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Laboratory Experiments on Dispersive Transport Across Interfaces: The Role of Flow Direction

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Abstract. We present experimental evidence of asymmetrical dispersive transport of a conservative tracer across interfaces between different porous materials. Breakthrough curves are measured for tracer pulses that migrate in a steady-state flow field through a column that contains adjacent segments of coarse and fine porous medium. The breakthrough curves show significant differences in behavior, with tracer migrating from fine medium to coarse medium arriving significantly faster than from coarse medium to fine medium. As the flow rate increases, the differences between the breakthrough curves diminish. We argue that this behavior indicates the occurrence of significant, time-dependent tracer accumulation in the resident concentration profile across the heterogeneity interface. Conventional modeling using the advection-dispersion equation is demonstrated to be unable to capture this asymmetric behavior. However, tracer accumulation at the interface has been observed in particle tracking simulations, which may be related to the asymmetry in the observed breakthrough curves.

1. Introduction

The correct accounting for the effects of interfaces across different porous materials is a longstanding issue in modeling advective-dispersive transport of contaminants in porous domains. While the continuity equation for the concentration $c = c(x, t)$,

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial j(x, t)}{\partial x} \quad (1)$$

dictates how the temporal change in the concentration is related to the divergence of the tracer flux, $j(x, t)$, the specific constitutive expression for flux remains an open question. At the interface between two different porous materials, the classical assumption is that of continuity of a Fickian type of flux, i.e.,

$$j(x, t) = v(x)c(x, t) - D(x)\frac{\partial c(x, t)}{\partial x}, \quad (2)$$

where v is the pore velocity and D is a coefficient of dispersion.

For simplicity, we focus here on the fundamental case of conservative tracer transport in a porous column consisting of two adjacent segments of different (coarse and fine) glass bead packs. As shown schematically in Figure 1, tracer transport can be considered in two directions, from the fine medium to the coarse medium (F-C direction), or from the coarse medium to the fine medium (C-F direction). With the assumption of flux and concentration continuity across

the interface, therefore, one might intuitively expect that breakthrough curves (BTCs) in the F-C and C-F directions will be similar because tracers experience equal lengths of subdomains in both directions.

Indeed, an often unspoken hypothesis in transport in heterogeneous media is that the spatial arrangement of the heterogeneity has very little influence on the upscaled transport behavior. Stochastic methods [Freeze, 1975; Zhang, 2002], for instance, base their predictions on geostatistical models of the heterogeneity, in combination with local implementations of the classical (constant coefficient) advection-dispersion equation (ADE).

Moreover, the implementation of random walk schemes (via numerical particle tracking methods) to treat transport usually involves solution of the diffusion and advection-dispersion equations with discontinuous coefficients (for diffusivity and porosity). In particular, [Labolle *et al.*, 1996, 2000] simulate transport between two porous materials with different porosities (i.e., in media with spatial discontinuities). Labolle and Zhang [2006] and Lim [2006] note that the random walk methods satisfy the ADE, but from examination of mass conservation in the vicinity of the discontinuities (interfaces), they raise concern over potential (and possibly unphysical) accumulation of mass around the interface between the materials, particularly in one-dimensional domains.

On the other hand, from analysis of solutions based on the ADE, Schwartz *et al.* [1999] find that a discontinuity in resident concentrations at the interface between a porous medium and the inlet or outlet reservoir may arise for low Péclet numbers (i.e., when the advective contribution is small compared to the diffusive and dispersive contributions). Also, van Genuchten and Parker [1985] suggest that concentration may not be continuous across an interface between two layers of porous medium. More recently, Hornung

et al. [2005] and *Marseguerra and Zoia* [2006] examine discontinuity effects at interfaces between two different porous materials, in terms of diffusion-only systems, finding that a physically-justified concentration discontinuity can indeed arise. Extending the analysis to advective-dispersive systems, *Marseguerra and Zoia* [2007] find similar discontinuities to arise. We return to discuss these results in Section 3.

There are few reports in the literature on tracer transport experiments in such composite media. *Sternberg* [2004] and references therein carried out experiments in one-dimensional columns containing layered segments of uniform glass beads with different sizes. They estimated first and second spatial moments from the measured concentration distribution along the column. The analysis of the experiments suggests that the discontinuities between the different segments can lead to different mixing behaviors, and that symmetry in concentration profiles is not reached when the order of the segments is changed. *Sternberg* [2004] also notes that the measured behavior is not consistent with that predicted by use of the ADE. Other experimental studies have focused on transport across the interface between a laboratory column and the inlet/exit reservoirs [e.g. *Novakowski*, 1992; *Schwartz et al.*, 1999].

Here, we focus on the case shown in Figure 1 and quantitatively measure tracer BTCs in the two directions of flow. Our emphasis is on examining whether and to what magnitude the interface between macroscopic heterogeneities can affect the transport, namely, the symmetry of the BTCs. In particular, we study if, and how, the direction of the flow at a sharp interface between two different geological units affects the transport of a non-reactive solute flowing across it. Despite its apparent simplicity, this problem has not received sufficient attention in the hydrogeological literature.

2. Column Experiments

A series of experiments focused on measuring BTCs for a conservative tracer migrating in a one-dimensional flow field, through an horizontal column containing two different sections of uniformly packed glass beads. A composite packing arrangement was achieved by filling a plexiglass column 40 cm long, with internal diameter of 2.54 cm. The inlet and outlet ends of the column were separated from the porous medium by thin nylon meshes with hydraulic conductivity larger than those of the glass beads. The effect of these meshes on the overall hydraulic conductivity and transport properties of the porous system can be considered negligible. Small open volumes between the meshes and the column closure caps served to promote tracer mixing and to further dampen subtle pulses in the injected liquid caused by the peristaltic pump. The filling materials included two sizes of uniform borosilicate glass beads, with diameters of 1 mm and 4 mm. In the following, we refer to these two filling materials as fine (F) and coarse (C), respectively.

Each column packing was carried out under saturated conditions, with (sequentially) small amounts of glass beads being poured through water and stirred with a thin stick to avoid air entrapment. During packing the column was in a vertical position. In addition, the glass beads were compacted and the column was shaken frequently during the process of packing. The column was filled half way (20 cm) with the fine glass beads. A thin nylon mesh (with hydraulic conductivity larger than that of the small diameter beads) was laid on the top layer, and the coarse glass beads were then packed above the fine material to fill the column, using the same procedure described above. The packing methodology ensured that the columns were as uniformly saturated and as homogeneous as possible. The final result was a

composite porous column with a sharp interface at the column midpoint. The porosity was controlled by weighing the amount of glass beads packed into a given column volume. Note that as the grains of both materials are spherical, the value of the porosity, n , does not change in the fine and coarse sections; $n \approx 0.3$. Thus, for the one-dimensional flow arrangement and fixed volumetric flow rate, the fluid velocity through the column remains constant.

The flow rate of the injected water and tracer (sodium chloride) was controlled by a peristaltic pump (Masterflex, USA) together with a flow dampener. A T-joint connected salt water and fresh water reservoirs, which enabled an immediate switchover between the different water supplies without interrupting the flow. In each experiment, fresh water was used to initiate and stabilize the flow, and to calibrate the background concentration. Salt water was then injected to displace the fresh water and to determine BTCs. The effluent conductivity was measured over time with an electrical conductivity (EC) meter (TWIN, Japan), with maximum measurement error of 1%, and then converted to tracer concentration values by using calibration curves. All tracer experiments were run until the effluent conductivity was steady and equal to the inflow concentration, at a constant room temperature of 23 °C. In all experiments, degassed fresh water was prepared from deionized water heated under vacuum; salt water contained 500 mg/L NaCl. In each experiment, the total volume of injected saltwater was 1.5 ml, after which fresh water was flushed through the column.

We investigated three different flow rates: 0.3, 0.4, and 1.0 ml/min. A first pair of tracer BTCs was measured by flowing the water in the fine-to-coarse (F-C) direction. A second pair of BTCs was then obtained by repeating the experimental procedure on the same column packing, but in the coarse-to-fine (C-F) direction. The column was thoroughly flushed and the flow allowed to restabilize after each experiment. To maximize the resolution and accuracy of the measurements, “dead volumes” of fluid (containing both tube volume and inlet volume of column) were accounted for in the treatment of the measurements.

The experimental results are presented in Figure 2. It can be seen that for a flow rate of 1 ml/min, the BTCs in the F-C and C-F directions do not differ significantly. For the smaller flow rates, however, the BTCs show a significant difference in the peak arrival times. The difference increases for lower values of the volumetric flux. The experimental results show that the BTCs in the C-F direction are slower and more disperse than their counterparts in the opposite F-C direction, which are faster and less disperse. Preliminary experiments suggest that the asymmetry in the BTCs decreases by decreasing the grain size contrast; precise quantification of this relationship will be considered in a separate study. Thus, our experimental results indicate that the BTCs depend both on (i) the overall volumetric flux, and (ii) on the degree of difference in hydraulic conductivity (and Fickian dispersivity) jump at the interface.

Moreover, separate experiments on 20 cm columns, packed individually with 1 mm or 4 mm glass, were carried out with a 0.3 ml/min flow rate. The BTCs were found to be reasonably well characterized by the ADE, with estimated dispersivity values of $\alpha = 1.3 \times 10^{-3}$ and 9.6×10^{-3} m, respectively.

3. Results and Discussion

3.1. Conceptual Interpretation

We begin by first providing a conceptual picture to interpret the measured BTCs. The C-F BTCs shown in Figure 2 have lower peaks and are broader (more disperse) than the corresponding F-C BTCs. We argue that these results suggest that there is significant accumulation of tracer at the

interface, in the C-F direction. In other words, tracer migrating through the coarse glass bead segment encounters difficulty crossing the interface and entering the fine glass bead segment. Thus, tracer accumulation at the interface causes a “slow release” into the fine glass bead segment, leading to a time shift and a more disperse BTC. As such, the common assumption of continuity in the Fickian flux at the interface and the usual definition of flux (equation (2)) deserve careful consideration: it is apparent that the expression for the flux depends nonlinearly on the accumulation of the tracer at the interface, and that the mass distribution near the interface is time-dependent. Moreover, tracer accumulation may lead to development of a very steep concentration gradient across the interface; the resident concentration profile across the interface may in some case be considered as discontinuous, although molecular diffusion acts against this.

As flow rate increases, differences in BTCs in the two directions become less significant; the advective transport evidently eliminates the tracer accumulation, suggesting that it is caused primarily by diffusive effects. More specifically, increasing the flow rate overrides back diffusion and accumulation at the interface, so that concentration continuity is reached. This point is also made by *Marseguerra and Zoia* [2007]. It is interesting to note that this behavior can be considered somewhat counter-intuitive, given that increased effects of diffusion (i.e., slower flow rates) might be expected to increase the degree of “homogenization” and thus eliminate any accumulation of tracer at the interface.

3.2. Partial Differential Equation Models of Transport

With the above interpretation of the BTC measurements, it is natural to ask if such behavior is expected using standard modeling methods, i.e., the ADE. In fact, the latter, with the assumption of Fickian flux continuity at the interface, does not provide for a difference in the arrival times for the BTCs in the two directions; in other words, transport is invariant upon a reflection symmetry. To illustrate this point rigorously, we consider the 1D form of the ADE.

Consider now a composite material consisting of two columns of equal length, and porosity (i.e., same fluid velocity v), but (in terms of the ADE) with different dispersivity, α_F and α_C (Figure 1): this can be achieved by using a composite packing of homogeneous spherical grains with two different diameters.

We can show that in this case an ADE description of transport predicts that there should be no difference in the shape and arrival times of the two BTCs in the F-C and C-F directions. For the sake of the argument, let the water flow from the fine material into the coarse material (F-C). When the boundary condition at the inlet of the column is given by a total flux $\tilde{j}_0(u)$, then the solution for the total flux at the left of the column interface (fine material, F) is given by the convolution of the inlet boundary condition with the Green’s function of the transport equation, $G(x=1, t, \alpha)$. Here the dispersivity is the ratio of the dispersion coefficient, D , to the pore velocity, $v = q/n$. The analytical solution for this problem can be written expediently as a product in the Laplace space of parameter u , i.e., $\tilde{j}^{(F)}(u) = \tilde{j}_0(u)G^{(F)}(u, \alpha_F)$.

The tracer flux at the interface can be now taken to be the boundary condition for the coarse segment of the column. The solution for the total flux at the outlet of the coarse column is thus

$$\tilde{j}^{(F-C)}(u) = \tilde{j}_0(u)G^{(F)}(u, \alpha_F)G^{(C)}(u, \alpha_C). \quad (3)$$

This is an exact analytical solution valid when the lengths and the pore velocity of the fine and coarse column sections are the same, and for the definition of flux given by (2). From this analytical solution it is obvious that reversing the order of the flow the solution does not change

as the product of the two Green functions G is commutative. It is also straightforward to see how this reflection-symmetry argument fails for a different definition of the flux. For example, with a Fokker-Planck flux expression $j(x, t) = v(x)c(x, t) - \frac{\partial D(x)c(x, t)}{\partial x}$, the space derivative of the dispersion coefficient $D(x)$ introduces a direction-dependent drift correction to the tracer velocity of the form $v - \frac{\partial D(x)}{\partial x}$ [*Cortis et al.*, 2004b].

To illustrate this argument further, we solve the classical ADE numerically for the case of flow in the C-F and F-C directions (Figure 1). As shown in Figure 3, the resident concentration profiles in the two directions differ significantly, but the resulting BTCs at the column outlets in the two directions are identical. The numerical solution in Figure 3 was obtained by means of a spectral collocation method in the Laplace space, and then inverted to the time domain. Alternative numerical schemes based on finite differences, finite volumes, and finite elements provided identical results.

We note that *Leij and van Genuchten* [1995] demonstrate a difference in BTCs, qualitatively similar to those shown in Figure 2, by solving the ADE under the assumption that the porosity (and thus the fluid velocity) and dispersivity (with relatively large values) change significantly between the two segments. However, applying this solution to match the same quantitative differences requires a change in porosity of a factor of about 1.5 – 2 (coarse beads to fine beads ratio), and values of dispersivity about ten times larger than those estimated for the individual columns (Section 2). Such values are clearly not realistic for the two glass bead media used in the experiments. Moreover, a porosity contrast cannot explain the flowrate-dependent differences in BTCs displayed in Figure 2.

The above argument demonstrates that use of the conventional ADE is inadequate to describe the observed differences in BTCs shown in Figure 2. The constraint of flux continuity at the interface is dictated by the continuity equation (1), and it cannot be prescribed otherwise. However, the actual definition of the flux can be different from the usual form (2). While the flux is continuous, it is time-dependent, and changes as the amount of accumulated tracer at the interface changes over time. Note, also, that this condition says nothing about the character of the resident concentration problem across the interface. Clearly, diffusion plays a role in modifying the time-dependence of this accumulation, but diffusion is not the primary driving force; rather, tracer accumulation is due primarily to the abrupt change in hydraulic conductivity at the interface.

Now, depending on the particular constitutive relationship for the flux j (e.g., Fickian as given by (2), or Fokker-Planck) an anomalous accumulation of the resident concentration at the interface may appear. In the experiments shown here, we argue that the resident concentration profile across the interface may display a sharp gradient or even discontinuity.

3.3. Model Evidence of Tracer Accumulation

As shown in the previous subsection, simply solving an ADE transport equation with Fickian flux continuity does not allow for tracer accumulation at the interface. We therefore consider particle tracking simulations of transport.

Hornung et al. [2005] employ particle tracking simulations within the context of a continuous time random walk (CTRW) framework [*Berkowitz et al.*, 2006]. Of particular interest is their discussion of discontinuity effects that arise in terms of diffusive-only systems. Specifically, *Hornung et al.* [2005] show that mass can indeed accumulate at the interface, so that $c_1 \neq c_2$. These authors suggest that, instead, the chemical potential is continuous. *Marseguerra*

and Zoia [2006] consider a similar approach using CTRW, and also find evidence for a concentration discontinuity at the interface.

Marseguerra and Zoia [2007] expand this modeling approach by considering also tracer transport in an advective flow field. In their simulations (especially Figure 10 in Marseguerra and Zoia [2007]), the first and second segments of the column have parameter values corresponding to domains with more and less dispersive properties, respectively. In other words, they consider a case corresponding to the C-F direction BTC in our experiments. These simulations show a clear accumulation of tracer at the interface, with a sharp concentration discontinuity, in the C-F direction. Reversing the values of the simulation parameters, no tracer accumulation appears at the interface [A. Zoia, personal communication, 2008]. However, these analyses have not yet been applied to consideration of BTCs such as displayed in Figure 2.

We note that tracer transport through a column of “homogeneous” porous medium may display non-Fickian behavior on small length scales, with a transition to ADE behavior over longer scales [e.g., Cortis *et al.*, 2004a]; this is controlled by the tracer residence time in the column. However, regardless of whether or not the overall transport in each column segment is described by the ADE, we suggest the possibility that non-Fickian (CTRW) effects may become manifest in the vicinity of the interface, as shown by the particle tracking methods. This would in essence lead to a change in the model flux condition at the interface. Preliminary results extending the PT simulations to determine BTCs confirm that asymmetry in the BTCs can result from the concentration discontinuities. A complete analysis with this approach will be reported in a separate study.

4. Concluding Remarks

Our experiments show clear flowrate-dependent differences in BTCs in a column consisting of two equal-length segments containing two kinds of uniform porous media, when the direction of flow is reversed. Furthermore, we have demonstrated that use of the Fickian form of flux, (2), in a transport model does not account for these differences. As a consequence, we argue that in such cases, the resident concentration profile across the heterogeneity interface displays significant, time-dependent accumulation of tracer, as a function of the flow rate. Clearly, it remains to obtain direct experimental measurements of tracer accumulation or a potential concentration discontinuity at the interface, to account for the flux appropriately, and to achieve a one-to-one quantitative correspondence between simulations and the experiment measurements. Particle tracking simulations accounting for non-Fickian transport near the interface may provide a means to quantify this behavior. Extension of these PT simulations to BTCs is in progress.

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Figure Captions

Figure 1. Schematic of the transport problem across a macroscopic heterogeneity interface. The column of length L consists of two adjacent, equal-length segments comprised of different porous materials; (F) fine glass beads; (C) coarse glass beads.

Figure 2. Experiments showing differences in breakthrough behavior for coarse to fine (C-F) and fine to coarse (F-C) directions of flow, at flow rates of 0.3 ml/min, 0.4 ml/min and 1 ml/min. The tracer input pulse times are 5 min, 3.75 min, 1.5 min and the sample collection intervals are 5 min, 3.75 min, 1.5 min, respectively. Solid symbols represent C-F direction, and open symbols represent F-C direction. Two experiments in each direction were measured

for the 0.3 ml/min and 0.4 ml/min flow rates. Each point represents an average of three measurements. The vertical axis shows electrical conductivity (EC), which is directly proportional to concentration.

Figure 3: Profiles of tracer resident concentration for the ADE model, for flow in the F-C (solid curves) and C-F (dashed curves) directions, at two times. The interface between the C and F segments lies at $x = 0.5$. In the calculations, all quantities are dimensionless with $v = 1.0$; $D = 0.05$ and $D = 0.40$ in the fine and coarse column segments, respectively. Significantly, the resulting BTCs at the column outlets in each of the F-C and C-F directions are identical.

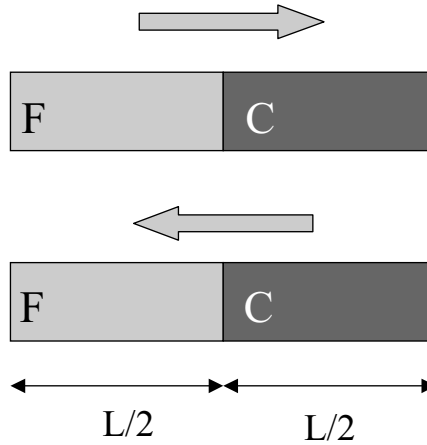


Figure 1.

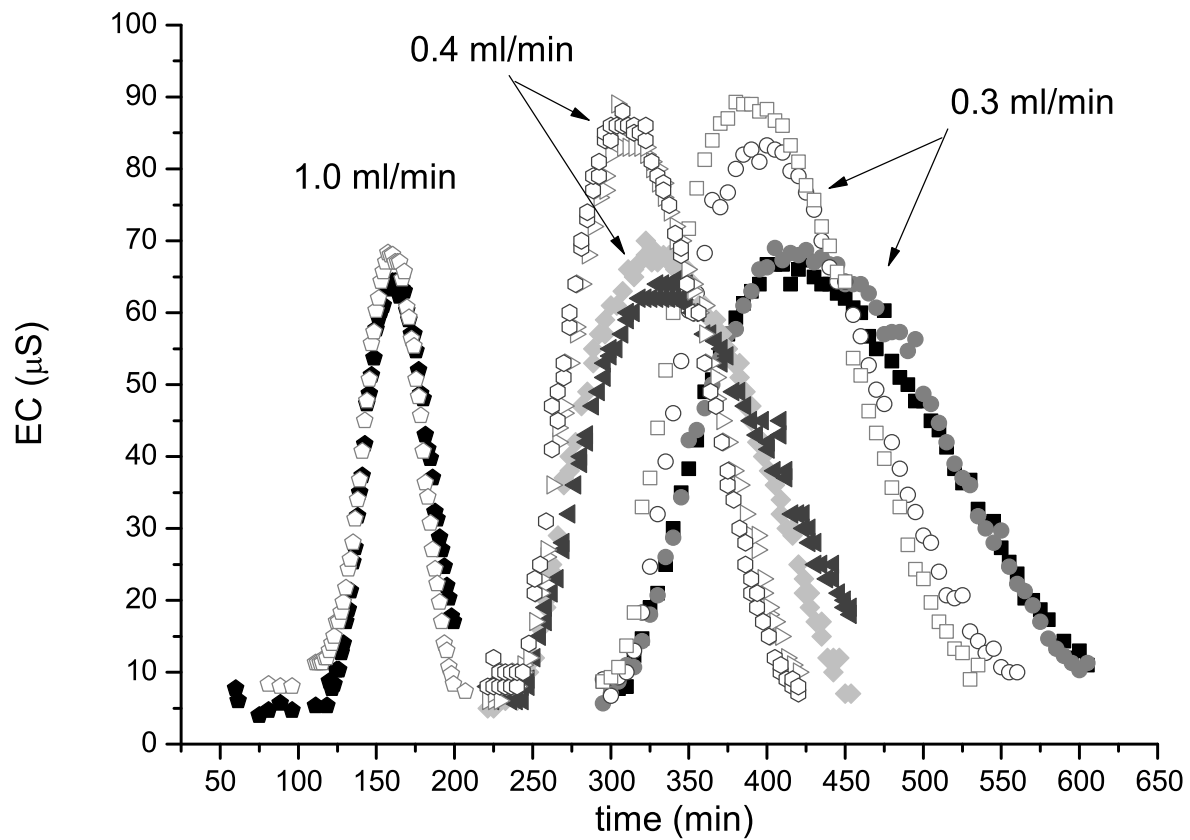


Figure 2.

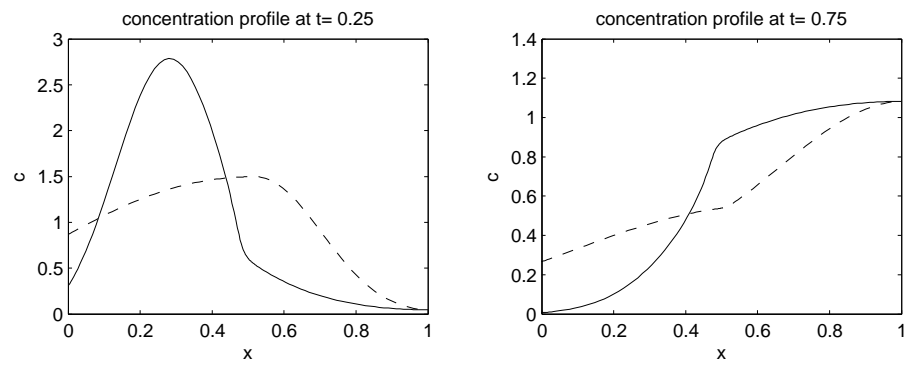


Figure 3.