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Peclet number as affected by molecular diffusion controls transient anomalous transport in alluvial aquifer–aquitard complexes

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ABSTRACT

This study evaluates the role of the Peclet number as affected by molecular diffusion in transient anomalous transport, which is one of the major knowledge gaps in anomalous transport, by combining Monte Carlo simulations and stochastic model analysis. Two alluvial settings containing either short- or long-connected hydrofacies are generated and used as media for flow and transport modeling. Numerical experiments show that 1) the Peclet number affects both the duration of the power-law segment of tracer breakthrough curves (BTCs) and the transition rate from anomalous to Fickian transport by determining the solute residence time for a given low-permeability layer, 2) mechanical dispersion has a limited contribution to the anomalous characteristics of late-time transport as compared to molecular diffusion due to an almost negligible velocity in floodplain deposits, and 3) the initial source dimensions only enhance the power-law tail of the BTCs at short travel distances. A tempered stable stochastic (TSS) model is then applied to analyze the modeled transport. Applications show that the time-nonlocal parameters in the TSS model relate to the Peclet number, P_e. In particular, the truncation parameter in the TSS model increases nonlinearly with a decrease in P_e due to the decrease of the mean residence time, and the capacity coefficient increases with an increase in molecular diffusion which is probably due to the increase in the number of immobile particles. The above numerical experiments and stochastic analysis therefore reveal that the Peclet number as affected by molecular diffusion controls transient anomalous transport in alluvial aquifer–aquitard complexes.

1. Introduction

Anomalous, or non-Fickian diffusion – which is characterized by a nonlinear scaling of the second centered moments of a contaminant plume – has been well documented at all scales (Berkowitz et al., 2006; Neuman and Tartakovsky, 2009). The late-time tailing behavior of solute breakthrough curves (BTCs), which is usually caused by the slow release of contaminants from relatively immobile zones, is a signature of anomalous transport. The BTC tails affect the first five integer-order spatial moments of the plume. For example, the plume mean displacement grows more slowly than linearly in time, and the plume variance expands faster than Fickian diffusion due to the plume stretching from the effects of the mean drift; see for example, Zhang et al. (2008a, 2013). The BTC late-time tails can also evolve in time and/or space, such as during the transition from anomalous to Fickian transport (Dentz et al., 2004), which results in *transient anomalous transport* (Meerschaert et al., 2008). Transient anomalous transport constrains the dissipation rate of contaminant mass, which may affect groundwater quality sustainability, and introduce challenges for remediation (LaBolle and Fogg, 2001). Quantifying the complex dynamics of transient

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anomalous transport and identifying its major controlling factors in regional-scale aquifer–aquitard complexes has importance for science and society, which motivates this study.

Both the medium properties and the chemical properties can affect the dynamics of transient anomalous transport of contaminants. On the one hand, the geometry of low-permeability zones, such as clay lenses (Guswa and Freyberg, 2000) and matrix (Haggerty et al., 2000), are known to affect the late-time shape of BTCs. Systematic Monte Carlo simulations that consider a wide spectrum of medium heterogeneity and architectures further show that the distribution of the thicknesses of low-permeability layers significantly affects the long-term dynamics of transient anomalous transport (Zhang et al., 2013, 2014). Typical alluvial settings consisting of both interconnected aquifer materials and surrounding aquitard deposits are common examples of aquifer–aquitard complexes that facilitate transient anomalous transport (Green et al., 2010; Lee, 2004; Weissmann et al., 2002). The vertical connectivity of diffusion-limited, low-permeability deposits has been found to be critical in the late-time behavior of contaminant transport (Zhang et al., 2007). On the other hand, chemical properties, such as the effective molecular diffusivity (D^*), are also expected to affect late-time transport by controlling the rate of diffusive mass transfer between aquifer and aquitard materials. Molecular diffusion was found to be the dominant transport property controlling sub-diffusion in a specific set of alluvial deposits (LaBolle and Fogg, 2001). In particular, LaBolle and Fogg (2001) observed a noticeable increase in the sequestration of contaminant mass with an increase in D^*, which led to a heavier late-time tail in the contaminant BTC. However, the sensitivity of transient anomalous transport to molecular diffusion has not been quantified systematically. The following study will show that the observation in LaBolle and Fogg (2001) is only valid at certain timescales due to the time-dependent impact of molecular diffusion on transient anomalous transport.

This study aims to expand on previous efforts by quantifying the dynamics of transient anomalous transport that respond to molecular diffusion under various alluvial architectures. The effect of diffusion is characterized by a Peclet number, a dimensionless number which is applicable for different scales and translatable across various problems. In Section 2, Monte Carlo simulations are conducted to explore transient anomalous transport in alluvial aquifer–aquitard systems with varying hydrofacies thickness and varying molecular diffusivity. In Section 3, stochastic models are applied to interpret the observed transport dynamics. In Section 4, we discuss the impacts of molecular diffusion, mechanical dispersion, and the initial source dimension on transient anomalous transport, and we also explore the quantitative relationship between stochastic model parameters and molecular diffusion or Peclet number. Conclusions are provided in Section 5.

2. Monte Carlo investigation of the influence of the Peclet number as affected by molecular diffusion on transient anomalous transport

In this section, we will briefly introduce the Monte Carlo approach, and then analyze the influence of the Peclet number (changing with diffusion) on transport dynamics.

2.1. Procedure of Monte Carlo simulations

Monte Carlo simulations are conducted to explore the influence of the medium architecture (i.e., the hydrofacies mean length) and the transport processes (focusing on molecular diffusion) on the long-term dynamics of tracer transport. The procedure of the Monte Carlo simulations is similar to that used by Zhang et al. (2013), except that 1) we double the length of the modeling domain in order to evaluate greater spatial and temporal scales of transient anomalous transport and 2) we explore the impact of molecular diffusion on transport.

There are three major steps in the Monte Carlo simulations. First, we model the heterogeneity of alluvial aquifer–aquitard systems using the three-dimensional transition probability model developed by Carle (1999). The resultant high-resolution hydrofacies models contain four facies – debris flow, floodplain, levee, and channel (Table 1) – that represent the alluvial setting observed at the Lawrence Livermore National Laboratory (LLNL) site (Carle, 1999). Zhang et al. (2013) found that the vertical mean length (i.e., thickness) of low-permeability floodplain layers has a greater effect on the transient anomalous transport than the other medium properties, including the juxtaposition tendency and hydraulic conductivity variability within each facies. This result prompts us to build two alluvial settings with different distributions of aquitard thicknesses. One setting contains small scale hydrofacies with short mean lengths (designated *Scenario Short*) and the other setting contains large scale hydrofacies with long mean lengths (designated *Scenario Long*). One hundred equally possible but different realizations are generated for each scenario. Fig. 1 shows the first realization for each scenario and Table 1 shows hydrofacies properties for *Scenario Long*. Hydrofacies properties for *Scenario Short* are similar to those for *Scenario Long*, except that *Scenario Short* has a facies mean length that is 16 times smaller than that for *Scenario Long*.

Second, three-dimensional, steady-state groundwater flow is simulated using the USGS software MODFLOW (Harbaugh and McDonald, 1996). The upgradient and downgradient boundaries of the model – which are perpendicular to the stratigraphic dip direction, or the *X* axis shown in Fig. 1(a) – are general-head boundaries that simulate inflow and outflow through the system (so that the boundary effect on solute transport can be minimized), whereas the other boundaries are no-flow conditions. The general-head gradient is 0.002, a value measured at the LLNL site. Hydraulic conductivity for each hydrofacies is shown in Table 1.

Third, solute transport through the regional-scale medium is solved using a Lagrangian solver, RWHet (LaBolle, 2006), in which the classic second-order, advection–dispersion equation (ADE) is used to describe diffusion in each grid cell. Particles are released from a cluster of channel cells (close to the upgradient boundary) that is built into each hydrofacies model (as hard conditioning data) to represent an initial point source in the mobile phase. Further details of the initial source property can be found in Zhang et al. (2013). The two general-head boundaries are assumed to be absorbing boundaries for solute particles (so that the solutes can move across the model boundaries freely) and the other boundaries are assumed to be reflective to represent the no-flow conditions. The effective molecular diffusivity is first defined as $D^* = 5.2 \times 10^{-5}$ m^2/day,