Solute transport in low-heterogeneity sandboxes: The role of correlation length and permeability variance

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Abstract This work examines how heterogeneity structure, in particular correlation length, controls flow and solute transport. We used two-dimensional (2D) sandboxes (21.9 cm × 20.6 cm) and four modeling approaches, including 2D Advection-Dispersion Equation (ADE) with explicit heterogeneity structure, 1D ADE with average properties, and nonlocal Continuous Time Random Walk (CTRW) and fractional ADE (fADE). The goal is to answer two questions: (1) how and to what extent does correlation length control effective permeability and breakthrough curves (BTC)? (2) Which model can best reproduce data under what conditions? Sandboxes were packed with the same 20% (v/v) fine and 80% (v/v) coarse sands in three patterns that differ in correlation length. The Mixed cases contain uniformly distributed fine and coarse grains. The Four-zone and One-zone cases have four and one square fine zones, respectively. A total of seven experiments were carried out with permeability variance of 0.10 (LC), 0.22 (MC), and 0.43 (HC). Experimental data show that the BTC curves depend strongly on correlation length, especially in the HC cases. The HC One-zone (HCO) case shows distinct breakthrough steps arising from fast advection in the coarse zone, slow advection in the fine zone, and slow diffusion, while the LCO and MCO BTCs do not exhibit such behavior. With explicit representation of heterogeneity structure, 2D ADE reproduces BTCs well in all cases. CTRW reproduces temporal moments with smaller deviation from data than fADE in all cases except HCO, where fADE has the lowest deviation.

1. Introduction

In the natural subsurface, solid materials of different properties are distributed unevenly with various spatial patterns [Allen-King et al., 1998; Barber et al., 1992; de Marsily et al., 2005; Scheibe et al., 2011; Sudicky et al., 2010; Zinn and Harvey, 2003]. Mineral spatial distributions vary from random and even configurations at one extreme to large and clustered zones or layers at the other end of the spectrum [Jin et al., 2013; Koltermann and Gorelick, 1996; Landrot et al., 2012; Li et al., 2011]. This leads to significant spatial variations in subsurface properties and has profound impacts on flow and solute transport [Desbarats and Bachu, 1994; Bao et al., 2014]. It is important to understand and quantify the role of heterogeneity structure in determining processes and effective parameters at large scales.

The effects of small-scale spatial variation on effective permeability have been examined extensively for more than four decades [Dagan, 1989; Dagan et al., 2013; Freeze, 1975]. Most studies quantify effective permeability with synthetic or imaged small-scale distribution using mathematical, numerical, geostatistical, or stochastic methods [Babadagli, 2006; Desbarats, 1987; Di Federico et al., 2010; Sun et al., 2011; Vemerey, 2012]. The effective permeability has been found to depend on the volume fraction of high permeability zones, pore connectivity, and the relative direction of mineral distribution to the main flow [Bernabe et al., 2003, 2004, 2011]. Effective permeability depends not only on the magnitude of permeability variation, but also on the spatial distribution characteristics [Desbarats, 1987]. Effective permeability can be calculated as the arithmetic average of different zones if the flow is parallel to the zonation, and as harmonic average if the flow is perpendicular to the zonation [Song and Renner, 2006]. These studies have provided the foundation for the quantification of effective permeability [Renard and deMarsily, 1997]. Compared to the large number of theoretical and numerical work, experimental studies are rather scarce. In particular, most experimental studies have used one specific spatial distribution without systematically vary heterogeneity structure to understand its role in controlling effective permeability.
Similarly, solute transport in heterogeneous media has been investigated extensively in numerical [Barth et al., 2001; Fernández-Garcia et al., 2005; Hoteit et al., 2002; Willmann et al., 2008], experimental [Chao et al., 2000; Cortis and Berkowitz, 2004; Levy and Berkowitz, 2003; Li et al., 1994; Ostrom et al., 1992; Silliman, 2001; Silliman and Zheng, 2001], and field studies [Adams and Gelhar, 1992; Garabedian et al., 1991; Vanderborght and Vereecken, 2002; Welty and Gelhar, 1994]. Extensive work has been done to capture the anomalous, non-Fickian behavior commonly observed in heterogeneous media using, for example, the dual porosity model [Gerke and Vangnuchten, 1993], multivariate mass transfer model [Haggerty and Gorelick, 1995; Haggerty et al., 2000], as well as nonlocal methods [Bolster et al., 2010; Deniz et al., 2011; Huang and Hu, 2001; Major et al., 2011; Willmann et al., 2010]. Berkowitz and coworkers developed the framework of Continuous Time Random Walk (CTRW) that is nonlocal in time [Berkowitz and Scher, 1998, 2001; Berkowitz et al., 2002, 2009; Di Donato et al., 2003]. Fractional Advection-Dispersion Equation (FADE) is nonlocal in space and has also been extensively used [Benson et al., 2000a, 2001; Huang et al., 2006; Pachepsky et al., 2000].

In general, there is a consensus that spatial patterns and heterogeneity structure play a critical role in determining solute transport [Beaudoin et al., 2010; de Dreuzy et al., 2007; Fiori et al., 2011; Gotovac et al., 2009; Janjovic et al., 2003, 2009; Pedretti et al., 2013; Ramasomanana et al., 2013; Sric et al., 2013]. Various numerical studies have identified connectivity and correlation length as key parameters that determine solute breakthrough [Renard and Allard, 2013; Willmann et al., 2008; Zinn and Harvey, 2003]. Zinn and Harvey [2003] showed that connectivity in low conductivity zones significantly increases dispersivity value. Pedretti et al. [2013] demonstrated that stratification induced by vertical layers of different permeability controls the shape of breakthrough curves. The BTC tailing becomes increasingly significant with increasing connectivity in low permeability zones [Willmann et al., 2008]. With the same global correlation length, long correlation lengths in low permeability zones leads to more significant increase in longitudinal dispersivity compared to those in high permeability zones [Fiori et al., 2010]. Non-normal transport has been observed when the travel distance is comparable to the correlation length regardless of permeability variation while normal transport occurs when the travel distance is more than 20 times longer than the correlation length [Gotovac et al., 2009].

Although connectivity and correlation length have been found to be critical in these modeling studies, they have not been systematically examined and confirmed experimentally. Existing experimental work on solute transport has mostly focused on single spatial patterns with one correlation length [Cortis and Berkowitz, 2004; Levy and Berkowitz, 2003; Silliman and Simpson, 1987; Sternberg et al., 1996; Zinn et al., 2004]. The objective of this work is to systematically understand and quantify the role of correlation length in determining effective permeability and solute transport using flow cell experiments and modeling approaches. The central questions we ask are: (1) how and to what extent does correlation length determine effective permeability and breakthrough curves under different permeability variation conditions? (2) Which model can reproduce the data under what conditions?

Heterogeneous porous media was represented by a series of 2D flow cells (21.9 cm × 20.6 cm × 1.0 cm) packed with the same 20% (v/v) fine sands and 80% (v/v) of coarse sands however in different patterns. The Mixed pattern contained uniformly distributed fine and coarse sand grains. Four-zone cases had four square fine zones (4.5 cm × 4.5 cm) embedded in coarse sand matrix. The One-zone cases had all fine grains in one square zone (9 cm × 9 cm) in the middle of the flow cell within the coarse sand matrix. Large correlation length corresponds to natural systems that are commonly characterized by layered structures or zones with distinct properties at length scales comparable to the scale of the whole domain [Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salehikhoo et al., 2013]. Three series of flow cells were studied with permeability variance σ²nK varying from 0.10 to 0.43 (here K refers to permeability). Compared to studies with orders of magnitude permeability difference between fine and coarse zones, the σ²nK here was relatively small. The extent of permeability variation differs significantly in different natural subsurface systems. For example, the Bordon site (Borden, Ontario) is well known as relatively homogenous with low σ²nK values around 0.20 [Mackay et al., 1986; Sudicky, 1986], while the Macrodispersion Experiment (MADE) site in Mississippi is known to be highly heterogeneous with σ²nK around 4.5 [Boggs et al., 1992].

Four modeling approaches were used here to capture the breakthrough curves. The 2D Advection-Dispersion Equation (ADE) explicitly incorporates the heterogeneity structure. The 1D ADE approach assumes homogeneous media using average porosity and permeability. The well-known and extensively used nonlocal in space FADE and nonlocal in time method CTRW framework were also used. These four methods were compared to understand which model works better under what conditions.
2. Methodology

2.1. Flow Cell Experiments

2.1.1. Spatial Distribution Patterns of Sandboxes

Quartz sands from Portage Lumber were packed into seven transparent Plexiglas sandboxes of the dimension $21.6 \text{ cm} \times 20.9 \text{ cm} \times 1.0 \text{ cm}$. The sand grains were packed into three spatial patterns (Mixed, Four-zone, and One-zone) that contained fine (black) and coarse zones (gray) as illustrated in Figure 1. The Mixed pattern contains homogeneously mixed fine and coarse sands. The Four-zone pattern has four fine zones of $4.5 \text{ cm} \times 4.5 \text{ cm}$ distributed in the center of each quarter of the sandbox. The One-zone pattern has one fine zone of $9 \text{ cm} \times 9 \text{ cm}$ in the middle of the flow cell. All fine zones align in parallel to the sides of the flow cell. In all three cases, the coarse sand occupies 80% (v/v) of the total volume, with the rest being the fine sand. The three patterns differ in their “dimensionless correlation length,” $\lambda / L$, defined as the ratio of the spatial correlation length [Kitanidis, 1997; Webster and Oliver, 2007] of the permeability field $\lambda$ over the length of the sandbox in the main flow direction $L$. The values of $\lambda / L$ were 0.001, 0.244, and 0.447 for the Mixed, Four-zone, and One-zone cases, respectively.

The size of the sand grains varies between 0.05 and 0.84 mm to represent the range in the natural subsurface, as shown in Table 1. The finest sand (FSI) and the coarsest sand (CSII) in Table 1 were used to generate...
the largest size and permeability contrast between fine and coarse zones in High Contrast series High Contrast Mixed (HCM), Four-zone (HCF), and One-zone (HCO). Another three sandboxes were packed using the fine sand FSII and the coarse sand CSI of lower size and permeability contrast for Low Contrast Mixed (LCM), Four-zone (LCF), and One-zone (LCO) cases. An additional medium contrast flow cell was packed using the medium sand size contrast (FSI and CSI) with the One-zone (MCO) pattern. As will be discussed later, the fine and coarse zones of each size range have their own permeability values. In each series, the global permeability variance $\sigma_{lnK}^2$, a measure of the extent of variation [Gelhar, 1993], is the same. The $\sigma_{lnK}^2$ values are 0.430, 0.260, and 0.100 for the HC, MC, and LC series, respectively. These variances are similar to those of low-heterogeneity natural geological formations such as Borden ($\sigma_{lnK}^2 = 0.29$) and Cape Cod ($\sigma_{lnK}^2 = 0.26$) [Leblanc et al., 1991; Mackay et al., 1986].

As shown in Figure 1d, the flow cell setup consists of 10 inlet injection ports, the sandbox, and 3 outlet sampling ports. A digital camera was used to qualitatively document the visualization tests where dyed water was injected from the inlet plane, as will be discussed later.

2.1.2. Wet Packing Procedure

A wet packing procedure [Minyard and Burgos, 2007] was used to prevent the trapping of air bubbles in the porous media that can lead to pore clogging and change of permeability. The packing was done layer by layer to remove air and to establish different zones. One side of the flow cell was removed and water was poured to a height of 2 cm. The sand was then added, shaken, and stirred to remove all trapped air bubbles. Plastic strips were planted in the cell before packing the fine sand zones to keep sands of different zones from mixing. After each fine sand zone was packed, the plastic strips were carefully removed. When all parts of the sandbox and connections were filled with sand and water, the removed side of the flow cell was screwed back on and the desired patterns in Figure 1 were verified visually. A small amount of sand was added to the sandbox from valves to make the packing as tight as possible. Silicone caulking was used to seal off the system and to avoid leakage. All connections to the cell and sampling points were covered with a fine mesh in order to prevent sand from flowing out of the system. The effect of the mesh on the flow was verified to be negligible by measuring changes in pressure drop before and after implementing the mesh in 1D columns.

2.1.3. Determination of Porosity and Permeability

The solid volumes of the fine and coarse zones were calculated from the weight and density of the sand. The porosity of each zone was determined based on the difference between the solid volume and the bulk volume estimated from the dimension of the zones. Values of porosity for each zone are shown in Table 1. The average porosity was calculated based on the volume of water used during the wet packing and the total volume of the sandbox.

Effective permeability was determined in two steps. First, one-dimensional columns were packed using each type of sand grains to determine permeability of the individual zones packed with each size range of sand. Pressure gradients along the sand columns were measured at five steady state flow rates, 0.10, 0.15, 0.20, 0.25, and 0.30 mL/min. A Crystal Engineering pressure gauge (XP2i-DP) that can measure a 15 psi differential pressure with the precision of 0.001 psi was used. To ensure steady state condition, each flow rate was kept constant until a differential pressure was stabilized for 15 min with a maximum variation of 0.005 psi. Using the measured flow rate and pressure gradient, Darcy’s law was used to calculate the absolute permeability of the columns.

The effective permeability of the Mixed cases was determined by measuring permeability of the 1D columns packed with sands of mixed grain size range using the above method. Attempts to measure pressure drop directly in the 2D flow cell failed due to the relatively short length of the flow cell compared to its width, which resulted in pressure fluctuation along the inlet plane. As an alternative, the effective permeability of Four-zone or One-zone cases was calculated using 2D numerical simulation in CrunchFlow. CrunchFlow can simulate the advective, dispersive, and diffusive transport processes coupled with chemical reactions [Molins et al., 2012; Singha et al., 2011]. The code essentially solves Darcy’s equation for the distribution of steady state flow velocity. The measured permeability values for the coarse and fine zones were used to set up the permeability distribution in the 2D model domain. The outlet side was set exactly the same as the experimental setup. That is, it was a no flow boundary except at the three outlets. Hydraulic heads were assigned at the inlet and outlet boundaries, with the left and right boundaries set as no flow.
boundary. The hydraulic head in the main flow direction was adjusted to be consistent with the flow rate data from the three outlets by minimizing the sum of squared residuals. The effective permeability was calculated using Darcy’s law with the measured overall flow rate data and the hydraulic gradient that matched the flow rate data. The effective permeability therefore represents the equivalent, averaged value assuming a homogeneous porous medium at the flow cell scale.

2.1.4. Flow Through Tracer Experiments

Tracer experiments were carried out by injecting a solution of $1.25 \times 10^{-4}$ mol/L sodium bromide through 10 inlets at a constant overall flow rate of 0.7 mL/min using a Harvard Apparatus syringe pump. The dye phenol red was used to visualize the process. This flow rate corresponds to an average velocity around 1.3 m/d, which is in the high end of natural groundwater flow velocity [Newell et al., 1990]. The residence times vary from 187 to 237 min, depending on the average porosity of the sandboxes. The effluents were collected through the three outlets every 15 min. Bromide concentrations were measured using the Dionex ICS2500 Ion Chromatography. Each experiment was carried out for 8.5 h, equivalent to approximately three pore volumes.

2.2. Modeling Approaches

2.2.1. The 2D and 1D Advection-Dispersion Equations (ADE): Determination of Local and Global Dispersivity

Transport modeling was used with two different approaches to understand solute transport and to determine the local (grid block) and effective dispersivity. In one approach, 2D ADE modeling was set up with the computational domain exactly like that of the flow cell experiment, with explicit distribution of measured permeability and porosity in fine and coarse zones. The model also explicitly set up the three outlets at the top boundary. The constraints were the three flow rates and the breakthrough curves from the three individual outlets. The explicit incorporation of spatial distribution enabled the simulation of heterogeneous flow fields and was used to obtain the dispersivity at the local grid block scale. In another approach, the 1D ADE was solved to simulate the whole flow cell as a homogeneous system as if we do not know the detailed heterogeneous distribution. The three outlets are combined into one overall outlet in the calculation with the total flow rate and the flow-rate-averaged tracer breakthrough curves as constraints. In this case, the effective or global dispersivity at the flow cell scale was obtained by matching the averaged breakthrough data.

2.2.1.1. The 2D ADE Modeling With Explicit Heterogeneity Structure: Local Dispersivity

The classical 2-D ADE equation was solved using CrunchFlow [Steefel and Lichtner, 1994]:

$$\frac{\partial C}{\partial t} + \nabla \cdot (-D \nabla C + vC) = 0$$

where $C$ is the solute concentration (mol/m$^3$), $t$ is the time (s), $D$ is the combined dispersion-diffusion tensor (m$^2$/s), $v$ (m/s) is the flow velocity vector and can be decomposed into $v_x$ and $v_z$ in the directions parallel and transverse to the main flow. The dispersion-diffusion tensor $D$ is defined as the sum of the mechanical dispersion coefficient and the effective diffusion coefficient in porous media $D^*(m^2/s)$. At any particular location (grid block) with flow velocities in longitudinal and transverse directions being $v_x$ and $v_z$, their corresponding $D_L$ and $D_T$ are the dispersion coefficients (m$^2$/s) given by

$$D_L = D^* + \alpha_L v_x$$
$$D_T = D^* + \alpha_T v_z$$

Here $D^*$ is the effective diffusion coefficient in porous media (m$^2$/s), $\alpha_L$ and $\alpha_T$ are the longitudinal and transverse dispersivity (m). The ratio of $\alpha_L/\alpha_T$ has been reported to be between 6 and 20 [Gelhar et al., 1992]. In this work, $\alpha_T$ was set to be 0.1 $\times$ $\alpha_L$ in all models. A common tortuosity value of 2.0 for unconsolidated porous media [Armatas, 2006; Salem and Chilingarian, 2000] was used to relate $D^*$ to the aqueous diffusion coefficient $D_0$ of $2.0 \times 10^{-9}$ m$^2$/s for bromide [Fetter, 1999].

In all cases, the size of grid block was 0.1 cm $\times$ 0.1 cm. The grid-size effect was eliminated by increasing the resolution to the extent that the produced BTCs do not change with increasing resolution. The total number of grid blocks is $209 \times 216$. Three outlets were established explicitly at the effluent boundary to have exactly the same setup as shown in Figure 1d. The local dispersivity values were obtained by matching the
breakthrough data from individual outlets. Although the dispersivity \( \alpha_l \) is the same for all grid blocks, \( D_l \) is different for each grid block due to the spatial variation in the flow field, as will be discussed later.

### 2.2.1.2. The 1-D ADE With Averaged Properties Assuming Homogeneous Systems: Global Effective Dispersivity

To obtain the effective dispersivity at the flow cell scale, the averaged breakthrough curves were obtained by flux averaging the concentrations from their respective outlets as follows:

\[
\overline{c} = \frac{\sum_{i=1}^{3} C_i Q_i}{\sum_{i=1}^{3} Q_i}
\]

where \( \overline{c} \) represents the flux-averaged concentration, \( C_i \) and \( Q_i \) are the experimentally measured concentration and flow rate from each outlet \( i \). Accumulated effluent water volume from each outlet was summed and divided by the experiment duration to determine the averaged flow rate. The averaged flow rate and breakthrough curve were used as constraints to obtain the global effective dispersivity for each sandbox using the 1-D form of the ADE equation (1). Averaged porosity and effective permeability values were used assuming homogeneous sandboxes without spatial variations in properties. The obtained dispersivity \( \alpha' \) therefore represents the effective dispersivity at the scale of the sandbox.

### 2.2.2. Continuous Time Random Walk (CTRW) Analysis

Here we use the CTRW framework to analyze the non-Fickian or “anomalous” behavior in the heterogeneous porous media [Berkowitz and Scher, 1997, 1998; Kosakowski et al., 2001]. The CTRW framework portrays the transport process as a series of transitions steps with displacements \( s \) and times \( t \) [Berkowitz et al., 2006]. It can capture non-Fickian behavior where the traditional ADE often fails. Detailed mathematical background can be found in literature [Berkowitz et al., 2000; Hatano and Hatano, 1998; Levy and Berkowitz, 2003].

Implementation of CTRW requires the identification of proper probability density function (pdf) \( \psi(s,t) \) that physically describes transport in a system. For transport in porous media, it is sometimes approximated as a pure power law form \( \psi(s,t)=t^{-1-\beta} \), where the use of a pure power law means that the non-Fickian transport will endure forever during transport through an infinite porous media with repeated spatial patterns such as the ones in Figure 1. Here we use the Truncated Power Law (TPL) form of \( \psi(t) \) that allows the quantification of the start and end time of non-Fickian behavior. It has been successfully used in understanding observations at multiple scales [Berkowitz et al., 2000, 2006, 2009; Bijeljic and Blunt, 2006; Deng et al., 2008; Xiong et al., 2006]. The decoupled pdf is approximated as \( \psi(s,t)=\phi(s)\psi(t) \), where \( \phi(s) \) is the probability distribution of the length of the jumps and \( \psi(t) \) is the probability rate for a transition time \( t \) between sites [Berkowitz and Scher, 2010]. This results in the following equation

\[
\frac{\partial c(s,t)}{\partial t} = \int_0^t M(t-t')|\psi| \cdot \nabla c(s,t') - D \psi \cdot \nabla \nabla c(s,t')|dt'\quad(5)
\]

where \( c(s,t) \) is the concentration normalized by the inlet concentration, \( \psi \), and \( D \) are the first and second moments of \( \phi(s) \) divided by the characteristic time \( \tau \), and \( M(t) \) is the memory function. The Laplace transform of the memory function is

\[
\tilde{M}(u) = \frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)}\quad (6)
\]

where \( \tilde{\psi}(u) \) is the Laplace transform of \( \psi(t) \)

\[
\psi(t) = \frac{\exp(-t/\tau_2)}{(1+t/\tau_1)^{1+\beta}}\quad (7)
\]

\[
N = \left[ \tau_1 \tau_2^{-\beta} \exp\left(\tau_2^{-1}\right) \Gamma(-\beta, \tau_2^{-1}) \right]^{-1}
\]

where \( \tau_1 \) and \( \tau_2 \) are the limits of the power law spectrum, \( \Gamma \) is the incomplete gamma function, and \( \tau_2 \equiv t_2/t_1 \).
The well-known conventional ADE is a specific form of CTRW where the value of \( \beta \) is larger than 2. The value of \( \beta \) is between 0 and 2 for non-Fickian transport. The deviation of \( \beta \) values from 2 is a measure of the non-Fickian behavior. Values of \( \beta \) between 1 and 2 indicate less extent of non-Fickian behavior than those between 0 and 1. The time scales \( t_1 \) and \( t_2 \) are the lower and higher time limits of the power law behavior that follow \( \psi(t) \propto (t/t_1)^{-1-\beta} \). The \( t_1 \) approximates the median transition time when the power law behavior starts, while the cutoff \( t_2 \) is the time where the power law behavior ends, which ensures that the transport evolves into a normal Fickian one when \( t > t_2 \). As such, the use of TPL form allows the quantification of the time needed to approach Fickian behavior.

It should be noted here that the statistical characteristics of uncorrelated velocity fields was used to project particle jumps in porous media. In some cases in our system, preferential flow paths are visible and the velocity field is correlated, as shown later in Figures 3b and 3c. As such, transport can be modeled using correlated velocity fields [Dentz and Bolster, 2010; Le Borgne et al., 2008a, 2008b, 2011]. The solution \( C(x,t) \) determines the first arrival times based on BTC as a function of the parameters \( \nu_x, D_x, \beta, t_1, \) and \( t_2 \). The parameters were adjusted simultaneously to reproduce the breakthrough curves using the CTRW tools [Cortis and Berkowitz, 2005].

### 2.2.3. Fractional Advection-Dispersion Equation (fADE)

Nonlocal in space methods such as fADE have been used to describe non-Fickian transport [Benson et al., 2000a, 2000b]. One of the most common fADEs for conservative solute transport is the following one-dimensional form [Meerschaert et al., 1999]:

\[
\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^{\alpha} C}{\partial x^{\alpha}}
\]

where \( \alpha \) is the order of the fractional differentiation typically between 1 and 2 and is normally represented as \( \alpha \) in fADE literature. Here we used \( \alpha \) to avoid confusion with the dispersivity \( \alpha \) in the ADE. With a continuous solute injection into a solute-free medium at the inlet, the analytical solution to equation (9) is as follows [Benson et al., 2000b; Huang et al., 2006]:

\[
C = C_0 \left[ 1 - F_{\alpha} \left( \frac{x - vt}{\left( \cos \left( \frac{\alpha}{2} \right) \right)^{\frac{\alpha}{2}}} \right) \right]
\]

where \( F_{\alpha} \) is the symmetric \( \alpha \)-stable probability function [Pachepsky et al., 2000] defined as

\[
F_{\alpha}(y) = \frac{\text{sign}(1-\alpha y)}{2} \int_0^1 \exp \left( -\frac{y}{\nu} \left| \sum_{i=1}^{\alpha} U_{\alpha}(\phi) \right| \right) d\phi
\]

where \( \phi \) is the integration variable, \( \text{sign}(1-\alpha y) \) is \(-1, 0, \) and \( 1 \) for \( \alpha y > 1, =1 \) and \( <1 \), respectively, \( U_{\alpha} \) and \( C(\alpha) \) are auxiliary functions of \( \alpha \). Here \( C(\alpha) \) is equal to 1 if \( \alpha > 1 \) and is equal to 0.5 if \( \alpha < 1 \) and

\[
U_{\alpha}(\phi) = \left[ \frac{\sin \left( \frac{\pi \alpha \phi}{2} \right)}{\cos \left( \frac{\pi \alpha \phi}{2} \right)} \right]^{\frac{\alpha}{\pi}}
\]

The analytical solution of the fADE formulation was applied and calibrated to the experimental data. The average velocity was first adjusted to match the mid arrival time of BTC. Other parameters, including \( D \) and \( \alpha \), were then adjusted to reproduce the BTC.

### 2.2.4. Optimization Methods

To capture the BTC tails and to keep consistency between different models for fair comparison, the best fit was obtained for all four models by minimizing \( \sum_{i=1}^{N} (\log \hat{C}_i - \log C_i)^2 \), the sum of squared residuals between the logarithms of concentration data and the model predicted concentrations. Here \( N \) is the number of data points, \( \hat{C}_i \) is the model predicted concentration, and \( C_i \) is the measured data. This is essentially a weighted minimization \( \sum_{i=1}^{N} W_i (\hat{C}_i - C_i)^2 \), where the weight \( W_i = 1/C_i^2 \) [Chakraborty et al., 2009]. This is different from minimizing \( \sum_{i=1}^{N} (\hat{C}_i - C_i)^2 \) that results in uniform fit to the model over the whole BTC. The logarithm minimization allows proper account of the fit to the BTC tails, which is important in solute transport in heterogeneous porous media. As will be pointed out later, the optimization method plays a large role in determining the performance of different models in capturing the BTCs.
### 2.2.5. Temporal Moment Analysis and Model Comparison

Characteristics of solute transport in porous media can be represented by key parameters such as first and second temporal moments [Dagan, 1990; Zhu and Yeh, 2006; Zhu et al., 2009]. Here we use the moment analysis to measure the similarity between the experimental data and the predictions from the ADE, CTRW, and fADE frameworks. Some key parameters are defined as follows [Dagan, 1990; Riva et al., 2008].

The first moment, $T_1$, is a measure of the mean advective time of fluid flow in porous media. It is defined as follows:

$$T_1 = \frac{\int_0^\infty t \ c(t) dt}{\int_0^\infty c(t) dt}$$

(13)

where $c(t)$ is the tracer concentration at time $t$.

The centered second-order moment, $T_2$, represents the width of the tracer plume around its center of mass. It is calculated as follow:

$$T_2 = \frac{\int_0^\infty (t-T_1)^2 c(t) dt}{\int_0^\infty c(t) dt}$$

(14)

Both temporal moments were calculated for the experimental data and modeling output from the ADEs, CTRW, and fADE. The differences between model predictions and data were quantified using the relative difference defined as follows:

$$\delta_v = \frac{|P_m - P_d|}{P_d}$$

(15)

where $\delta_v$ is the relative difference between $P_m$, the moment from the model, and $P_d$, the moment from the data. A $\delta_v$ value of 0 means no difference between data and model prediction. The larger the $\delta_v$ value, the larger the difference.

The relative difference between the prediction and data for the overall BTC was calculated as follows:

$$\delta_v(BTC) = \frac{\int_{t=0}^\infty |c_m - c_d| dt}{\int_{t=0}^\infty c_d dt}$$

(16)

where $c_m$ and $c_d$ are the predicted and measured concentration, respectively. This value compares the prediction of the overall breakthrough curves from different models, while $\delta_v$ values for $T_1$ and $T_2$ calculated from equation (15) focus on the BTC characteristics.

### 2.3. Results and Discussion

#### 2.3.1. Average Porosity and Effective Permeability

As shown in Table 1, the two Mixed cases (LCM and HCM) have lower porosity than other sandboxes, similar to observations in other studies [Li et al., 2014; Salehikhoo et al., 2013]. In other cases, the coarse zones have larger porosity compared to the fine zones. Surprisingly, the CSII sand zone has slightly lower porosity than the CSI sand zone, likely due to the larger size range of CSII grains (0.59–0.84 mm) compared to the relatively narrower size range (0.42–0.50 mm) of the CSI sand. In general, the LC series has higher average porosity than the HC cases.

Measured permeability values for sand grains of different sizes are shown in Table 2 together with their standard deviation. As expected, permeability values are relatively small for fine sands and larger for coarse
sands. Measured permeability values of sand grains vary between $0.305 \times 10^{-12} \text{ m}^2$ for FSI (0.05–0.09 mm) and $1.576 \times 10^{-12} \text{ m}^2$ for the CSII (0.59–0.84 mm). Also shown in Table 2 and illustrated in Figure 2, the effective permeability of all sandboxes fall between that of their composing sand grains. The Mixed patterns (LCM and HCM) have relatively lower permeability than the other two cases for both LC and HC cases. This is a common observation even with the mixing of difference types of mineral grains [Li et al., 2014; Salehi-khoo et al., 2013]. This is because the fine grains can fill in the pore volumes between coarse grains in the Mixed cases. The LCF and LCO cases have the same effective permeability values that are close to the permeability of the coarse sand. This also occurs in the HCF and HCO cases. With the same One-zone distribution, the LCO case has an effective permeability similar to that of the MCO, primarily because they share the same coarse sand. The HCO case has much higher permeability than the LCO and MCO cases because it has much larger coarse sand grains. This indicates that when the correlation length is sufficiently large, the effective permeability is dominated by that of the coarse zone, which results in increasing effective permeability with increasing correlation length under the same permeability variance conditions.

The effective permeability of a heterogeneous porous medium can be calculated using various averaging techniques, including arithmetic ($K_{\text{eff}} = \sum_{i=1}^{n} x_i k_i$), harmonic ($1/K_{\text{eff}} = \sum_{i=1}^{n} x_i / k_i$), and geometric mean ($K_{\text{eff}} = \sqrt[n]{\prod_{i=1}^{n} k_i}$) of permeability in individual zones [Babadagli, 2006; Dagan, 1989; Jensen, 1991; Song and

---

### Table 2. Measured Permeability of Coarse and Fine Zones and Calculated Effective Permeability of 2-D Sandboxes

<table>
<thead>
<tr>
<th>Case Description</th>
<th>Grain Size (mm)</th>
<th>Perm Ratio</th>
<th>Permeability ($10^{-12} \text{ m}^2$)</th>
<th>Arithmetic Mean</th>
<th>Harmonic Mean</th>
<th>Geometric Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSI</td>
<td>0.05–0.09</td>
<td>0.305</td>
<td>0.019</td>
<td>0.970</td>
<td>0.876</td>
<td>0.732</td>
</tr>
<tr>
<td>FSI</td>
<td>0.10–0.21</td>
<td>0.491</td>
<td>0.027</td>
<td>0.970</td>
<td>0.876</td>
<td>0.732</td>
</tr>
<tr>
<td>CSI</td>
<td>0.42–0.50</td>
<td>1.090</td>
<td>0.006</td>
<td>0.933</td>
<td>0.720</td>
<td>0.577</td>
</tr>
<tr>
<td>CSII</td>
<td>0.59–0.84</td>
<td>1.576</td>
<td>0.012</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>Low contrast, Mixed (LCM) FSI+CSI</td>
<td>2.21</td>
<td>0.756</td>
<td>0.016</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>Low contrast Four-zones (LCF) FSI+CSI</td>
<td>2.21</td>
<td>0.877</td>
<td>0.070</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>Medium contrast, One-zone (MCO) FSI+CSI</td>
<td>3.57</td>
<td>0.807</td>
<td>0.031</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>High contrast, Mixed (HCM) FSI+CSII</td>
<td>5.17</td>
<td>0.823</td>
<td>0.019</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>High contrast, Four-zones (HCF) FSI+CSII</td>
<td>5.17</td>
<td>1.140</td>
<td>0.070</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
<tr>
<td>High contrast, One-zone (HCO) FSI+CSII</td>
<td>5.17</td>
<td>1.317</td>
<td>0.070</td>
<td>1.322</td>
<td>0.860</td>
<td>0.693</td>
</tr>
</tbody>
</table>

*Perm ratio is the permeability of the coarse zone divided by that of the fine zone.

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**Figure 2.** Measured permeability (filled black squares) for each sand type (first four cases) and for the Mixed cases (LCM and HCM), and the calculated effective permeability for the 2-D sandboxes (filled black squares). Also shown are the arithmetic average (open circle), harmonic average (open triangle), and geometric mean (open diamond).
Renner, 2006]. Here $k_i$ is the permeability and $x_i$ is the volume fraction or layer thickness of the composing zone $i$. The $K_{eff}$ values can be quantified using harmonic averaging if the main flow direction is perpendicular to the orientation of different permeability zones (cross layers) and by arithmetic averaging when the main flow is parallel to the orientation of the different zones (flow along stratification). The geometric mean can be used to estimate $K_{eff}$ when both parallel and perpendicular flows exist relative to the direction of zonation. That is, when there is not a dominant flow direction relevant to the zonation.

As shown in Table 2 and Figure 2, due to similar permeability values in the fine and coarse zones, the LC sandboxes have similar arithmetic and harmonic means and effective permeability. In contrast, the $K_{eff}$ values in the HC cases are much closer to the arithmetic mean. This is because the resistance to the flow is high with the low-permeability fine sands. As a result, water preferentially flow through the coarse zone and the system acts if there are layers in parallel to the main flow direction. In contrast to observations in literature [Babadagli, 2006; Berg and Illman, 2011], the $K_{eff}$ values in all cases are higher than the geometric mean, indicating well-connected high permeability zones [Zinn and Harvey, 2003]. In the LCM case, flow occurs in all directions due to the lower permeability contrast and the mixing pattern, leading to the similarity between different types of averaged permeability values.

### 2.3.2. Visualization Test

The tracer experiments were carried out in the three LC cases, with the main flow direction from the bottom to the top. The fluid flow was visualized using phenol red. Figure 3 compares the dye distribution during the water-injection test (top) and the predicted bromide concentration profile (bottom) by the 2-D ADE at 0.45 pore volumes. In these LC cases with the permeability ratio of 2.21, the difference between the two zones is visible, verifying successful packing of different zones. The predicted spatial profiles of Br concentration agree qualitatively with the images, with the formation of concentration gradients shaped by the spatial zonation. The images also show unevenness and irregularities at the fronts even in the “homogeneous” LCM case, while the model predicts smooth front in a perfectly homogeneous medium. This emphasizes the importance of small-scale, unresolved heterogeneity that actually affects solute transport.

### 2.3.3. Solute Transport in High Contrast (HC) Cases

Figure 4 shows the measured and simulated Br breakthrough curves (first row) and the calculated flow velocity field (second row) from 2-D ADE for the HC cases. The calculated flow velocities in the low and high permeability zones from the 2-D ADE are within the same order of magnitude because the permeability ratio is only a factor of 5.1, much lower than the orders of magnitude permeability difference in studies for
highly heterogeneous porous media [Levy and Berkowitz, 2003; Zinn et al., 2004]. As expected, the HCM case has the homogeneous distribution of flow velocities except at the sampling outlets where relatively fast flow occurred because all flow converged to the outlets. As a result, the BTCs from the three outlets overlap. In the HCF and HCO cases, the fine zones have lower flow velocities compared to the coarse zone. The HCF case has a slightly higher flow channel in the middle and therefore slightly earlier breakthrough compared to the side outlets. In the HCO case, the flow rates are lower in the middle fine zone and higher at the sides. This results in earlier breakthrough from the sides starting at about 0.5 pore volumes and much later breakthrough from the middle outlet starting at around 1.0 pore volume. The difference in the breakthrough time from the side and middle outlets is much larger in HCO than in HCF.

The predicted flow velocity distribution shows that the setup of the outlet boundary, or the presence of the three outlets, affects flow distribution in regions up to about 3–5 cm distant from the outlet plane in all three cases. The flow field further away from the outlet plane is not affected. Although not shown here, we also compared the output of 2-D ADE with an open outlet boundary (without three outlets) to that with three outlets using the same set of parameters obtained from matching data. The comparison shows that the overall breakthrough curves in these two cases are almost identical with or without the three outlets, except that an open boundary led to about 5% earlier breakthrough in average than that with three outlets in the HC cases, which is considered negligible.

The local longitudinal dispersivity values from the 2-D ADE are 0.03, 0.38, and 0.45 cm for the HCM, HCF, and HCO cases, respectively. From a theoretically point of view, the local dispersivity values represent the intrinsic property of porous media because the heterogeneous flow fields are explicitly simulated and therefore should be the same in all cases. However, this seems not the case here. The $\alpha_L$ values for the HCF and HCO cases are relatively similar and are much higher than that of the HCM case. This may indicate intrinsic difference between cases with very small and large correlation lengths. The longitudinal local dispersivity $D_L$ also vary spatially (not shown here), the distribution of which is exactly the same as that of the flow rates as indicated by equation (2).

Figure 5 shows the evolution of the overall breakthrough data and the prediction from the models. The data look significantly different between cases. In the HCM case, the bromide breaks through between 0.9 and 1.1 pore volumes and reached more than 99.9% of inlet concentration ($\log(1 - C/C_0) = -3$) within approximately 1.2 pore volumes. In contrast, the breakthrough in the HCO starts much earlier, at approximately 0.5 pore volumes. The outlet concentration reached 99% of the inlet concentration at about 2.5 pore volumes ($\log_{10}(1 - C/C_0) = -2$). The early breakthrough has a slope not as sharp as that in HCM, indicating slower breakthrough than the HCM case. The BTC shows an apparent "step" at around 1.0 pore volume, the time when the breakthrough from the middle outlet starts, as shown in Figure 4c. This early breakthrough...
is primarily due to the “fast advection” from the higher flow channels at the sides with a characteristic median breakthrough time of 0.75 pore volumes, consistent with the medium arrival time from the side outlet shown in Figure 4c. Another step, or change in slope, occurs at around 2.0 pore volumes, when the breakthrough from the middle outlet ends. This second stage breakthrough is caused by the “slow advection” from the fine zone with a median arrival time of 1.5 pore volumes that is consistent with that from the side outlets shown in Figure 4c. After that, log(1−C/C₀) decreases much slower. This last stage is likely due to the “slow diffusion” because of the large size of the fine zone and small-scale heterogeneity. These different stages are similar to the observation in the fast flow high permeability contrast cases in [Zinn et al., 2004]. The major difference is that the BTC from slow diffusion here is caused by the large fine zone, not by very low permeability zones.

The breakthrough of the HCF case is somewhat between those of HCM and HCO. It does not have three distinct stages. However, a slight change in slope does occur at approximately 1.2 pore volumes. In fact, it can be characterized by two stage breakthrough, with most breakthrough between 0.7 and 1.5 pore volumes because the three outlets do not have very distinct breakthrough times. Later breakthrough due to diffusion occurs at much lower rates after about 1.6 pore volumes. In fact, the rates of the late breakthrough look similar between HCF and HCO, indicating this is not necessarily caused by the zonation. Instead it is probably more related to the small-scale, unresolved heterogeneity in the system.

With the exact setup of the heterogeneity structure, the 2-D ADE (equation (1)) captures detailed stages in the BTC well. Although the 1-D ADE does not capture the detailed breakthrough stages in HCO, it captures the “average” behavior of the BTC surprisingly well. It obtains a large α’ value of 1.96 cm for HCO and a much smaller value of 0.15 cm in the HCM case. The 2-D ADE also reproduces the shape of the HCF case almost perfectly, while the 1-D ADE does not capture the later stage of the HCF breakthrough.

The CTRW reproduces the HCM and HCF curves almost perfectly, however, not the HCO curve. In the latter case, the CTRW curve describes the early breakthrough and the long tail well, however, not the second stage characterized by the “slow advection” from the fine zone. This is expected because the HCO has distinct zones at the scale comparable to the domain, which represents a nonstationary domain [Berkowitz et al., 2006]. This is one of the CTRW limitations. Relatively large size of the low permeability zone in the HCO case separates exponential tails from each zone, which hinders the formation of a power law tail that a TPL model can often capture precisely [Willmann et al., 2008]. Values of β for the HCM, HCF, and HCO cases are 1.93, 1.72, and 1.56, respectively. Values of t₁ (10⁻⁶₄ min) are the same for HCF and HCO, both of which
are higher than that of HCM. Larger $t_2$ values mean longer time to approach the Fickian behavior. This transition occurs much later in the HCO ($\sim 6300$, $10^{3.6}$ min) and HCF ($\sim 2500$, $10^{3.4}$ min) compared to the HCM ($\sim 398$, $10^{2.6}$ min), indicating longer time needed to reach asymptotic Fickian behavior with increasing correlation length.

Compared to CTRW, the fADE does a much better job in reproducing the HCO data probably owing to the fact that the HCO case has large fine zone with lower permeability than that of the coarse zone, which facilitates the formation of the preferential flow path and channels. This is largely confirmed by the fact the fADE does not reproduce the data as well in the HCF case, where the preferential flow path is not as obvious in the HCO case.

### 2.3.4. Solute Transport in the Low Contrast (LC) Cases

The BTCs of the LC cases from the three outlets are similar to that of the HC cases, as shown in Figure 6. However, the difference between the breakthrough times from different outlets is much smaller compared to the HC cases. The LCM case has longer tail than the HCM case, indicating a more heterogeneous system although they are both packed in mixed pattern. The BTC of LCF does not show staged breakthrough, while the LCO case does show an early fast breakthrough and long tail later. However, no “steps” are observed in the BTC due to the relatively small permeability contrast between zones. CTRW reproduces the data well in all cases, as shown in Figures 6d–6f. The 2D ADE also does a reasonable reproduction of the data. Both 1-D ADE and fADE reproduce early part of the BTC, however, significantly underestimate the tails in LCM and LCF cases. In the LCO case, the fADE predicts a much earlier breakthrough than the data.

### 2.3.5. Effects of Permeability Variance

To quantify the effect of permeability variance, the three One-zone cases are compared in Figure 7. As shown in Figures 7a–7c, the difference in breakthrough times between the middle and the side outlets increases with increasing permeability contrast. Correspondingly, the small-scale dispersivity values increase with increasing variance, with 0.34, 0.55, and 0.45 cm, respectively, for the LCO, MCO, and HCO cases.

The overall breakthrough curves become wider with earlier breakthrough and longer tails as the permeability variance increase. Correspondingly, the observed stages or steps in the BTCs become increasingly obvious from the LCO to HCO cases. As expected, the 1-D ADE typically misses the tail. Surprisingly, it does better in the HCO case than in the LCO and MCO cases. Both 2-D ADE and fADE reproduce the data increasingly better with increasing permeability variance while CTRW does better in the LCO and MCO cases than in the HCO case. The value of $t_1$ remains the same $10^{-0.4}$ (0.4) min for all cases while the cutoff time $t_2$ increases with increasing permeability variance. This is expected because the travel time and
distance for approaching Fickian typically increase linearly or nonlinearly with permeability variance [Fiori et al., 2010].

2.3.6. Moment Analysis and Model Comparison
The first moment $T_1$ measures the mean advection time of the plume center; the second moment $T_2$ measures the time scale relevant to the width of the plume. As shown in Figure 8, the $T_1$ values vary between approximately 240 and 300 min, comparable to the range of residence times between 188 and 237 min. The $T_1$ values increase with correlation length, with larger increase in the HC cases than in the LC cases.

![Figure 7](image1.png)

**Figure 7.** Measured (symbols) and predicted (lines) local breakthrough for (a) LCO, $\lambda_c = 0.34$ cm, (b) MCO, $\lambda_c = 0.55$ cm, and (c) HCO, $\lambda_c = 0.45$ cm. Overall breakthrough and model output of 2-D ADE, 1-D ADE, fADE, and CTRW for (d) LCO; (e) MCO; (f) HCO.

![Figure 8](image2.png)

**Figure 8.** (a) First moment $T_1$ and second moment $T_2$ as a function of dimensionless correlation length ($\lambda/L$); relative difference between data and modeling output ($\delta$) for (b) breakthrough curves, (c) $T_1$, and (d) $T_2$. 

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Values of $T_2$ increase significantly from approximately 1000 to 8000 min$^2$ in the HC cases and from 1000 to 2400 min$^2$ in the LC cases, indicating the significant impact of correlation length and permeability variance on solute plume.

To quantitatively compare different models, the relative difference between the data and model outputs were calculated for the overall breakthrough curves (equations (15) and (16)) and the two moments (equations (13) and (14)). As shown in Figure 8b, in most cases, CTRW and 2D ADE have the smallest deviation from data while 1D ADE and fADE have relatively larger deviation for the overall BTC curves. Interestingly, the fADE predictions have smaller $\delta_v$ in all HC cases than in the LC cases. Within each permeability contrast series, the $\delta_v$ (BTC) values increase with correlation length in all models, emphasizing the challenge in capturing the overall breakthrough with increasing correlation length.

Figure 8c shows that most models capture the first moment well with $\delta_v$ values within 10%. Figure 8d shows that 2D ADE reproduces the closest $T_2$ in almost all cases. CTRW does better than fADE and 1D ADE in the LC cases. Consistent with observations in Figure 5, CTRW has larger deviation in the HC cases, especially in the HCO, where its $\delta_v$ is the largest among all models.

The fADE has larger $\delta_v$ values than CTRW in all cases except in the HCO case. Similar to observations in Figure 8b, the $\delta_v$ values of fADE for the moments decrease with increasing permeability contrast, as shown in the trend from LCO, MCO, to HCO. This can be attributed to the fact that fADE captures solute transport well when there is well-connected low permeability zones with channel formation [Benson et al., 2000a]. In cases other than HCO, the permeability contrast and/or the correlation length are not sufficiently large to form channels, which may explain why fADE does not do as well as other models in these cases.

The 1D ADE reproduces $T_1$ reasonably well. However, it generates the largest $\delta_v$ ($T_2$) among all models in most cases. Interestingly, the 1-D ADE has the largest $\delta_v$ values for $T_1$ in the LCM case and for $T_2$ in the HCM case, where the sandboxes are expected to be homogeneous. This is consistent with the irregular shaped fronts and concentration gradients observed in Figure 3, which emphasizes the importance of the smaller-scale heterogeneity. Surprisingly, 1D ADE does well in the HCO case compared to other cases.

It is important to mention here that the optimization scheme plays a large role in determining the performance of all models. Note that here we compare models optimized by minimizing the residuals of logarithm of concentrations to capture the tail and to keep consistency for comparison. If the models are optimized by minimizing the residual of concentration, the ADEs do better for the overall shape of the breakthrough curves than CTRW and fADE, as shown in Figure A2a in Appendix A. However, they generate the largest deviation for both $T_1$ and $T_2$, as shown in Figures A2c and A2d. In addition, the C residual minimization also leads to much smaller dispersivity values, as shown in Table A1.

2.3.7. Conditions for Non-Fickian Behavior

To put our work in the context of others and to quantify conditions under which the non-Fickian behavior arises, we followed the method of Zinn et al. [2004] and defined two dimensionless numbers, the Pecllet (Pe) and Damkohler (Da) numbers. The Pecllet number is the ratio of the time scale of diffusion to the time scale of advection through the fine zones. The Damkohler number has various definitions in literature. For easy comparison, here we use Zinn et al.’s [2004] definition that $Da$ is the ratio of the time scale of advection across the whole flow cell to the time scale of diffusion through the fine zone. Quantitatively, they are defined as follows:

$$Pe = \frac{v_{cz} R^2}{RD}$$

$$Da = \frac{LD}{v_{cz} R^2}$$

where $D$ is the diffusion coefficient of bromide in porous media, $L$ is the length of the flow cell, $R$ is the characteristic length of the heterogeneity structure. For the Mixed case, the mean grain size was used for $R$. For the Four-zone and One-zone cases, the length of the fine zones was used. The $v_{cz}$ and $v_{cz}$ are the velocities in the fine and coarse zones, respectively. Velocities were calculated using the permeability ratio of the fine ($K_{fz}$) and coarse zones ($K_{cz}$) and the average linear flow velocity of the flow cell. The average linear flow
velocity was calculated as follows using the total flow rate ($Q$), average porosity ($\phi$), height ($h$), and width ($w$) of the flow cell:

$$v_f = \frac{K_f K_c}{K_c} \times \frac{Q}{hw}$$

(19)

$$v_c = \left(1 - \frac{K_f}{K_c}\right) \times \frac{Q}{hw}$$

(20)

When the time scale of diffusion in the fine zone is smaller than that of advection in the flow cell, we expect limited tailing and the flow is close to Fickian. This essentially would be the top light gray region of the Figure 9 labeled with “Fickian region” ($Pe > Da^{-1}$ or $Pe > 1$). Tailing and non-Fickian flow are pronounced when advection or diffusion in the fine zone is much slower than advection in the flow cell, essentially the bottom left medium gray region labeled with “Advective mass transfer” for $Pe > 1$ and $Pe < Da^{-1}$ and the bottom dark gray region labeled with the “diffusive mass transfer” domain for $Pe < 1$.

Here the Pe and Da numbers for the seven cases in this work were calculated and plotted with those from Zinn et al. [2004] and others in Figure 9 (also listed in Table 3). Compared to other studies, our work provides a unique set of data that fill in the variable space with high Pe and a wide range of Da values. The Pe values cover a relatively narrow high range due to the single high flow rate used. The Mixed cases have large Da values due to their small fine zones and R values. The One-zone cases have low Da values because of their large fine zone and R values. Both Mixed cases (HCM, LCM) are in the Fickian zone defined in Zinn et al. [2004], while the LCF and LCO are close to or at the Fickian-advevtive transition line. The HCO and MCO cases are in the advective mass transfer zone, however, very close to the transition line. Note that although HCM, LCM, LCF, and LCO cases are all within the “Fickian” region defined by Zinn et al. [2004], their breakthrough curves indicated non-Fickian transport, with $\beta$ values between 1.97 and 1.88 and $\alpha$ values lower than 2.0. This indicates that the division between Fickian and non-Fickian region should be a gray zone instead of a rigid line. In our case, it seems that the division line Pe = Da^{-1} need to be moved up by 2 logPe units. This may also indicate that although the division line works well for porous media with small correlation lengths, it may not work as well for media with large correlation length.

It is known that the extent of non-Fickian behavior increases when permeability contrast increases, which was what Zinn et al. [2004] focused on by having orders of magnitude contrast between the high and low

| Table 3. Characteristic Parameters for Solute Transport in Sandboxes |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cases           | $\lambda/L$     | $\phi_k$        | Local $x^e$ (cm)| Global $x^g$ (cm)| $\alpha_f$ | $\beta$ | $t_1$ (min) | $t_2$ (min) | log(Pe) | log(Da) |
| LCM 0.001       | 0.10            | 0.02            | 0.13            | 1.96            | 1.92 | $10^{-1.2}$ | $10^{-2.6}$ | 2.65 | $-0.92$ |
| LCF 0.224       | 0.10            | 0.07            | 0.27            | 1.84            | 1.89 | $10^{-1.2}$ | $10^{-3.1}$ | 3.19 | $-2.52$ |
| LCO 0.447       | 0.10            | 0.34            | 0.51            | 1.80            | 1.88 | $10^{-0.4}$ | $10^{-3.5}$ | 3.51 | $-3.12$ |
| MCO 0.447       | 0.26            | 0.55            | 0.93            | 1.74            | 1.65 | $10^{-0.4}$ | $10^{-3.7}$ | 3.33 | $-3.27$ |
| HCM 0.001       | 0.43            | 0.03            | 0.15            | 1.91            | 1.93 | $10^{-1.1}$ | $10^{-2.6}$ | 2.86 | $-1.33$ |
| HCF 0.224       | 0.43            | 0.38            | 0.76            | 1.78            | 1.72 | $10^{-0.4}$ | $10^{-3.4}$ | 2.88 | $-2.70$ |
| HCO 0.447       | 0.43            | 0.45            | 1.96            | 1.58            | 1.56 | $10^{-0.4}$ | $10^{-3.8}$ | 3.21 | $-3.37$ |

*From 2D ADE optimized by minimizing residual of the logarithm of concentrations.

*From 1D ADE optimized by minimizing residual of the logarithm of concentrations.
permeability zones. Compared to their maximum contrast by a factor of 1800, our maximum permeability contrast was a factor of 5.17. Our results indicate that even with relatively low permeability variance, non-Fickian behavior can be pronounced if the length of the fine zone is comparable to the domain length. This is particularly important because the non-Fickian behavior largely depends on the time scale of diffusion in and out of the fine zone. The time scale of diffusion depends on the characteristic length of the fine zone in quadratic form \((t_{\text{diff}} = \frac{R^2}{D})\) instead of linear form. Therefore, the time scale for diffusion increases with length much faster than that of advection.

2.3.8. Dispersivity Parameters
Table 3 summarizes the parameters that characterize the heterogeneity structure, permeability variance, and solute transport for all seven cases. Figure 10 maps the global dispersivity \(\alpha'\) and dispersion parameter \(\beta\), (c) \(t_1\), and (d) \(t_2\).

Figure 10. Dispersion parameters as a function of dimensionless correlation length and permeability variance. (a) Global dispersivity \(\alpha'\), (b) dispersion parameter \(\beta\), (c) \(t_1\), and (d) \(t_2\).

permeability zones. Compared to their maximum contrast by a factor of 1800, our maximum permeability contrast was a factor of 5.17. Our results indicate that even with relatively low permeability variance, non-Fickian behavior can be pronounced if the length of the fine zone is comparable to the domain length. This is particularly important because the non-Fickian behavior largely depends on the time scale of diffusion in and out of the fine zone. The time scale of diffusion depends on the characteristic length of the fine zone in quadratic form \((t_{\text{diff}} = \frac{R^2}{D})\) instead of linear form. Therefore, the time scale for diffusion increases with length much faster than that of advection.

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Figure 10a also shows that with similar small correlation length, increasing permeability variance leads to much more increase in dispersivity values when the permeability variance is below 1.5. Once the permeability variance is larger than 1.5, the permeability variance has relatively low impact on dispersivity values. This
indicates that as long as the permeability variance is sufficiently large that the fine zone acts as the immobile zone and is dominated by the diffusion process, further increase in permeability variance has relatively minor impact.

Similarly, the extent of non-Fickian behavior also increase significantly with the correlation length, as shown in Figure 10b with the increasing deviation of $\beta$ from 2. Comparison of our $\beta$ values to those from Levy and Berkowitz [2003] shows that they had a larger extent of non-Fickian behavior with relatively small correlation length due to the large $\sigma_{lnK}^2$ values up to 2.1. The use of TPL form in CTRW allows the quantification of the time scales for the onset and the end of the non-Fickian behavior. As shown in Figure 10c, values of $t_1$ are all within a minute and are lower under low permeability variance and short correlation length conditions. Values of $t_2$ increase with correlation length and permeability variance. Based on stochastic theory, the travel time to approach Fickian transport depends on permeability variance and on correlation length for low-heterogeneity media [Dagan, 1989]. In the HC cases, $t_2$ increases from $10^{2.6}$ to $10^{3.8}$ min for HCM to HCO, an increase of 1.2 orders of magnitude. In the LC cases, the value of $t_2$ increased from $10^{2.6}$ to $10^{3.5}$ min for LCM to LCO, an increase of 0.9 orders of magnitude. For the three One-zone cases with the same correlation length, the $t_2$ values increase from $10^{3.5}$ to $10^{3.8}$ min, almost a factor of 2, when $\sigma_{lnK}^2$ increases from 0.10 to 0.43. This indicates that the correlation length plays a significant role in determining the time needed to approach the asymptotic, Fickian transport regime.

### 3. Discussion and Conclusions

This work presents the first set of flow cell experiments that systematically measure the control of the correlation length on effective permeability and non-Fickian solute transport [Cortis and Berkowitz, 2004; Levy and Berkowitz, 2003]. Seven sandboxes (21.6 cm × 20.9 cm × 1.0 cm) were packed with sand grains of different size range in three spatial patterns of fine and coarse zones with dimensionless correlation length varying from 0.01 to 0.45. The sandboxes have three relatively low permeability variance $\sigma_{lnK}^2$, 0.10, 0.26, and 0.43, respectively, for the low (LC), medium (MC), and high contrast (HC) cases. This work provides a unique set of data under low permeability variance and increasing correlation length conditions where experiments have been rarely carried out. We chose to study low-heterogeneity media due to their relevance in many geological settings and field sites [Leblanc et al., 1991; Mackay et al., 1986]. The goal is to answer two questions: (1) how and to what extent does correlation length control effective permeability and breakthrough curves (BTC)? (2) Which model can best reproduce data under what conditions?

Effective permeability $K_{eff}$ in general increase with correlation length due to the formation of flow channels in high permeability zones. Values of typically fall between the arithmetic and harmonic mean of permeability of the fine and coarse zones. The $K_{eff}$ values of the HC flow cells are closer to the arithmetic mean, indicating the formation of preferential flow path in the coarse zone. The $K_{eff}$ values of the LC flow cells, however, are closer to the harmonic mean, which can be attributed to the cross-layer type of flow distribution due to similar permeability between different zones. The geometric mean is far from the $K_{eff}$ values for most cases, possibly due to the correlation in high permeability zones.

While the cases with short correlation length exhibits relatively low extent of non-Fickian transport, those with long correlation length shows significant tailing and non-Fickian transport. In particular, the HC One-zone (HCO) case shows distinct steps and stages of breakthrough arising from fast advection in the coarse zone, slow advection in the fine zone, and slow diffusion. With the same correlation length, the LCO and MCO cases do not exhibit the staged breakthrough, indicating that the permeability contrast between zones has to be sufficiently large in order for the correlation length to be important.

Four models have been used to simulate solute transport and reproduce the BTCs by minimizing the residual of logarithm concentrations. These include the 2D ADE that explicitly takes into account the heterogeneity structure, the 1D ADE that assumes homogeneous media with average porosity and permeability, and the nonlocal in time CTRW and nonlocal in space fADE. Comparing these models, 2D ADE typically has the lowest deviation from data. However, it is important to note that 2D ADE is also more data “expensive” because the exact heterogeneity structure has to be part of the input. In reality, we rarely have this kind of luxury. It is interesting to note that the relative deviation $\delta_r$ of 2D ADE for the first and second moments are the largest in the HCM case that is expected to be homogeneous. This highlights the importance of the
small-scale, unresolved heterogeneity in controlling the solute transport in apparently "homogeneous" media.

CTRW reproduces the data and moments well in most cases except the HCO case. This is expected because the CTRW framework involves taking ensemble average over the entire domain assuming the heterogeneity length is much smaller than the domain length [Berkowitz et al., 2006]. The HCO case, however, is actually a nonstationary domain with comparable length scales of heterogeneity and the domain. It is possible that a correlated CTRW can reproduce the BTC in HCO case better, because the flow pattern in Figure 4 shows correlated flow channels. In addition, the Peclet number in the HCO case is 10^{1.21}, which is within the suggested flow conditions (Pe > 100) where incorporating correlation can be critical [Bolster et al., 2014].

In contrast, for the HCO case, the fADE does not reproduce the BTC as well as CTRW in most cases. However, it reproduces the data the best among all models. In fact, fADE reproduces the BTC increasingly well with increasing permeability contrast. This largely confirms that fADE is strong in reproducing BTCs well with high permeability contrast and well-connected media. In other cases, the conditions do not allow the formation of channels and preferential flow path so that the fADE does not do well. Stratified low-permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface [Koltermann and Gorelick, 1996; Li et al., 2014; Pedretti et al., 2013; Salekhkoo et al., 2013]. It is expected that fADE will work better under these conditions. As has been argued in literature, both non-local in time and nonlocal in space methods have their strengths and limitations. It has been argued that may be non-local models both in time and space are needed to fully capture non-Fickian transport [Neuman and Tartakovsky, 2009].

With the optimization minimizing the residual of the logarithm concentration, even 1D ADE reproduces the average behavior of HCO BTC relatively well, although it does not capture the detailed stages of the breakthrough. The 1D ADE, however, also has the largest deviation for the 2nd moment of data for most cases, especially in the HCM case. It is important to note here that these conclusions are based on the optimization scheme that minimizes the residual of logarithm concentrations. With minimization of residual of concentration, the ADEs tend to have much larger deviation from the data for the prediction of moments, especially the second moment, as shown in Appendix A.

With the permeability variance of 0.43, the correlation length strongly controls the effective dispersivity and the extent of non-Fickian behavior, with the global dispersivity varying from 0.15 cm in the HCM case to 1.96 cm in the HCO case. Similarly, β values from CTRW vary from 1.97 in the HCM case to 1.56 in the HCO case. Values of t₂, which represent the time scale needed to reach asymptotic dispersivity, increase with the correlation length from 10^{-6} min in the HCM cases to 10^{18} min in the HCO case. In the LC cases, however, the effects of the correlation length are negligible. This indicates that the permeability variance needs to be sufficiently large for correlation length to be important in determining solute transport. This also implies that the solute needs to travel a longer time in a more heterogeneous media to experience sufficient heterogeneity to reach asymptotic, Fickian behavior—a major finding in the subsurface stochastic hydrology in the past decades [Dagan, 1989].

Our comparison with literature data shows that the control of correlation length on the solute transport is potentially as strong as, if not stronger than, that of permeability variance. This is because effective dispersivity and non-Fickian behavior depends largely on the time scale of diffusion in the fine zone, which increases fast with the characteristic length scale of the fine zone in the form of R²/D. On the other hand, as long as the permeability variance is sufficiently large that the fine zone acts as the immobile zone, further increase in permeability variance has relatively minor impact. Interestingly, all our data fall in the Fickian region or the boundary of the Fickian and Adveactive mass transfer regime defined by Zinn et al. [2004]. However, non-Fickian transport is observed in all cases.

Stratified low permeability layers and clay lenses with comparable length scale as the domain length are very common in natural subsurface. Numerical studies have emphasized the importance of connectivity and correlation length in controlling solute transport. For example, Pedretti et al. [2013] concluded that the degree of stratification primarily control the late time distribution of the concentrations in convergent flow field tracer tests in realistic three-dimensional settings. In our work, we observe significant non-Fickian transport in the HCO case with relatively low permeability variance (0.43). Existing experimental work has mostly focused on porous media with short correlation length. Our work points to the need of studying systems with comparable correlation length to the domain of interest.
Appendix A: Comparison Between Measured Data and Model Prediction by Minimizing the Residual of Concentrations for 1-D ADE and 2-D ADE

With the minimization of concentration residual, the 2D ADE (equation (1)) captured the BTC curves well in the HCO case up to about 2.0 pore volumes when the first two stages end. Beyond that it quickly drops and cannot capture the later tails likely caused by the diffusion process associated with unresolved heterogeneity at scales smaller than the zonation. The 1D ADE captures the “average” behavior of the BTC in HCO, as shown in Figure A1c, however, not the detailed stages in the tails shown in Figure A1f. The 1D ADE obtains a large $\alpha'$ value of 1.04 cm for HCO and a much smaller value of 0.08 cm in the HCM case. These values are much smaller than the 1.96 and 0.15 cm, respectively, for HCO and HCM, obtained by minimization of logarithm concentration, as shown in the comparison in Table A1. This indicates the importance of optimization method in reproducing the BTC curves.

As can be observed in Figure A2a, with the concentration residual minimization, the 2-D ADE has the smallest deviation from the overall breakthrough. However, its deviation from the data is much larger than the CTRW and fADE with logC residual minimization. The comparison of this figure and Figure 8 in the main text indicates that the ADE curves, especially 2-D ADE, capture the tails much better when they are optimized by minimizing residuals of logarithm concentration.

Figure A1. Comparison of overall breakthrough data with predicted curve using 2D ADE, 1D ADE, CTRW, and fADE for (a) HCM: $\alpha_f = 1.91$, $\beta = 1.93$, $t_1 = 10^{-1.1}$ min, $t_2 = 10^{-0.9}$ min, $x' = 0.08$ cm, (b) HCF: $\alpha_f = 1.78$, $\beta = 1.72$, $t_1 = 10^{-0.4}$ min, $t_2 = 10^{-0.4}$ min, $x' = 0.47$ cm, and (c) HCO: $\alpha_f = 1.58$, $\beta = 1.56$, $t_1 = 10^{-0.4}$ min, $t_2 = 10^{-0.8}$ min, $x' = 1.04$ cm. Here the 1D and 2D ADE curves are obtained by minimizing the residual of concentrations, while the CTRW and fADE are still the ones from minimizing the residual of logarithm concentrations.

Figure A2. Relative difference between data and modeling output ($\delta$) for the (a) overall breakthrough, (b) first moment, and (c) second moment for all models. Here the 1-D and 2-D ADE curves are obtained by minimizing the residual of concentrations, while the CTRW and fADE are still the ones from minimizing the residual of logarithm concentrations.
Table A1. Characteristic Parameters for Solute Transport in Sandboxes

| Cases | \( \Delta s \) | \( s_{1,3}^2 \) | Local \( s^* \) (cm) | Local \( s'' \) (cm) | Global \( s^* \) (cm) | Global \( s'' \) (cm) |
|-------|--------------|-------------|----------------|----------------|----------------|----------------|-------|--------|--------|--------|--------|--------|
| LCM   | 0.001        | 0.10        | 0.02           | 0.08           | 0.13            | 0.08            |
| LCF   | 0.224        | 0.10        | 0.07           | 0.22           | 0.27            | 0.28            |
| LCO   | 0.447        | 0.10        | 0.34           | 0.16           | 0.51            | 0.24            |
| MCO   | 0.447        | 0.26        | 0.55           | 0.21           | 0.93            | 0.67            |
| HCM   | 0.001        | 0.43        | 0.03           | 0.08           | 0.15            | 0.08            |
| HCF   | 0.224        | 0.43        | 0.38           | 0.21           | 0.76            | 0.47            |
| HCO   | 0.447        | 0.43        | 0.45           | 0.29           | 1.96            | 1.04            |

*From 2D ADE with log C residual minimization.
(2) From 2D ADE with C residual minimization.
(3) From 1D ADE with log C residual minimization.
(4) From 1D ADE with C residual minimization.

Appendix B: Raw Data From Sandbox Experiments

Appendix B contains the raw experimental data from the sandboxes. Table B1 is raw bromide breakthrough data from each outlet (left, middle, and right) for all seven sandboxes. Table B2 is the flow rate data from each outlet for all seven cases.

Table B1. Breakthrough Data in the Form of \( C/C_0 \) From Individual Outlets (Left, Middle, and Right)

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<th>MCO</th>
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Table B2. Flow Rates From Three Different Outlets of Sandboxes

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Acknowledgments

The raw data and some figures generated using models by minimizing residuals of concentration for 1-D ADE and 2-D ADE are shown in the Appendix A and B. This work is supported by the Department of Energy and the Environment (PSEIE) and by the Department of Energy Office of Sciences Subsurface Biogeochemical Research (SBR) Program under the project DE-FOA-0000311. We thank the Associate Editor Daniel Fernández-Garcia and four anonymous reviewers for their persistence in seeing a better paper out of this work and their diligent, meticulous, insightful, thought-provoking, and constructive comments that have significantly improved the paper. We thank Andrea Cortis for valuable discussion on CTRW and optimization schemes.

References


