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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

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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.

Key words: Molecular diffusion, Mass transfer, Alluvial settings, Sub-diffusion

PACS:

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 slower 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 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 (Weissmann et al., 2002; Lee, 2004; Green et al., 2010). 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.

Table 1

Hydrofacies properties for *Scenario Long*, including mean length (m) along the strike, dip, and vertical directions (denoted as L_{Strike} , L_{Dip} , and L_{Vertical} , respectively, and corresponding to y , x , and z axes shown in Figure 1a); global volumetric proportion; hydraulic conductivity K (m/day); and average Peclet number P_e (where the Peclet number was calculated using the method proposed by LaBolle and Fogg (2001) with a diffusion coefficient of 10^{-5} m²/day). The hydrofacies mean lengths and hydraulic conductivities were estimated by Carle (1999).

Hydrofacies	L_{Strike}	L_{Dip}	L_{Vertical}	Proportion (%)	K	P_e
Debris Flow	32	96	4.4	7	0.432	2.4×10^4
Floodplain	108	268	8.4	26	0.432×10^{-5}	2.1×10^{-1}
Levee	24	80	3.2	19	0.173	7.9×10^3
Channel	40	200	5.2	48	5.184	5.9×10^5

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. Figure 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 down-

Fig. 1. Three-dimensional view of hydrofacies model realization #1 for *Scenario Short* (a) and *Scenario Long* (b). The bottom plots show the inside view of the top plots with the length of the X axis reduced for a better view.

gradient boundaries of the model—which are perpendicular to the stratigraphic dip direction, or the x axis shown in Figure 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 classical 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 $D^* = 5.2 \times 10^{-5} \text{ m}^2/\text{d}$, as suggested by LaBolle and Fogg (2001), and is then adjusted to represent changes in the Peclet number. An isotropic dispersivity ($\alpha_L = \alpha_T = 0.01 \text{ m}$) is used as recommended by LaBolle and Fogg (2001). The impact of mechanical dispersion will be discussed in section 4.

It is noteworthy that the average Peclet number for each hydrofacies (Table 1) shows that transport in the relatively immobile zones of the floodplain facies is diffusion dominated, while transport through all the other facies is advection dominated. Here the average Peclet number for facies is calculated by (LaBolle and Fogg, 2001):

$$P_e = \frac{KJa}{D^* \theta}, \quad (1)$$

where J [dimensionless] denotes the regional hydraulic gradient, a [L] is the characteristic length scale for the hydrofacies, and θ (0.35) [dimensionless] is the effective porosity. In the following sections when we explore the influence of D^* on anomalous transport, we also refer to P_e since this dimensionless number is more general.

2.2 Simulated flow and transport

One example of simulated flow field for realization #1 for the two scenarios (i.e., short and long) is shown in Figure 2. In *Scenario Short*, flow along channel deposits exhibits channeling behavior (Figure 2a), whereas the surrounding floodplain deposits change the local flow direction and magnitude. The simulated flow is mainly along the interconnected channel deposits. For *Scenario Short*, the proportion of flow is 3.817% (mean of the 100 realizations), 0.014%, 8.778%, and 87.391% in the debris flow, floodplain, levee, and channel deposits, respectively. For *Scenario Long*, the proportion of flow is 0.967%, 0.004%, 1.531%, and 97.498% in the debris flow, floodplain, levee, and channel deposits, respectively. Therefore, more water flows in channel facies in *Scenario Long*

Fig. 2. *Scenario Long* (left) and *Scenario Short* (right): (a) and (e) show the simulated particle plumes for realization #1 at time $t = 10$ yrs, where the hydrofacies distributions are shown in gray-scale, the modeled hydraulic head contours are shown as green lines, and the green rectangle shows the initial source location; (b) and (f) show the closest analogy of the transport behavior (i.e., mass transfer between high-permeability zones and low-permeability layers), where the white areas denote the mobile domains, and the black areas denote the relatively immobile domains; and (c) and (g) show the semi-analytical approximation of the late-time concentration in the BTC for (b) and (f), respectively. In (d) and (h), the thick red line represents the ensemble average of BTCs for all 100 realizations and the thin line represents the modeled BTC for the first 20 realizations.

than in *Scenario Short*, which is probably due to the greater interconnectivity of the longer channel networks in *Scenario Long*.

Figure 3 shows the velocity probability density function (PDF) for realization #1 for

Table 2

The average Peclet number (P_e) and Damköhler number (D_a) for floodplain hydrofacies in *Scenario Long* and *Scenario Short*. Here the Damköhler number is calculated as the ratio between the maximum sorption time (as represented by the maximum residence time) and the average convection time scale; see eq. (3) in Section 3 for details.

Scenario	Hydrofacies	a	D^*	P_e	D_a
		[m]	[m ² /day]	[dimensionless]	[dimensionless]
<i>Long</i>	Floodplain	8.4	5.2×10^{-4}	4.0×10^{-3}	4.7×10^2
<i>Long</i>	Floodplain	8.4	5.2×10^{-5}	4.0×10^{-2}	4.7×10^1
<i>Long</i>	Floodplain	8.4	5.2×10^{-6}	4.0×10^{-1}	3.7×10^1
<i>Short</i>	Floodplain	0.5	5.2×10^{-4}	2.4×10^{-4}	3.3×10^2
<i>Short</i>	Floodplain	0.5	5.2×10^{-5}	2.4×10^{-3}	5.4×10^1
<i>Short</i>	Floodplain	0.5	5.2×10^{-6}	2.4×10^{-2}	7.2×10^0

Fig. 3. Velocity PDF for realization #1 for *Scenario Short* (a) and *Scenario Long* (b).

the two scenarios. If the effective molecular diffusivity is $D^* = 5.2 \times 10^{-5}$ m²/day, then the Peclet number is much smaller than 1 (see Table 2) and therefore molecular diffusion dominates transport in the floodplain layers. For example, even for the thinnest layer with a thickness of $dz = 0.5$ m (i.e., the floodplain layer consists of one cell) and a mean velocity 1×10^{-6} m/day (see Figure 3), the corresponding P_e (≈ 0.01) is so small that the average diffusive time required for a particle to vertically exit the floodplain layer is two orders of magnitude smaller than the advective time required for the particle to flow out of the cell.

Figure 2a shows the simulated particle cloud for *Scenario Long*, which is negatively skewed due to channeling flow in the interconnected channel facies and the simul-

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taneous sequestration occurring in floodplain layers. Here “sequestration” denotes the
near-source mass hold-up effect (LaBolle and Fogg, 2001; Zhang et al. 2013). Therefore,
the resultant BTC is also positively skewed (with tailing at larger values) (Figure 2d).
The closest analogy of transport for this scenario might be the process of multi-rate
mass transfer between layered aquifers/aquitards with variable thicknesses (Figure 2b),
where the resultant BTC is the summation of several exponential functions corre-
sponding to the exponential decline of tracer mass during each mass exchange process
(Figure 2c) (Zhang et al., 2007).

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For *Scenario Short*, both the simulated particle cloud (Figure 2e) and the BTC (Fig-
ure 2h) are much more symmetrical than those in *Scenario Long* due to greater mixing
of particles in high- and low-permeability facies. For *Scenario Short*, solute particles
can transfer relatively easily between channel and floodplain facies (Figure 2f). This
process can be approximated by a single-rate mass transfer process (Figure 2g) which
results in the fast decline of the late-time BTC shown in Figure 2h.

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It is noteworthy that both analytical and numerical approaches had been developed
to relate the flow velocity to anomalous transport. For example, Dentz and Bolster
(2010) found that 1) power-law distributed, uncorrelated velocities (with a density
 $p_v(v) \propto v^{\rho-1}/(1 + v/v_c)^{1+\rho}$, where v_c is a characteristic drift and the exponent $\rho > 0$)
lead to sub-diffusion (for $0 < \rho < 0.5$) or super-diffusion (for $0.5 < \rho < 2$), and 2) a
power-law correlated velocity field results in super-diffusion or a mixture of sub- and
super-diffusion. Herrick et al. (2002) and Kohlbecker et al. (2006) found that the heavy
tailed (i.e., power-law distributed) and long-range dependent hydraulic conductivity
field causes the heavy tailed solute displacement (i.e., super-diffusion), a conclusion
consistent with the analytical solution in Dentz and Bolster (2010). Our study and
previous Monte Carlo simulations in Zhang et al. (2007, 2013, 2014) further reveal
that an exponentially correlated facies field, where an average hydraulic conductivity
is assigned to each hydrofacies (and the resultant velocity does not need to distribute
as a power-law function; see for example Fig. 3), can generate a broad distribution of
the thicknesses of low-permeability deposits, resulting in transient anomalous diffusion.

The following section is an exploration of the possible influence of the Peclet number (due to molecular diffusion) on transport that considers the various factors related directly or indirectly to molecular diffusion.

2.3 Influence of the Peclet number on transient anomalous transport in floodplain layers with different thicknesses

To further understand the influence of the Peclet number on late-time transport behavior, we conduct additional numerical experiments to quantify the long-term temporal evolution of solute particle partitioning in all phases (i.e., mobile, immobile, and total). For *Scenario Short*, numerical results show that more particles are trapped by the immobile phases (which consist of floodplain hydrofacies (Zhang et al., 2014)) than the mobile phase (represented by non-floodplain hydrofacies) at late times (such as time $t \geq 200$ yrs) (Figure 4a). Only when the transport time is longer than the maximum residence time of immobile particles, will the trailing edge of the immobile plume leave the source area and move downstream (see Figure 4b,c). Note that in a standard mobile-immobile transfer model (Haggerty et al., 2000), an immobile particle can exit the immobile domain and become mobile again when the elapsed time is larger than the trapping period. At this time, sequestration ceases. The trailing edge of the mass in all phases distributes as an exponential function in space with the same rate of concentration decrease for all phases, as shown by Figure 4e,f.

Plume snapshots for *Scenario Long* differ from those for *Scenario Short* in several respects. First, the sequestration in *Scenario Long* lasts a great deal longer, due to the much thicker floodplain layers (Figure 5). Second, tracer particles in different phases (i.e., mobile or immobile) exhibit different behaviors. For example, when the mobile phase plume moves downstream, the immobile phase is still trapped near the source location (Figure 5a). Additionally, the trailing edge of the immobile phase plume is much heavier (i.e., more pronounced) than that of the plume in the mobile phase (Figure 5d,e).

Fig. 4. Snapshots of *Scenario Short* along the longitudinal direction at time $t = 200$ yrs (a), 800 yrs (b), and 1,000 yrs (c). The right column shows the semi-log plot of the left column. The diamond at $X_0 = 115$ m in each plot shows the initial position of contaminants. The symbols represent the ensemble average of Monte Carlo simulations, and the lines represent the TSS model (2) solutions.

Therefore, both the Peclet number (changed mainly with diffusion in this study) and the immobile block properties can affect the persistence of tracer sequestration at the initial source position by controlling the rate of backward diffusion (here “backward diffusion” means that particles trapped previously by immobile phases slowly exit the immobile domain due to molecular diffusion) for solute particles trapped in floodplain layers. For a given medium, molecular diffusion can dominate late-time anomalous transport. This finding generalizes the conclusion in LaBolle and Fogg (2001), who found a critical role of molecular diffusion in contaminant migration in a specific alluvial system.

Fig. 5. Snapshots of *Scenario Long* along the longitudinal direction at time $t = 2,000$ yrs (a), 4,000 yrs (b), and 6,000 yrs (c). The right column shows the semi-log plot of the left column. The symbols represent the ensemble average of Monte Carlo simulations, and the lines represent the TSS model (2) solutions. Here “resident concentration” refers to the concentration of all solutes (mobile or immobile) present at the sampling location (Zhang et al., 2006). The parameter $1/\lambda$ is equal to 2000 yrs. The noise in the TSS model solution is due to small numbers of particles in narrow X -intervals.

2.4 Influence of the Peclet number on sub-diffusion

A single Peclet number (corresponding to a molecular diffusivity $D^* = 5.2 \times 10^{-5}$ m²/day) was used in the above Monte Carlo analysis. In this section, we test a wide range of P_e and evaluate its contribution to sub-diffusive transport.

Figure 6 shows the Monte Carlo simulation of BTCs for *Scenario Short* with various diffusivities. Three main transport behaviors related to molecular diffusion can be observed. First, in most cases the late-time BTC transitions gradually from power law

to exponential, and the transition time decreases with an increase in D^* (Figure 6b,c). For the smallest P_e (2.4×10^{-4} ; with $D^* = 5.2 \times 10^{-4}$ m²/day) considered in this study, the transition time is so small that most of the observation time of the BTC is longer than the transition time. Therefore, the power-law segment of the BTC is too short to be observed in Figure 6a. The observed transition from anomalous to normal transport is consistent with the temporal behavior of solute transport observed by Dentz et al. (2004). It is also noteworthy that for all of the other cases, the slope of the power-law segment of the BTC remains the same for all P_e . In other words, the power-law slope of the late-time BTC does not change with P_e . Zhang et al. (2014) found that the BTC slope is dominated by the distribution of thicknesses of diffusion-limited, low-permeability layers, which explains this behavior.

Second, the transport behavior may not be stable at short travel distances (such as the green symbols shown in Figure 6c). For example, at a travel distance of 20 m, the simulated BTCs exhibit noise that is probably due to 1) local variations of the floodplain layer thicknesses near the source and 2) strong variation of preferential flow paths (consisting of channel deposits) from the source zone to the control plane.

Third, the BTC peak appears later for a smaller Peclet number (Figure 6d,e,f), which might be due to the enhanced vertical trapping effect. There is a greater probability that solute particles will enter the surrounding floodplain layers vertically, particularly when P_e is smaller. Therefore, particles can be trapped for a longer period, which results in a later BTC peak. At the same time, the plume front may exhibit a slower leading edge along the longitudinal direction for a smaller P_e , which is also due to enhanced vertical trapping of solute particles. This behavior can be seen in Figure 7, where the leading edge of the plume for $P_e = 2.4 \times 10^{-4}$ (Figure 7a) moves downstream slower than the plume for $P_e = 2.4 \times 10^{-2}$ (Figure 7c).

Monte Carlo simulations for *Scenario Long* (Figure 8) show similar behaviors, except for a longer and heavier power-law decline of the late-time BTC due to thicker floodplain layers.

Fig. 6. The BTCs of *Scenario Short* at four control planes (perpendicular to the general flow direction) with the Peclet number $P_e = 2.4 \times 10^{-4}$ (a), 2.4×10^{-3} (b), and 2.4×10^{-2} (c). The right column plots are linear-linear versions of the left column plots. The vertical dotted lines are at the time $t = 1/\lambda$ (where λ is the truncation parameter in time) and the thick black line in (b)~(c) shows the power-law slope of the BTC. The symbols are for the Monte Carlo simulations and the lines are for the TSS model (2) solutions. The long-dashed vertical line in the right column is used to compare the peak position for the BTC at $L = 100$ m shown in (d), (e), and (f).

Figure 9 shows plume snapshots for *Scenario Long* with different P_e at time $t = 100$ yrs. The plume peak is higher for a larger P_e , which is the opposite of the effect observed for *Scenario Short* (see Figure 7). This difference might be caused by greater interconnectedness of preferential flow paths in *Scenario Long*. As discussed in section 2.2, a majority of solute particles can move along the thick channel “pipe” and generate a negatively skewed snapshot (Figure 2a). Therefore, the plume peak shown in Figure 9

Fig. 7. Snapshots of *Scenario Short* along the longitudinal direction at time $t = 100$ yrs with the Peclet number $P_e = 2.4 \times 10^{-4}$ (a), 2.4×10^{-3} (b), and 2.4×10^{-2} (c). The right column plots are linear-linear versions of the left column plots. The symbols represent the Monte Carlo simulations and the lines represent the TSS model (2) solutions. The initial source is located at $X_0 = 115$ m. The vertical dashed line in the right column is used to compare the peak position for the snapshots shown in (d), (e), and (f).

is also part of the plume front, which can be heavier for a larger P_e due to the enhanced vertical trapping effect discussed above.

To further interpret and understand the nature of anomalous dynamics simulated by the Monte Carlo approach, we apply a stochastic model to quantify anomalous transport as affected by the Peclet number in the following section. The above Monte Carlo simulations of tracer BTCs and snapshots are treated as “measurements” to check the applicability of the stochastic model discussed below.

Fig. 8. The BTCs of *Scenario Long* at three control planes with the Peclet number $P_e = 4.0 \times 10^{-3}$ (a), 4.0×10^{-2} (b), and 4.0×10^{-1} (c). The right column plots are linear-linear versions of the left column plots. The vertical dots in each plot represent time $t = 1/\lambda$ and the thick black line in (a)~(c) shows the power-law slope of the BTC. The symbols represent the Monte Carlo simulations and the lines represent the TSS model (2) solutions.

3 Stochastic model to quantify effects of Peclet number on transient anomalous transport

In this section, we adopt the following tempered stable stochastic (TSS) model proposed first by Meerschaert et al. (2008):

$$\frac{\partial C_T}{\partial t} + \beta e^{-\lambda t} \frac{\partial^\gamma}{\partial t^\gamma} [e^{\lambda t} C_T] - \beta \lambda^\gamma C_T = -\frac{\partial}{\partial x} \left[V C_T - D \frac{\partial C_T}{\partial x} \right] + \beta C_0(x) \int_t^\infty e^{-\lambda \tau} \frac{\tau^{-\gamma-1}}{\Gamma(-\gamma)} d\tau, \quad (2a)$$

$$\frac{\partial C_M}{\partial t} + \beta e^{-\lambda t} \frac{\partial^\gamma}{\partial t^\gamma} [e^{\lambda t} C_M] - \beta \lambda^\gamma C_M = -\frac{\partial}{\partial x} \left[V C_M - D \frac{\partial C_M}{\partial x} \right], \quad (2b)$$

Fig. 9. Snapshots of *Scenario Long* along the longitudinal direction at time $t = 100$ yrs with the molecular diffusivity $D^* = 5.2 \times 10^{-4} \text{ m}^2/\text{d}$ (a), $5.2 \times 10^{-5} \text{ m}^2/\text{d}$ (b), and $5.2 \times 10^{-6} \text{ m}^2/\text{d}$ (c). The right column plots are linear-linear versions of the left column plots. The symbols represent the Monte Carlo simulations and the lines represent the TSS model (2) solutions. The vertical dashed line in the right column is used to compare the peak position for the snapshots shown in (d), (e), and (f). The initial source is located at $X_0 = 115 \text{ m}$.

where C_T and C_M [ML^{-3}] are the concentration of the solute in the total and mobile phases, respectively; $0 < \gamma < 1$ [dimensionless] is the scale index in time; β [$T^{\gamma-1}$] is the fractional capacity coefficient; $\lambda > 0$ [T^{-1}] is the truncation parameter in time; V [LT^{-1}] is the advective velocity; D [L^2T^{-1}] is the dispersion coefficient; $\Gamma()$ is the Gamma function; and $C_0(x)$ [ML^{-3}] is the initial concentration in the mobile phase.

It is noteworthy that other physical models, such as the well-known continuous time random walk (CTRW) framework (Berkowitz et al., 2006), can also efficiently describe the transition from anomalous to normal transport (Dentz et al., 2004). The

Table 3

The best-fit model parameters (except for the Peclet number P_e which is calculated by formula (1)): γ - the time index; β - the fractional capacity coefficient; λ - the time truncation parameter; V - the effective velocity; and D - the effective dispersion coefficient.

Scenario	P_e	γ	β	λ	V	D
	dimensionless	dimensionless	$\text{yr}^{\gamma-1}$	$1/\text{yr}$	m/yr	m^2/yr
<i>Scenario Long</i>	4.0×10^{-3}	0.62	0.20	5.0×10^{-3}	19.9	2.8
<i>Scenario Long</i>	4.0×10^{-2}	0.62	0.11	5.0×10^{-4}	19.0	6.8
<i>Scenario Long</i>	4.0×10^{-1}	0.62	0.07	4.0×10^{-4}	17.5	10.5
<i>Scenario Short</i>	2.4×10^{-4}	0.75	1.2	6.0×10^{-2}	9.9	55
<i>Scenario Short</i>	2.4×10^{-3}	0.75	1.0	9.8×10^{-3}	11.0	70
<i>Scenario Short</i>	2.4×10^{-2}	0.75	0.75	1.3×10^{-3}	11.1	75

TSS model (2) is functionally equivalent to the CTRW model with an exponentially truncated memory function. Model (2) is selected in this study because it not only efficiently captures transient anomalous transport in aquifer-aquitard systems (Zhang et al., 2014), but also distinguishes particle status in mobile and immobile phases, which is critical for anomalous transport in alluvial systems where abundant aquitard materials form immobile domains.

The TSS model (2) is first used to fit the Monte Carlo simulation of the BTC at the travel distance of 100 m for each value of P_e (see Figures 6 and 8). Each model parameter has a distinct impact on the resultant BTC, and therefore the model parameters can be fitted using the BTC, as demonstrated by Zhang et al. (2014). For example, the index γ controls the power-law slope of the late-time BTC (Zhang et al., 2007), the truncation parameter λ defines the inverse of the time transition from power-law to exponential in the late-time BTC (Meerschaert et al., 2008), the capacity coefficient β determines the mass ratio between immobile and mobile particles (Zhang et al., 2014), the velocity V affects the BTC peak position, and the dispersion coefficient D captures the overall expansion of the BTC. Because parameters γ , λ , and β define the time-nonlocal process and anomalous sub-diffusive transport, they can be referred to as “time-nonlocal” parameters (Zhang et al., 2014).

Table 3 shows the best-fit parameters for all scenarios and all Peclet numbers. The best-fit parameters are calculated based on the breakthrough curves at 100 m and are then used to predict all the other BTCs measured at the other travel distances. Results show that the TSS model (2) solutions generally match the Monte Carlo simulation of BTCs, except for the BTC at the shortest travel distance of 20 m where the measured BTC contains apparent noise (see the lines shown in Figures 6 and 8). Model (2) can also reliably predict the spatial distribution of particles in all phases, as shown in Figures 7 and 9.

We also calculate the Damköhler number D_a [dimensionless] using the truncation parameter λ :

$$D_a = \frac{\lambda}{KJ/(a\theta)}, \quad (3)$$

where the chemical reaction time for desorption is represented by the maximum residence time. The average Damköhler number for the floodplain hydrofacies is listed in Table 2. All Damköhler numbers are larger than 1, showing that the trapping of particles, a physical analog for chemical sorption, dominates contaminant transport process in floodplain layers.

4 Discussion

4.1 *Twofold impact of the Peclet number as affected by diffusion on transient anomalous transport*

The Peclet number as affected by molecular diffusivity affects transient anomalous transport by defining both forward diffusion (i.e., diffusion of mobile solutes from aquifers to aquitards) and backward diffusion (representing the release of immobile mass). On one hand, a large molecular diffusivity D^* (corresponding to a small P_e) enhances forward diffusion by facilitating anomalous transport at early times and can accelerate the mass exchange between aquifer and aquitard materials. Therefore, so-

lute particles originating from the mobile phase can easily diffuse into the immobile zones and increase the solute mass partitioning in the immobile phases. This impact is consistent with the conclusions of LaBolle and Fogg (2001), who found that a larger D^* increases sequestration of contaminant mass.

On the other hand, a larger D^* (resulting in a smaller P_e) leads to a larger backward diffusive rate because the residence time of immobile particles in floodplain layers is shortened. Therefore, anomalous transport should approach its normal asymptote faster for a larger D^* . In other words, a larger D^* decreases sequestration at late timescales, which is the opposite of the early-time impact. This late-time behavior can be observed in Figure 7a, in which the largest D^* (i.e., the smallest P_e) for *Scenario Short* causes the weakest sequestration of particles near the source at a time of 100 yrs due to the fast backward diffusion of trapped particles. This result generalizes the conclusions of LaBolle and Fogg (2001) and shows that molecular diffusion has a twofold and timescale-dependent impact on transient anomalous transport.

4.2 Change of stochastic model parameters due to the change of Peclet number

Figure 10 shows that the best-fit truncation parameter λ increases nonlinearly with a decrease in the Peclet number P_e . The negative correlation between the two variables may be explained by the relationship between λ and D^* . As shown by Table 3, λ increases with an increase in D^* , a positive correlation which is consistent with the empirical assumption proposed by Zhang *et al.* (2013, 2014):

$$\lambda \propto D^*/(Z^*)^2, \quad (4)$$

where Z^* is the effective thickness of the low-permeability layers. For a given medium, Z^* is likely to remain constant while P_e changes with hydraulic and chemical conditions. As discussed in Section 4.1, a decrease in P_e (due to an increase in D^*) enhances the diffusive transport rate and solute particles stay for shorter periods in immobile layers,

Fig. 10. The best-fit parameter λ for different scenarios and P_e .

which corresponds to a larger λ .

The link between β and P_e is more complicated. The mass ratio between immobile and mobile particles is defined by β , as discussed by *Zhang et al.* (2014). When P_e decreases due to an increase in D^* , particles originally located in the mobile phase diffuse into the immobile phase more easily, resulting in a larger mass ratio for immobile particles when transport reaches a dynamic equilibrium. Therefore, a smaller P_e should result in a larger β , but the exact functional formula remains unknown. Further experiments are needed to build a quantitative relationship between β , P_e , and the medium properties.

It is also noteworthy that *Scenario Short* has a larger λ and β than *Scenario Long*. This discrepancy might be due to the relatively uniform mixing between high- and low-permeability deposits in *Scenario Short*, in which solute particles released from the mobile phase can diffuse into the adjacent immobile zones more easily, resulting in a larger β (which indicates that there are more particles in the immobile phase). In addition, the thinner layers in *Scenario Short* compared to those in *Scenario Long* result in shorter residence times, and therefore a larger λ .

4.3 Relative contributions of molecular diffusion and mechanical dispersion to anomalous transport

Hydrodynamic dispersion containing both local-scale molecular diffusion and mechanical dispersion were considered in the above Monte Carlo simulations. In this section, we conduct additional Monte Carlo simulations to distinguish the relative contributions of the two different local-scale mechanisms to anomalous solute transport.

Figure 11 shows the impact of mechanical dispersion on tracer BTCs and snapshots for *Scenario Short*. Solute transport dynamics can be separated into three stages. At early timescales, the well-mixed mobile and immobile blocks (shown in Figure 2e) cause the fast-moving particles to be deposited in floodplain deposits before they arrive at the control plane and form the early segment of the BTCs (Figure 11a,b) and the leading edge of the snapshots (Figure 11c,d). Mechanical dispersion enhances the penetration of particles in floodplain layers, which results in a slightly later arrival of the fast-moving particles than without mechanical dispersion. This mechanism may explain the slightly delayed early-timescale BTC with a dispersivity of $\alpha = 0.01$ m (i.e., with mechanical dispersion; see the line in Figure 11b) compared to the case of $\alpha = 0$ (i.e., without mechanical dispersion). At the intermediate timescale, more particles can be trapped by the immobile blocks for a larger α , resulting in a higher peak concentration of particles in the immobile phase (see the green symbols and line in Figure 11c). Finally, at late timescales, forward and backward diffusive fluxes in floodplain layers reaches an equilibrium due to the finite thickness of each floodplain layer. At this final stage, molecular diffusion dominates the diffusive displacements because of the negligible velocity in floodplain deposits (Figure 3a). Therefore, the resultant late-time BTC is not sensitive to the magnitude of mechanical dispersion, which can be seen by the fact that the BTCs for both $\alpha = 0.01$ m and $\alpha = 0$ shown in Figure 11a,b exhibit the similar late-timescale rate of decline.

Similar behavior can be observed for *Scenario Long* (Figure 12), except at early timescales.

Fig. 11. Impact of mechanical dispersion for *Scenario Short*: Monte Carlo simulations of the tracer BTC (a) and snapshots at all phases (c); (b) is the log-log plot of (a) and (d) is the semi-log plot of (c), which shows the tailing behavior. In the legend, “ α ” is the (isotropic) dispersivity. $P_e = 2.4 \times 10^{-3}$ with the effective diffusivity $D^* = 5.2 \times 10^{-5} \text{ m}^2/\text{day}$.

Scenario Long contains large-scale preferential flow paths consisting of interconnected channel deposits (Figure 2a). It is possible for the fast moving particles to arrive at the control plane without contacting the surrounding floodplain layers, and therefore the very early segment of the resultant BTC is not sensitive to α (Figure 12a,b). For some particles adjacent to the floodplain layers, mechanical dispersion forces them to contact the immobile phases, resulting in a smaller peak in both the BTC and the snapshot (Figure 12).

Therefore, mechanical dispersion tends to affect the dynamics of tracer transport at the early and the intermediate timescales, whereas molecular diffusion dominates the late-timescale, transient anomalous transport in alluvial aquifer-aquitard complexes.

Fig. 12. Impact of mechanical dispersion for *Scenario Long*: Monte Carlo simulations of the tracer BTC (a) and snapshots at all phases (c); (b) is the log-log plot of (a) and (d) is the semi-log plot of (c), which shows the tailing behavior. In the legend, “ α ” is the (isotropic) dispersivity. $P_e = 4.0 \times 10^{-2}$ with the effective diffusivity $D^* = 5.2 \times 10^{-5} \text{ m}^2/\text{day}$.

4.4 The influence of the initial source dimensions on late-time transport behavior

Source locations in the above Monte Carlo simulations are in high-permeability channel deposits conditioned by geostatistical simulations (see section 2.1). If part of the initial contaminant source is located in the relatively immobile phase, the transient anomalous transport may be affected by the slow mass release from these source locations. In this section, we conduct additional Monte Carlo simulations by expanding the previous point source to an area source with the dimension of $100 \times 200 \text{ m}^2$ ($Z \times Y$ axes) perpendicular to the main flow direction (X axis).

Figure 13 shows the impact of the initial source dimension on the late-time transport behavior. When the travel distance is relatively small (e.g., shorter than the mean longitudinal length of channel deposits), an increase of the initial source dimension can significantly enhance the power-law, late-time tailing of transport for *Scenario Long* (Figure 13c). Contaminant particles released initially in the floodplain deposits exit

Fig. 13. Impact of the initial source dimension on the BTCs for *Scenario Short* (a) and *Scenario Long* (c), where the control plane is located at $L = 160$ m and $1,495$ m, respectively; (b) and (d) are the log-log plots of (a) and (c), respectively, that show the peak. $P_e = 2.4 \times 10^{-3}$ for *Scenario Short* and 4.0×10^{-2} for *Scenario Long*, respectively, with the effective molecular diffusivity $D^* = 5.2 \times 10^{-5}$ m²/day. In the legend, “Point source” means the source particles are located in the channel cluster discussed in section 2.1, and “Area source” means the source particles are located in an upstream area perpendicular to the general flow direction. The “flux concentration” describes solute particles moving irrevocably past the control plane, which is the standard definition of a BTC (Zheng et al., 2006).

slowly, which is exhibited by increased sequestration in the Monte Carlo simulations (see Figure 14 and further discussion below), and provide a continuous source that broadens the distribution of mobile-immobile mass transfer rates, resulting in a more pronounced late-time tail in the BTC (Zhang et al., 2014). However, such an enhancement in the power-law tail is not evident for *Scenario Short* (Figure 13a), because its BTC does not contain any power-law segment due to the relatively short transition time $1/\lambda = 102$ yrs.

If the travel distance is much larger than the correlation scale of hydrofacies, the impact of the initial source size on transient anomalous transport can be minimized, as shown by the BTCs at the travel distance of $L = 1,495$ m shown in Figure 13. The corresponding travel time is typically long enough to reach the order of the transient time $1/\lambda$, when the late-time tail of the BTC is no longer enhanced by the solute par-

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ticles initially trapped near the source area because all the particles exit the immobile phase at a time $t \geq 1/\lambda$ (for an example, see Zhang and Meerschaert (2011)). At a later time $t \gg 1/\lambda$, transient anomalous transport approaches its asymptote, and therefore all cases (with different initial source dimensions) exhibit the same exponential rate of decline (see $L = 1,495$ m shown in Figure 13a,b). Therefore, the initial source dimension only affects the early stage of transient anomalous transport, especially for systems in which the travel distance is equal or shorter than the mean channel lengths or correlation distance of heterogeneity.

In addition, we explore whether the anomalous transport model parameters remain the same regardless of the initial source dimension. As a preliminary test, we apply model (2) to capture the Monte Carlo simulations with an area source. This test contains three steps. First, model (2) is generalized to allow a general initial condition using the fractal mobile/immobile concept proposed by Schumer et al. (2003), where contaminants initially distribute in both immobile and mobile domains (with a mass ratio denoted as R). Second, the time-domain Langevin approach proposed by Zhang et al. (2008b) is adopted to approximate the fractional-derivative model, where particles released to the system are defined as mobile or immobile. Finally, the resultant model and Lagrangian solver are used to quantify various snapshots for both *Scenario Short* and *Scenario Long*. All model parameters estimated in Section 3 (with a point source) are used here, leaving R as the only fitting parameter. Figure 14 shows the numerical result. For *Scenario Short*, the mass ratio $R = 0.2$ fitted by the first snapshot at time $t = 10$ yrs (Fig. 14a) is then used to predict the snapshot at time $t = 100$ yrs (Fig. 14b). Both the Monte Carlo simulations and the model solution identify the concentration peak near the initial source due to the enhanced sequestration. At late times (e.g., $t = 1000$ yrs) much larger than the maximum retention time ($1/\lambda = 102$ yrs), all initial source particles exit the source area and move downstream, minimizing the impact of the initial source dimension on anomalous transport (Fig. 14c). Similar behavior is observed for *Scenario Long*, except that the last snapshot (at $t = 1000$ yrs) still contains a significant amount of mass near the source, due to the longer retention time

($1/\lambda = 2000$ yrs) (Fig. 14f). Although the model captures the general trend of each snapshot, it cannot characterize the smooth decline and expansion of immobile mass around the initial source. This subtle difference might be due to the discrepancy between the physical model (2) and the Monte Carlo simulation for an area initial source. First, in the Monte Carlo simulations, particles start from a wide range of zones with different velocities, including not only mobile and relatively immobile zones, but also intermediate zones with velocities transitioning from mobile to immobile. In model (2), however, particles can only start from mobile or immobile phases. Second, in the Monte Carlo simulation, the source particles trapped by the relatively immobile domains keep moving due to molecular diffusion (which is similar to a dual-permeability model for transport in fractured media); while the immobile particles described by model (2) remain motionless (i.e., similar to a dual-porosity model). We will explore the above hypothesis and develop the corresponding physical model in a future study.

This study considers the variation of P_e caused mainly by the diffusive transport rate, while the advective transport rate only changes with the correlation of hydrofacies spatial distributions. In addition, the low hydraulic conductivity for floodplain facies represents the average conductivity measured at the LLNL site (Carle, 1999), which may not be indicative of other floodplain deposits. If the advective transport rate increases (due to for example an increase in the hydraulic gradient and/or conductivity), both the property of the transient anomalous transport and the applicability of the TSS model may need to be re-evaluated. The capacity coefficient β and truncation parameter λ might be sensitive to P_e changing with advection, while the power-law slope of the BTC (which is related to γ) might not vary significantly, since this slope is affected mainly by the medium properties (i.e., the thickness distribution of the low-permeability layers that ranks and assembles backward diffusion) (Zhang et al., 2013, 2014). We will check the above hypothesis systematically by exploring the possible influence of the advective transport rate on transient anomalous transport in a future study.

Fig. 14. Snapshots of *Scenario Short* (a, b, and c) and *Scenario Long* (d, e, and f) at different times ($t = 10, 100$, and 1000 yrs, respectively), with an area source. The effective molecular diffusivity D^* is equal to 5.2×10^{-5} m²/day for all cases, with the corresponding P_e shown in Table 2.

5 Conclusions

This study applies Monte Carlo simulation and stochastic model analysis to explore the influence of the Peclet number as affected by molecular diffusion on the dynamics of pre-asymptotic transport, especially the transition from non-Fickian to Fickian transport, in complex aquifer-aquitard systems represented by high-resolution hydrofacies models. Two scenarios of alluvial settings are considered—one representing short mean lengths (*Scenario Short*) and the other representing long mean lengths (*Scenario Long*)—because previous studies by Zhang et al. (2013, 2014) found that the facies connectivity is a

major medium property affecting sub-diffusive transport. Four factors are considered in the Monte Carlo simulations: the variations in thicknesses of the low-permeability layers, the molecular diffusivity, the dispersivity, and the initial source dimensions. The Monte Carlo simulations are also analyzed using a tempered stable model. The combined analysis using numerical and stochastic models reveal five major conclusions that can improve our understanding of the role that the Peclet number as affected by molecular diffusion plays in the transient anomalous dynamics for contaminant transport in alluvial aquifer-aquitard systems.

First, sequestration around the source area affected by molecular diffusion is an important sign of persistent pre-asymptotic transport. When solute particles begin to leave the source area, pre-asymptotic transport exhibits an apparent temporal transition to its asymptote. During this process, molecular diffusion defines the rate of backward diffusion and the low-permeability layers with various thicknesses act as a filter that ranks and assembles backward diffusion. Therefore, long-term monitoring of sequestration behavior might be useful for optimizing contaminant remediation.

Second, for a given alluvial medium, the Peclet number as affected by molecular diffusion has a twofold, timescale-dependent impact on transient anomalous transport. A smaller P_e due to a larger D^* not only enhances the mass exchange between mobile and immobile phases (and therefore facilitates anomalous transport at the early timescale), but also accelerates backward diffusion by shortening the residence time of immobile particles and enhances the transfer from anomalous to normal diffusion at the late timescale. Therefore, the Peclet number as affected by molecular diffusion affects both the duration of the power-law segment of the late-timescale BTCs and the transition rate from anomalous to normal diffusion. Additionally, the power-law slope of the BTC remains relatively stable for solute transport at different travel distances and various Peclet numbers.

Third, compared to mechanical dispersion, molecular diffusion has a significantly stronger influence on the late-time tailing behavior of the tracer BTCs for alluvial settings with

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either short or long mean lengths. This difference is likely due to the near negligible velocity in the floodplain layers.

Fourth, fitting and prediction exercises show that the tempered stable model can generally reproduce the simulated pre-asymptotic transport. The TSS model (2) contains three parameters that control the late-timescale transport behavior with a point source in the mobile phase. The index γ is not sensitive to P_e because the power-law slope of the BTC is affected mainly by the medium properties (i.e., the thickness distribution of the low-permeability layers that ranks and assembles backward diffusion). The truncation parameter λ and the fractional capacity coefficient β increase with a decrease in P_e , which is likely due to the decrease in the mean residence time and the increase in the number of immobile particles (when diffusion is enhanced), respectively. When the advective transport rate changes significantly, the variation of λ and β with respect to P_e should be evaluated systematically. This evaluation will be the topic of a future study.

Fifth, the increase of the initial source dimensions enhances the late-time tail of the BTCs for *Scenario Long* for a short travel distance due to the increased initial mass in immobile zones. Source dimensions do not significantly affect the pre-asymptotic transport at a relatively long travel distance due to the reduced sequestration at late timescales. When the travel time is sufficiently long, the late-time tail of the BTC is no longer significantly affected by sequestration, and therefore the transport is less sensitive to the initial source dimension. Here the dividing time between the early- and late-timescale can be approximated by the maximum residence time, which is denoted as $1/\lambda$ where λ is the truncation parameter. At early times $t < 1/\lambda$, the transport model captures the general trends of anomalous transport, but misses the spatial expansion of immobile mass around the source due to diffusion. At late times $t > 1/\lambda$, the anomalous transport model parameters remain the same regardless of the initial source dimension.

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