i(\mathbf{x}, t)$ approaching $g_i^{eq}(\mathbf{x}, t)$. For solute transport, the concentration is the only variable to be simulated. To improve computational efficiency, we allow the solute particles to move only in seven directions with velocities $\xi_0 = (0, 0, 0)$, $\xi_{1,2} = (\pm \delta x / \delta t, 0, 0)$, $\xi_{3,4} = (0, \pm \delta y / \delta t, 0)$, and $\xi_{5,6} = (0, 0, \pm \delta z / \delta t)$. As shown previously [Kang *et al.*, 2007], the associated equilibrium distribution function for particle moving with velocity ξ_i is

$$g_i^{eq}(c, \mathbf{u}) = w_i c [1 + 3.5 \xi_i \cdot \mathbf{u}], \quad (7)$$

where the weighting coefficient $w_i = 1/7$, $\mathbf{u}$ is the bulk fluid velocity calculated from (5), and c is the concentration, calculated from $c = \sum_{i=0}^6 g_i(\mathbf{x}, t) = \sum_{i=0}^6 g_i^{eq}(\mathbf{x}, t)$. As proven by Zhang *et al.* [2008], the above LBE model simulates solute transport in a velocity field of $\mathbf{u}$ with a diffusion coefficient of $D_0 = \delta x^2(\tau_c - 0.5)/3.5\delta t$.

[12] The LBE model for solute also involves a collision step and a streaming step to advance one time step. The collision step is to calculate the right-hand side of (6) as $g_i(\mathbf{x}, t)^* = g_i(\mathbf{x}, t) - [g_i(\mathbf{x}, t) - g_i^{eq}(\mathbf{x}, t)]/\tau_c$, and the streaming step is to move the collision result to $\mathbf{x} + \delta t \xi_i$ at the end of each time step to become $g_i(\mathbf{x} + \delta t \xi_i, t + \delta t) = g_i(\mathbf{x}, t)^*$. Similar to fluid flow, the distribution functions of solute particles were also located at the center of each voxel, and the solute-solid interface was solved by the bounce-back method.

2.3. Calculation of Solute Flux at Pore Scale

[13] From the way the LBE model works, it can be seen that the solute flux at each voxel can be directly calculated from all the particles present in the voxel. However, unlike the LBE model for fluid flow where the collision conserves both momentum and mass, the collision in the LBE model for solute transport, as shown in the appendix, conserves only mass due to the diffusion. As a result, the momentum of the solute particles is not equivalent to solute flux. We assumed that the solute movement through the void space is a Brownian motion, which can be described by the advection-diffusion equation. As proven in the appendix,

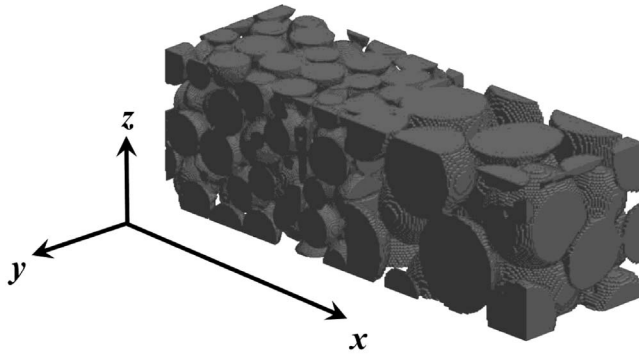


Figure 1. Image of the two-layer system used for the 3D simulations.

under this condition the three components of the solute flux in each voxel can be calculated as follows:

$$\begin{aligned} q_x &= (f_1 - f_2)(1 - 0.5/\tau_c) + 0.5u_x c/\tau_c, \\ q_y &= (f_3 - f_4)(1 - 0.5/\tau_c) + 0.5u_y c/\tau_c, \\ q_z &= (f_5 - f_6)(1 - 0.5/\tau_c) + 0.5u_z c/\tau_c. \end{aligned} \quad (8)$$

[14] We validated (8) against the movement of a pulse of tracer in three dimensions within a velocity field of $u_x = 0.1$ and $u_y = u_z = 0$ with a molecular diffusion coefficient of $D_0 = 0.143$, both in lattice units. The solute flux calculated from the analytical solution agreed well with the LBE simulations (results not presented) calculated from (8).

3. Simulations

[15] Figure 1 shows the 3D column simulated in this paper. It was based on the packing of glass beads used by *Chen et al.* [2009]. The three-dimensional image was acquired by X-ray computed tomography [*Chen et al.*, 2008], and the average diameter of the glass beads is 200 μm . The original image used by *Chen et al.* [2009] was uniform, and we made the two-layer system by enlarging the original image 2 times in all directions and then sticking the original and the enlarged images together prior to trimming it to the image shown in Figure 1. The average porosity of both the fine and the coarse media is approximately 39%, and the length of each medium is 230 voxels. To mimic the column displacement experiments, 10 layers of liquid were added to each end of the column in the x direction to represent the inlet and outlet reservoirs. The final length of the column used for simulations is therefore 480 voxels in the x direction as shown in Figure 1. Overall, the size of the simulated column is $480 \times 150 \times 150$, and the number of void voxels is 4.1 million.

[16] Fluid flow through the column was driven by a pressure drop imposed in the x direction by keeping constant pressures at the inlet and the outlet, respectively. Different pore-water velocities could be simulated by changing the pressure drop. The other four faces of the column were treated as periodic boundaries in which any particle exiting from one face of the column was returned to the column through its opposite face without changing its mass and

momentum. The displacement experiments were conducted once the fluid flow was deemed to have reached steady state. The tracer was injected into the inlet reservoir instantly in such a way that the tracer concentration in the first five layers of the reservoir was 1000 in lattice unit. The tracer was then flushed by tracer-free fluid by keeping the velocity field in the reservoir and the column unchanged. In all simulations, the inlet boundary was treated as an impermeable boundary for solute and the outlet boundary was treated as an adsorbing boundary where the concentration gradient was assumed to be zero; both boundaries were solved using the method proposed in our previous work [*Zhang et al.*, 2002]. During each simulation, both resident concentration and solute flux at each fluid voxel were sampled; they were then averaged in the y - z planes as shown in Figure 1 to generate volume-average and flux-average concentrations, respectively, in the x direction. The volume-average concentration (referred to as “resident concentration” hereafter) and the flux-average concentration (referred to as “flux concentration” hereafter) were calculated from

$$C(x, t) = \sum_{k=1}^{N_z(x)} \sum_{i=1}^{N_y(x)} c(x, y_i, z_k) / N_y(x) N_z(x) \quad (9)$$

and

$$C_f(x, t) = \sum_{k=1}^{N_z(x)} \sum_{i=1}^{N_y(x)} q_x(x, y_i, z_k) / \sum_{k=1}^{N_z(x)} \sum_{i=1}^{N_y(x)} u_x(x, y_i, z_k), \quad (10)$$

respectively, where x is the distance from the inlet boundary, $N_y(x)$ and $N_z(x)$ are the number of pore voxels in the y and z directions, respectively, in a y - z plane at location x as shown in Figure 1; $c(x, y_i, z_k, t)$ is the concentration at the voxel located at (x, y_i, z_k) and time t , and $q_x(x, y_i, z_k, t)$ is the x component of solute flux at the voxel located at (x, y_i, z_k) and time t . In each simulation, the breakthrough curve at the bottom of the column was calculated from (10) by setting $x = L$, where L is the length of the column in the x direction. In the following analysis, the time t is made dimensionless by $T' = tU/L$, where U is the average water velocity in the x direction.

4. Result Analysis

4.1. Spatial Distribution of the Flux Concentration

[17] The three flux components calculated by (8) are the mass of solute moving in the x , y , and z directions in each fluid voxel. The flux concentration calculated by (10) is the ratio between the mass of solute and the volume of fluid flowing through the y - z plane as shown in Figure 1 during a period of unit time. Because of the mass conservation requirement for both solute and fluid, the flux concentration calculated by (10) must be continuous, regardless of the media structure and water flow direction. As an example to illustrate that the model correctly captures this, Figure 2 shows the dimensionless flux concentration profiles calculated from simulations with an averaged pore-water velocity of $U = 0.0175$ and a molecular diffusion coefficient of $D_0 = 0.1429$, both measured in lattice units. In Figure 2 and what follows, the concentration is made dimensionless by $C' = C/C_0$, where C_0 is the initial concentration of the solute injected into the inlet reservoir. It is evident that the flux

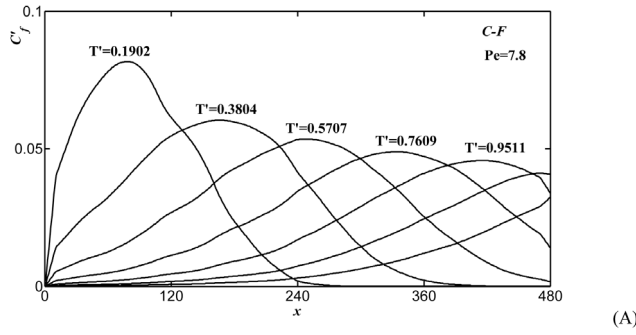


Figure 2. Dimensionless flux concentration for solute transport through the image shown in Figure 1 when water flowed in the C-F direction. The media interface was at $x = 240$.

concentration is continuous at the interface between the two media, as well as at the two reservoir-column interfaces.

4.2. Spatial Distribution of the Resident Concentration

[18] Figure 3 shows the distribution of the dimensionless concentration along the column for average velocity of $U = 0.0175$ and Peclet number $Pe = d_0 U / D_0 = 7.8$, where d_0 ($d_0 = 64$) is the average diameter of the glass beads and $D_0 = 0.143$ is the molecular diffusion coefficient. As shown in Figure 3A, when solute moves from the coarse medium to the fine medium (referred to as “C-F” hereafter), there is a considerable mass accumulation at the media interface as well as at the reservoir-column interfaces. Although the solute also accumulated at these two interfaces when flowing from the fine to the coarse media (referred to as “F-C” hereafter), the accumulation is less significant, as schematically illustrated in Figure 3B. These are consistent with the conjectures of Berkowitz *et al.* [2009] that when solute migrates in the C-F direction, it encounters extra difficulty and thus accumulates, giving rise to a discontinuous resident concentration. Because of such mass accumulations, the time it took the solute to break through the column was longer when moving in the C-F direction than in the F-C direction as shown in Figure 3C. This is again consistent with the experimental results of Berkowitz *et al.* [2009] and the theoretical simulations of Cortis and Zoia [2009].

[19] We also investigated the impact of the Pe number on mass accumulations at the media interface and reservoir-column interfaces. The simulations were carried out under the same velocity field as in the above example but by reducing the molecular diffusion coefficient to 0.0357, giving a Pe number of 31.2. The resident concentration profiles are shown in Figure 4. It is evident that the mass accumulation indeed became less significant at the media interface when the Pe number increased from 7.8 to 31.2, consistent with the conjecture of Berkowitz *et al.* [2009]. The simulated results revealed that, with an increase in Pe number, there was also an increase in mass accumulation at the reservoir-column interface. Such a mass accumulation made the breakthrough curves measured under different flow directions continue to differ considerably as shown in Figure 4C.

[20] The reason there is an increase in mass accumulation at the inlet reservoir as the molecular diffusion decreases is

because the tracer was uniformly applied into the reservoir. Since the surfaces of the glass beads at the reservoir-column interface are barriers to water flow, the water velocity in the inlet reservoir is highly nonuniform. The simulated velocity field indicated that the water in the regions between the surfaces of glass beads and the inlet boundary was much less mobile or even stagnant. Such less mobile and stagnant water made the tracer initially applied into this region difficult to move into regions where water is more mobile with a decrease in molecular diffusion, thereby giving rise to an increased mass accumulation at the column-reservoir interface.

[21] The way to apply the tracer into the inlet reservoir in column displacement experiments could vary. To show how this might affect solute movement (also to be more consistent with the experiment of Berkowitz *et al.* [2009]), we assumed that the tracer is not uniformly applied into the inlet reservoir, but is proportional to the velocity at each voxel at the inlet boundary as follows:

$$C(y_j, z_j) = \frac{M \sqrt{u_x^2(y_j, z_j) + u_y^2(y_j, z_j) + u_z^2(y_j, z_j)}}{\sum_{i=1}^N \sqrt{u_x^2(y_i, z_i) + u_y^2(y_i, z_i) + u_z^2(y_i, z_i)}}, \quad (11)$$

where M is the mass of tracer applied to the inlet reservoir, N is the number of voxels at the inlet boundary, and (y_j, z_j) is the coordinate of the center of the j th voxel at the inlet boundary. Simulations were carried out with the same velocity $U = 0.026$ and two diffusion coefficients, 0.143 and 0.0429; the associated Pe numbers are 10.9 and 36.3, respectively. Figures 5A and 5B show the resident concentration distributions simulated with the two Pe numbers. It is evident that, with an increase in Pe number, the mass accumulation at both the reservoir-column interface and the media interface decreases. Because of the decrease in mass accumulation at the column-reservoir interface, the differences between the breakthrough curves measured under different flow directions also become less significant in comparison with that shown in Figure 4. Further, Figures 5C and 5D indicate that when the Pe number increased from 10.9 to 36.3 the breakthrough curves measured under different flow directions are closer to each other, consistent with the experimental result of Berkowitz *et al.* [2009]. Because of the limitation of the numerical method, we were unable to further increase the Pe number.

4.3. Solute Movement in Stratified Media with High Porosity

[22] The results of the above simulations indicated that, when solute moved from one medium into another, there was a mass accumulation at the media interface, and such accumulation leads to a discontinuous resident concentration. In addition, we also found mass accumulation at the reservoir-column interface. These mass accumulations resulted in the breakthrough curve dependent on flow direction in that it took more time for the solute to break through the column when flowing in the C-F direction than in the F-C direction.

[23] In practice, it might be interest to know if the mass accumulation at the media interface can be fully characterized by the transport parameters of the two media. To investigate this, we simulated solute movement in an idealized 2D

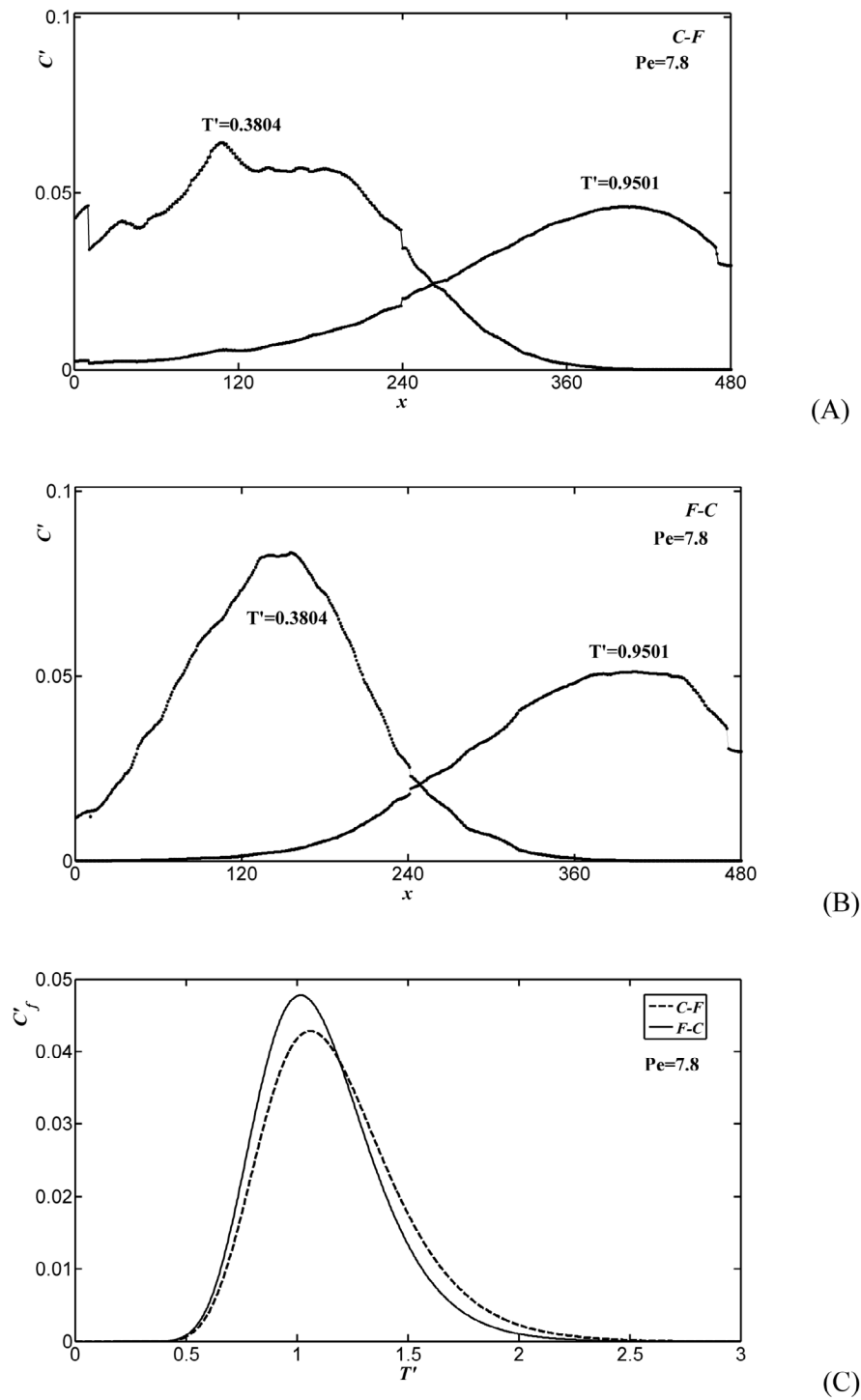


Figure 3. Mass accumulation at the media interface ($x = 240$) and at the reservoir-column interface for solute moving (A) in the C-F direction and (B) in the F-C direction, as well as (C) their impact on break-through curves, when tracer was uniformly applied into the inlet reservoir.

column with high porosity as shown in Figure 6. The column was packed with different rectangular solids in such a way that the porosity is a constant along the flow direction. The length and width of the fine and coarse media are the same, both being 1995 and 252 pixels, respectively; the porosity is 64.9%. In all simulations, 20 layers of fluid were added to each end of the column to represent the inlet and

outlet reservoirs. Overall, the length of the column was 4030 pixels. Fluid flow through the column was also driven by a pressure drop along the column. The simulation conditions were the same as in the 3D example except that we did not allow the tracer to accumulate at the reservoir-column interface. Two velocities, 0.0107 and 0.0524, with associated Pe number of 1.31 and 6.42, respectively, were

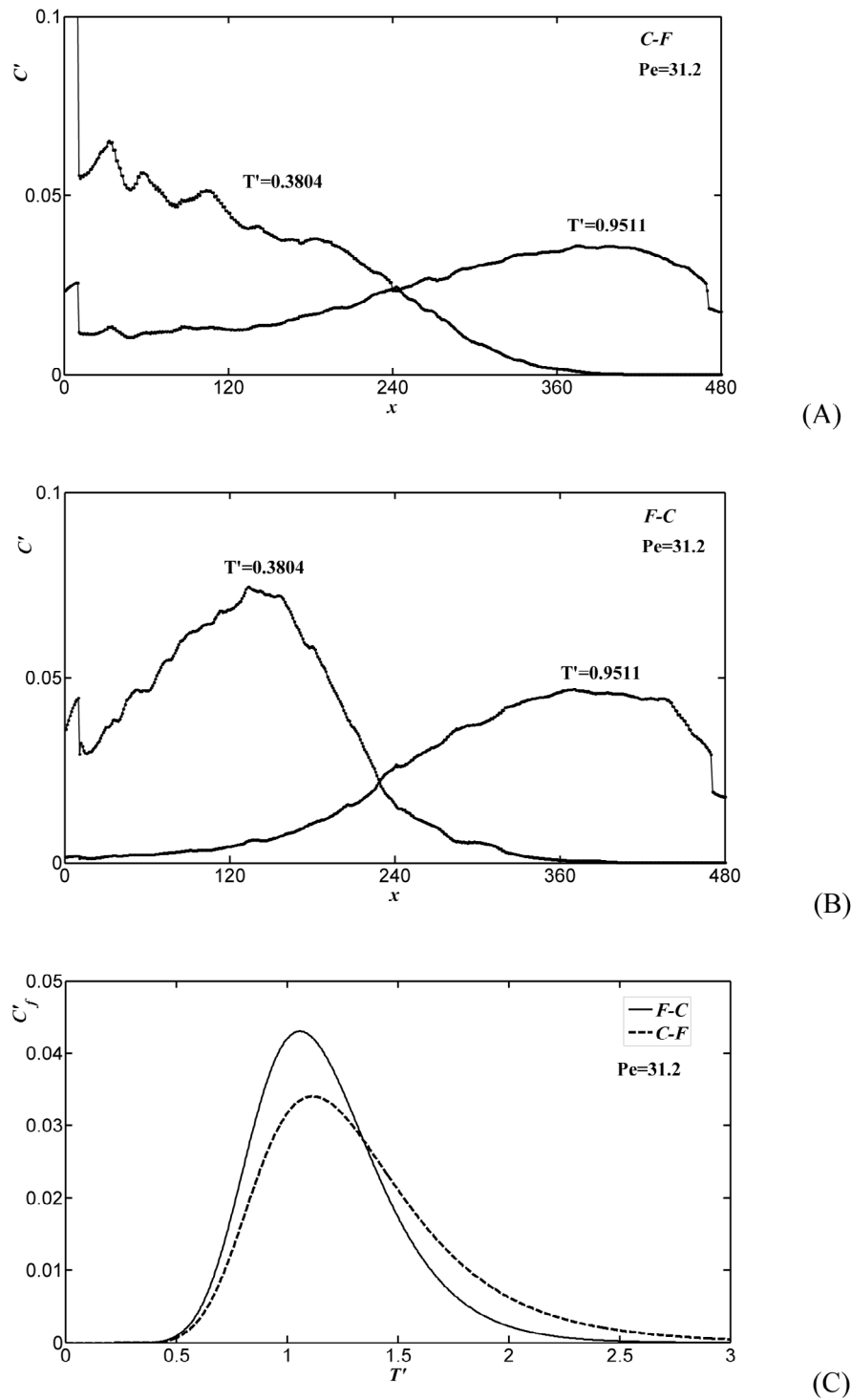


Figure 4. Schematic illustration of the impact of an increase in Pe number on mass accumulations at the media interface ($x = 240$) and at the reservoir-column interface for solute moving (A) in the C-F direction and (B) in the F-C direction, as well as (C) their impact on the breakthrough curves, when the tracer was uniformly applied into the inlet reservoir.

simulated; the Pe number was defined as $Pe = LU/D_0$, where L is the average width of the rectangular solids shown in Figure 6. For each velocity, the tracer movement in the fine and coarse media was simulated separately, and the resident concentration was found to be Gaussian. The associated hydrodynamic dispersion coefficients for each

medium were estimated using the moment method based on the simulated resident concentration; the results are shown in Table 1 for each of the two Pe numbers.

[24] Figure 7A shows the resident concentration distributions along the column when water flowed in the C-F direction. It is evident that, although the dispersive proper-

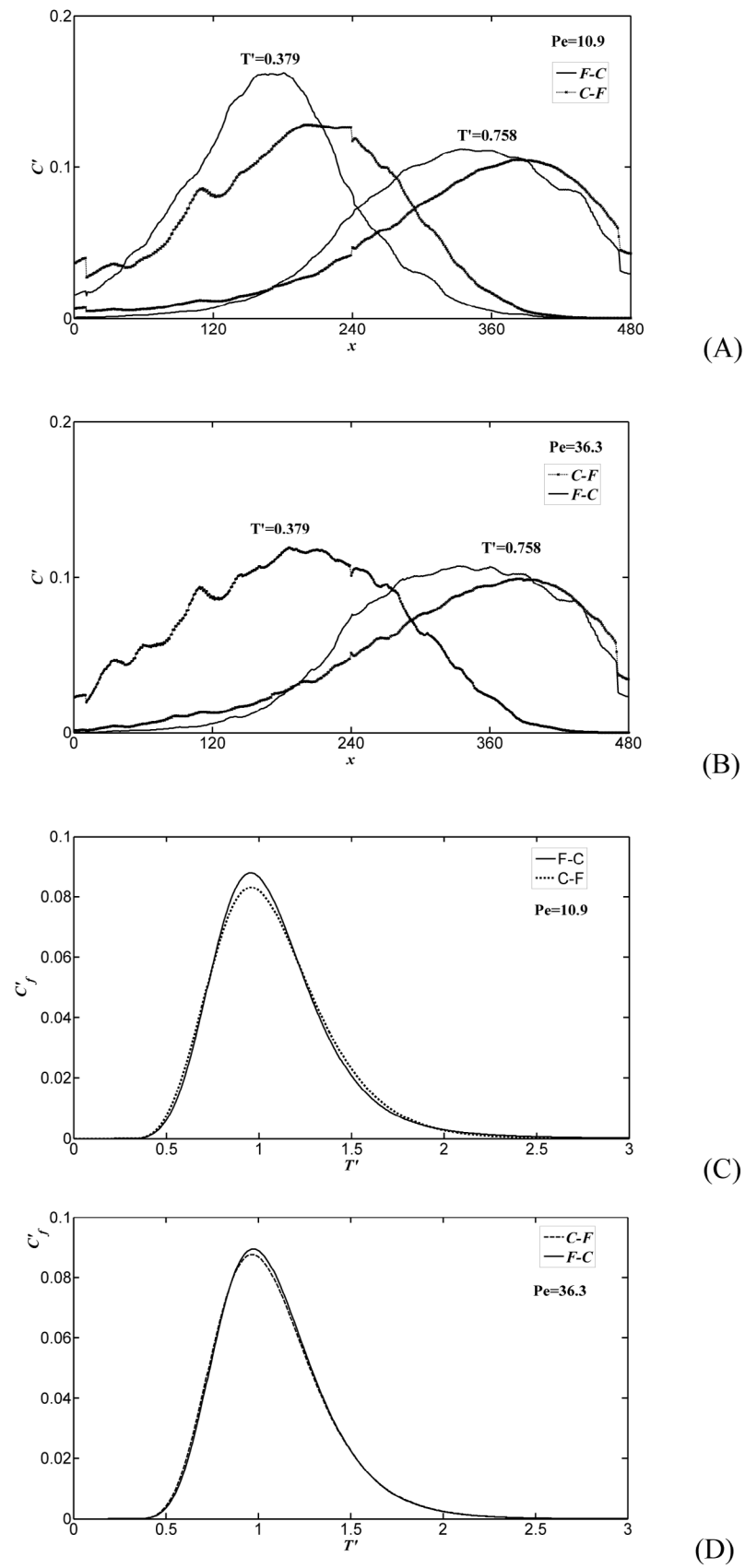


Figure 5. Schematic illustration of the effect of Pe number (A, B) on the mass accumulation at the reservoir-column and media interfaces and (C, D) on the breakthrough curves when the tracer was not uniformly applied into the inlet reservoir.

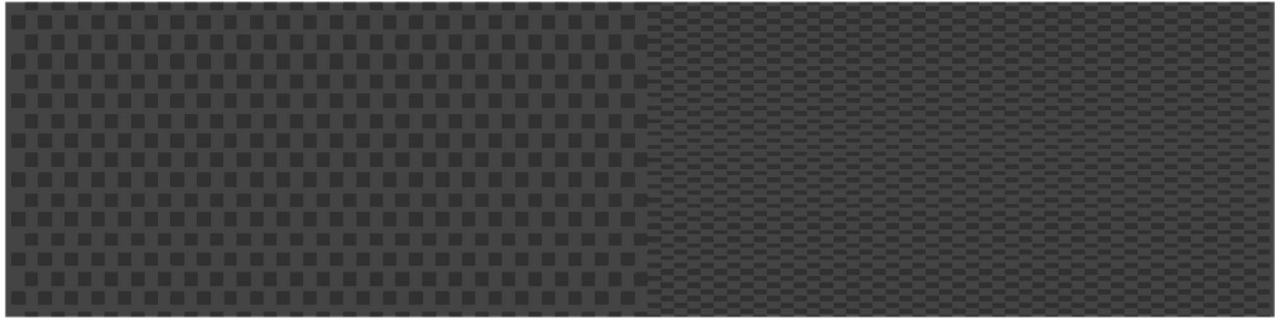


Figure 6. Idealized 2D column packed with different rectangular solids.

ties of the two media differ considerably, there is no mass accumulation at the media interface and the resident concentration is continuous. Figure 7B shows that for each of the two Pe numbers the breakthrough curves measured under different flow directions are the same. To test if a mass accumulation is essential to give rise to a difference in solute arrival time, we ran some simulations allowing the tracer to accumulate at the reservoir-column interface. The simulated results (not presented) indeed showed a mass accumulation at the reservoir-column interface, and such accumulation results in the breakthrough curves dependent on the water flow direction as shown in Figure 7C.

[25] The above 2D results indicate that knowing the macroscopic transport properties of two adjacent materials alone might not be sufficient to tell if the mass could accumulate at their interface, at least for high-porosity media as the above 2D example.

5. Summary and Discussion

[26] Solute transport in stratified porous media is critical to understanding contaminant migration in groundwater as most natural soils and aquifers are inherently heterogeneous. In stratified media, the transport parameters could endure an abrupt change at the interface between two materials. However, the impact of such a change on chemical transport is an issue that has not yet been fully understood due to the difficulty of measuring solute concentration at pore scale in the vicinity of the media interface.

[27] In most macroscopic models, including the stochastic analysis of chemical movement in heterogeneous media, both concentration and solute flux are assumed to be continuous across sharp interfaces. While the solute flux must be continuous because of the requirement of mass conservation, there is no similar requirement for solute concentration. In fact, there have been conjectures that, although the concentration is continuous at pore scale, a spatial average could result in a discontinuous volume-average concentration at an interface between two materials. Such conjectures were supported by some displacement experimental results, which showed that the classical advection-dispersion equation failed to reproduce the measured breakthrough curves if the concentration was assumed to be continuous at the sharp interfaces. However, since it is difficult to measure noninvasively the solute concentration at the pore scale, there has been no experimental evidence to show the existence of such discontinuous concentration. Some theoretical analyses provided evidence of mass accu-

mulation at media interfaces, but they were based on random walk models and simulated the particle movement above the REV scales.

[28] Pore-scale modeling was used in this paper to study the change in macroscopic concentration when solute moves from one material into another based on a 3D X-ray image and an idealized 2D column. The simulations for the 3D image were to investigate if there is a mass accumulation (and hence discontinuous resident concentration) at the media interface, making the solute movement in stratified media depend on the water flow direction. The idealized 2D column was to test if knowing the transport properties of two media alone is sufficient to determine a possible mass accumulation at the media interface.

[29] The simulated results from the 3D column with various Pe numbers revealed that solute did accumulate at the media interface, and the accumulation was more significant when solute migrated in the C-F direction than in the F-C direction. Also, there is a mass accumulation at reservoir-column interfaces; this is expected because in an extreme case the two reservoirs can be seen as another highly permeable medium. Such mass accumulations lead to a discontinuous resident concentration, making solute move through the column quicker when moving in the F-C direction than in the C-F direction.

[30] The simulation results from the 2D column revealed that, although the dispersive properties of the two media differ considerably, there was no mass accumulation and the resident concentration was continuous at the media interface. As a result, the breakthrough curves measured under different flow directions are same, indicating that knowing the transport properties alone might not be sufficient to determine if mass could accumulate.

[31] This work was motivated by the experimental results and theoretical analysis of *Berkowitz et al.* [2009] and *Cortis and Zoia* [2009], respectively. Our simulations based on the real 3D media did prove the conjectures of *Berkowitz et al.* [2009] that mass accumulation develops at the sharp interfaces when solute migrates from one medium to another.

Table 1. Change in Hydrodynamic Dispersion Coefficients with the Pe Number for the Two Media in Figure 6

Pe Number	Hydrodynamic Dispersion Coefficient	
	Fine Medium	Coarse Medium
6.42	0.2324	1.362
1.31	0.1694	0.558

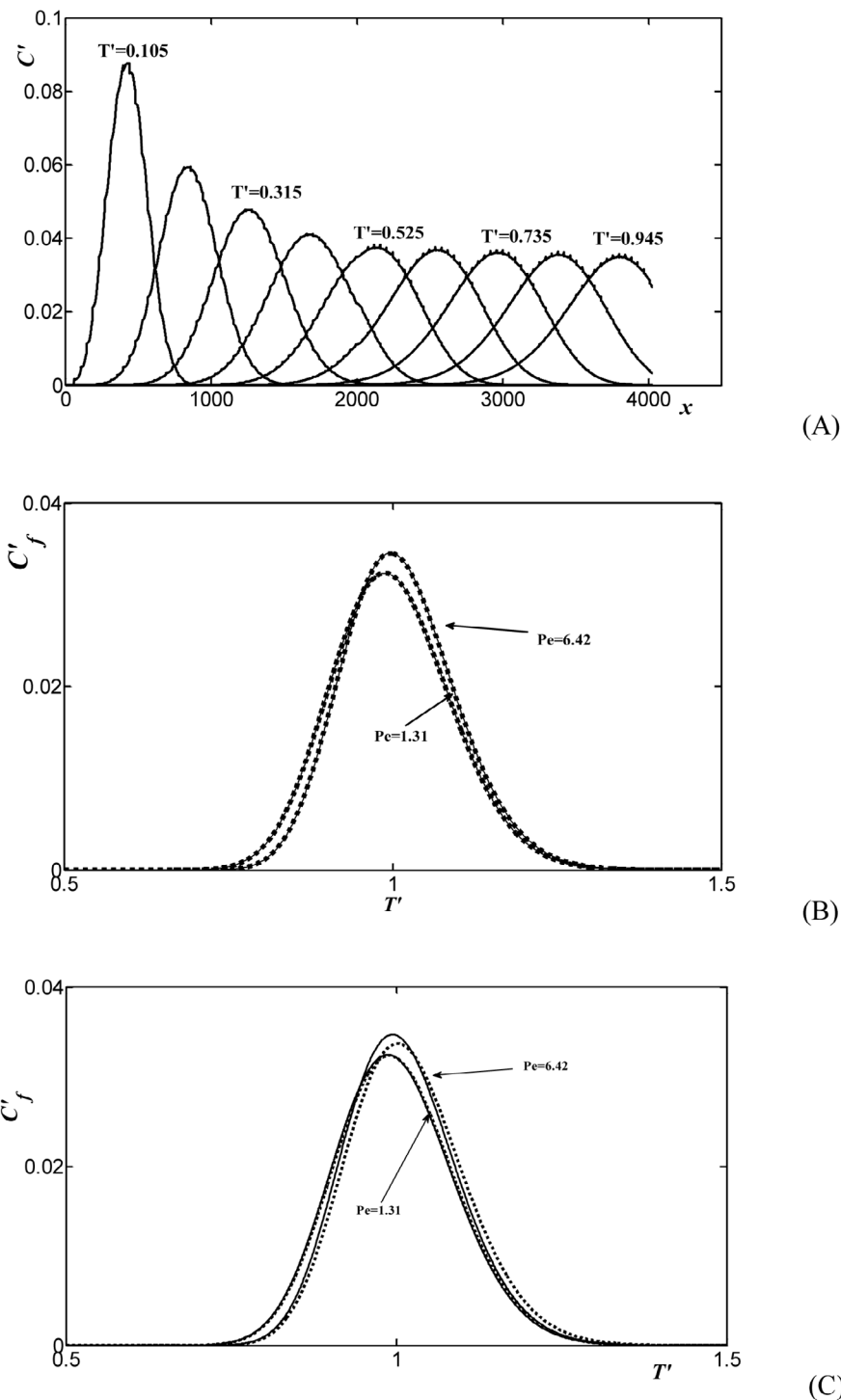


Figure 7. (A) Resident concentration profiles when solute moved in the C-F direction through the column shown in Figure 6. (B) Breakthrough curve for tracer moving in the C-F direction (broken lines) in comparison with that in the F-C direction (solid lines) when the tracer was not allowed to accumulate at the reservoir-column interface. (C) Same as Figure 7B, but the tracer in the inlet reservoir was allowed to accumulate at the column-reservoir interface.

The simulations found that the solute accumulated when water flowed in both directions, but the accumulation was more significant when solute migrated in the C-F direction than in the F-C direction. Because of the mass accumulation, the breakthrough curve measured when water flowed

in the C-F direction was delayed and broad in comparison with that measured when water flowed in the F-C direction. This is consistent with the experimental results of Berkowitz *et al.* [2009]. The finding that the mass also accumulated at the reservoir-column interface is consistent

with the conjectures and experimental results of other researchers [Novakowski, 1992b; van Genuchten and Parker, 1984].

[32] In comparison with natural media, the 3D glass beads and the 2D idealized columns simulated in this work are very simple. In natural media, the two adjacent materials often overlap each other to generate some microstructures, which are hydraulically and geometrically different from the pores in each medium. Such microstructures are very likely to trap part of the solute molecules, resulting in a mass accumulation and hence discontinuous resident concentration at the media interface. Although the behavior of solute in real media is more complicated than the examples investigated in this paper, our simulation results did provide some insight into the behavior of solute when it transports in stratified media. First, we showed that solute indeed accumulates at the sharp interfaces and confirmed the conjectures of Berkowitz *et al.* [2009], as demonstrated by the 3D example. Second, our simulations also suggest that the knowledge of the macroscopic transport properties of two adjacent materials alone might not be sufficient to determine if a mass accumulation would develop.

Appendix A

[33] It can be proven, by multiplying both sides of (6) by ξ_i and then summing all the terms over i , that the consequent results on the left- and right-hand sides are not equal, meaning that the collision in (6) does not conserve momentum. This appendix contains the derivation of the formulas to calculate the solute flux at pore scale based on the particle distribution functions. The derivation is based on the following expansion in terms of a small parameter ε and an assumption that the molecular diffusion in the void space is Gaussian:

$$\begin{aligned} g_i(\mathbf{x} + \xi_i \delta t, t + \delta t) &= \sum_{n=0}^{\infty} \frac{\varepsilon^n}{n!} (\partial_t + \xi_i \cdot \nabla)^n g_i(\mathbf{x}, t), \\ g_i(\mathbf{x}, t) &= \sum_{n=0}^{\infty} \varepsilon^n g_i(\mathbf{x}, t)^{(n)}, \\ \partial_t &= \sum_n \varepsilon^n \partial_{t_n}. \end{aligned} \quad (A1)$$

Substituting (6) into (A1) and keeping the terms up to second order ($n = 2$) gives

$$\begin{aligned} \varepsilon \partial_t g_i^{(0)} + \varepsilon^2 \partial_{t_0} g_i^{(1)} + \varepsilon^2 \partial_{t_1} g_i^{(0)} + \varepsilon \xi_i \cdot \nabla g_i^{(0)} + \varepsilon^2 \xi_i \cdot \nabla g_i^{(1)} \\ + \frac{1}{2} \varepsilon^2 (\partial_{t_0} + \xi_i \cdot \nabla) g_i^{(0)} = \frac{1}{\tau_c} (g_i^{eq} - g_i^{(0)} - \varepsilon g_i^{(1)} - \varepsilon^2 g_i^{(2)}). \end{aligned} \quad (A2)$$

Collecting terms up to second order with respect to ε gives the following relationships:

$$g_i^{(0)} = g_i^{eq}, \quad (A3)$$

$$\partial_{t_0} g_i^{(0)} + \xi_i \cdot \nabla g_i^{(0)} = -g_i^{(1)} / \tau_c, \quad (A4)$$

$$\partial_{t_0} g_i^{(1)} + \partial_{t_1} g_i^{(0)} + \xi_i \cdot \nabla g_i^{(1)} + \frac{1}{2} (\partial_{t_0} + \xi_i \cdot \nabla)^2 g_i^{(0)} = -g_i^{(2)} / \tau_c. \quad (A5)$$

Multiplying (A4) by ε and then adding the result to (A5) yields

$$\begin{aligned} (\partial_t + \xi_i \cdot \nabla) g_i^{eq} + (\partial_{t_0} + \xi_i \cdot \nabla) (g_i^{(1)} - g_i^{(1)} / \tau_c) \\ = -g_i^{(1)} / \tau_c - \varepsilon g_i^{(2)} / \tau_c. \end{aligned} \quad (A6)$$

Summing (A6) over i yields

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{u}c) + \nabla \cdot \sum_i (1 - 1/2\tau_c) \xi_i \varepsilon g_i^{(1)} = 0. \quad (A7)$$

If the solute transport is Gaussian, the solute flux is given by

$$\mathbf{q} = \mathbf{u}c - \sum_i (1 - 1/2\tau_c) \xi_i \varepsilon g_i^{(1)}. \quad (A8)$$

As $g_i^{(1)}$ can be approximated by $g_i^{(1)} \approx (g_i - g_i^{eq}) / \varepsilon$, the solute flux is then given by

$$\mathbf{q} = \mathbf{u}c - \sum_i (1 - 0.5/\tau_c) \xi_i (g_i - g_i^{eq}) = \sum_i \beta \xi_i g_i + 0.5 \mathbf{u}c / \tau_c, \quad (A9)$$

where $\beta = 1.0 - 0.5 / \tau_c$.

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