



# Effects of compound-specific dilution on transient transport and solute breakthrough: A pore-scale analysis



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## ABSTRACT

This pore-scale modeling study in saturated porous media shows that compound-specific effects are important not only at steady-state and for the lateral displacement of solutes with different diffusivities but also for transient transport and solute breakthrough. We performed flow and transport simulations in two-dimensional pore-scale domains with different arrangement of the solid grains leading to distinct characteristics of flow variability and connectivity, representing mildly and highly heterogeneous porous media, respectively. The results obtained for a range of average velocities representative of groundwater flow (0.1–10 m/day), show significant effects of aqueous diffusion on solute breakthrough curves. However, the magnitude of such effects can be masked by the flux-averaging approach used to measure solute breakthrough and can hinder the correct interpretation of the true dilution of different solutes. We propose, as a metric of mixing, a transient flux-related dilution index that allows quantifying the evolution of solute dilution at a given position along the main flow direction. For the different solute transport scenarios we obtained dilution breakthrough curves that complement and add important information to traditional solute breakthrough curves. Such dilution breakthrough curves allow capturing the compound-specific mixing of the different solutes and provide useful insights on the interplay between advective and diffusive processes, mass transfer limitations, and incomplete mixing in the heterogeneous pore-scale domains. The quantification of dilution for conservative solutes is in good agreement with the outcomes of mixing-controlled reactive transport simulations, in which the mass and concentration breakthrough curves of the product of an instantaneous transformation of two initially segregated reactants were used as measures of reactive mixing.

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## 1. Introduction

The characterization of solute transport in porous media needs to distinguish between the spreading caused by the variability of advective velocity and true dilution and reactive mixing processes. Dilution represents the distribution of a conservative solute over an increasingly larger volume or water flux. Reactive mixing occurs when initially segregated reactants occupy the same volume or water flux, allowing a reaction between the chemical species to proceed. Both dilution and reactive mixing are ultimately determined by aqueous diffusion, which is the only process that allows mass exchange between different streamlines and leads to the increase of the entropy of the plume and to the decrease of its peak concentration [1,2]. Besides its fundamental physical importance,

the role of diffusion and local dispersion (at the continuum scale) is also critical from a mathematical standpoint since in the partial differential equations governing solute transport, diffusion/dispersion coefficients multiply the higher order derivative terms, which determine the nature of the equation. Thus, the diffusion coefficients play a crucial role independently of how small in numerical value they may be perceived to be.

At the local scale, a number of experimental studies focusing on transverse mixing have shown that aqueous diffusion plays a quantitatively important role for the hydrodynamic dispersion coefficient both at low and at high flow velocities. In particular, in advection-dominated regimes concentration gradients and incomplete dilution develop in the pore channels and determine the direct dependency of the mechanical dispersion term on the solute aqueous diffusivity and a non-linear relation with the average flow velocity [3,4]. These effects observed for conservative transport have been proven to be important also for mixing-controlled reactive transport [5], for the interpretation of isotopic

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signatures of organic contaminants in groundwater [6,7] and for transport of dissolved ionic species [8,9].

At the larger field scale, an increasing number of applied studies at different sites have shown the important role of diffusion as the principal mechanism of solute exchange controlling contaminant segregation and release into and from low permeability silt and clay aquitards (e.g. [10–12]). Also some modeling studies have highlighted the relevance of diffusive processes for transport in heterogeneous formations (e.g. [13–17]); however, in most quantitative descriptions of solute transport the role of diffusion is often neglected and/or masked by large, diffusion-independent mechanical dispersion terms. In a recent contribution [18] we observed that a significant degree of variability characterizes the aqueous diffusion coefficients of dissolved species in groundwater and showed that compound-specific effects are relevant not only at the pore and local scales but also in complex heterogeneous domains at larger field scales typical of contaminated sites.

In this study we focus on the effects of compound-specific diffusivity on solute breakthrough. Flux-averaged, vertically integrated solute breakthrough curves are a common tool for the characterization of solute transport and they are widely measured in practical applications both at the laboratory and at the field scales. Therefore, their analysis has been extensively performed in the subsurface hydrology literature and the results allowed capturing experimental observations as well as developing transport theories. In fact, breakthrough curves are highly informative about flow and transport processes occurring in subsurface formations. For instance, the frequently observed tailing of such curves and their deviation from the Gaussian profile characteristic of Fickian behavior is a primary feature of anomalous transport determined by the kinetically-controlled solute exchange between high and low flow velocity zones. Such behavior cannot be captured by the traditional advection–dispersion equation and requires more complex mathematical formalisms. Some of the formulations proposed that were successful in describing anomalous transport include dual and multirate mass transfer models (e.g. [19]); fractional derivatives (e.g. [20]), memory function models (e.g. [21]) and continuous time random walk (e.g. [22]). More recently there has been some debate on the potential to transfer the successful results of such formulations for conservative transport to mixing-controlled reactive transport. For instance the studies of Ederly et al. [23] and Willmann et al. [24] have shown good performance of macroscopic descriptions based, respectively, on the continuous time random walk framework and on a multirate mass transfer formulation, in capturing anomalous reactive transport behavior. Instead, Luo and Cirpka [25] argued that the success of macroscopic one-dimensional models to characterize reactive transport is more limited since such formulations cannot properly quantify the concentration fluctuations within the solute flux (e.g. [26,27]).

Aiming at contributing to the discussion on the interpretation of solute breakthrough curves, on their dilution and on the transfer of conservative results to reactive transport we adopt a pore-scale modeling approach. Pore-scale investigations have been increasingly applied to study flow and transport processes in porous media. Microfluidic experiments and pore-scale modeling approaches have been proposed to improve the understanding of flow and transport problems relevant for subsurface applications such as dissolution and displacement of non-aqueous phases (e.g. [28–31]), transient conservative and reactive transport (e.g. [32–36]), mixing in the longitudinal and transverse directions (e.g. [4,37,38]), mineral precipitation and dissolution (e.g. [39–43]), bio-reactive transport and microbial growth (e.g. [44–47]). A great advantage of sub-continuum pore-scale descriptions is their capability to illuminate the direct coupling between physical and (bio)reactive processes. This allows to deepen our understanding of subsurface processes and also to recognize the limitations and,

thus, to improve macroscopic continuum formulations that are necessary to describe solute transport in practical applications at larger scales.

The main objective of this study is to investigate the effect of compound-specific aqueous diffusion on plume dilution and to propose appropriate metrics to accurately quantify the degree of dilution from breakthrough measurements. The analysis is performed in two pore-scale domains with distinct characteristics of flow variability and connectivity that effectively show the interplay between the fundamental physical processes of advection and diffusion and their impact on solute and dilution breakthrough curves. Finally, a simple transient reactive transport problem is selected to illustrate the impact of compound-specific aqueous diffusion on reactive mixing in a representative range of groundwater flow velocities.

## 2. Problem setup and modeling approach

The setup of this study consists of two-dimensional liquid–solid domains representing granular porous media. We considered two different 2-D pore-scale domains, hereafter denoted as porous medium 1 (PM1) and porous medium 2 (PM2), each with a length of 7.25 cm and a width of 4 cm. Their geometry is specified following the method described by Hochstetler et al. [5]: circles describing solid grains are randomly selected from a truncated lognormal distribution with a geometric mean of 1.25 mm and a standard deviation of 0.25 mm, the location of the grains is determined using a quasi-random procedure [48] from a starting staggered array, and the grain sizes are determined by random sampling from the truncated distribution. In the case of PM1 the grains are located at a minimum distance and any overlapping is prevented. This last step was not applied to create the geometry of PM2 in which a partial overlap of the solid particles was allowed. The obtained pore-scale domains, PM1 and PM2, are shown in Fig. 1. While the two media were generated from the same distribution of grain sizes, the different procedure adopted resulted in porous media with different characteristics. PM1 is a mildly heterogeneous pore-scale domain with a porosity of 0.40. PM2 has a slightly higher porosity, 0.42, but the different arrangement of the grains results in significant differences in the geometry of the pore channels and in their connectivity. As can be observed in Fig. 1, PM2 is characterized by preferential flow channels formed by arrangements of large and highly-connected pores. These characteristics of PM2 reproduce transport features typically observed in soil macropores and in highly heterogeneous porous media (e.g. [49,50]); therefore, in the remainder we will identify PM2 as highly heterogeneous pore-scale domain whereas PM1 will be denoted as mildly heterogeneous pore-scale medium.

In the pore-scale analysis conducted in this study, we show that the differences in geometry and pore channels connectivity between PM1 and PM2 have remarkable effects on pore-scale flow and transport processes.

### 2.1. Flow model

In the pore-scale domains the flow is described by the Stokes and the continuity equations:

$$\begin{aligned} -\rho g \nabla \varphi + \mu \nabla^2 \mathbf{u} &= 0 \\ \nabla \cdot \mathbf{u} &= 0 \end{aligned} \quad (1)$$

where  $\rho$  is the fluid density ( $\text{M L}^{-3}$ ),  $g$  is the acceleration due to gravity ( $\text{L T}^{-2}$ ),  $\varphi(L)$  is the hydraulic head,  $\mu$  is the dynamic viscosity ( $\text{M L}^{-1} \text{T}^{-1}$ ), and  $\mathbf{u}$  is the velocity vector ( $\text{L T}^{-1}$ ). The boundary conditions of the flow problem are schematically illustrated in Fig. 1 and include: zero-velocity (no-slip and no-flow) conditions at the

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