Linking aquifer spatial properties and non-Fickian transport in mobile-immobile like alluvial settings

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Abstract

Time-nonlocal transport models can describe non-Fickian diffusion observed in geological media, but the physical meaning of parameters can be ambiguous, and most applications are limited to curve-fitting. This study explores methods for predicting the parameters of a temporally tempered Lévy motion (TTLM) model for transient sub-diffusion in mobile-immobile like alluvial settings represented by high-resolution hydrofacies models. The TTLM model is a concise multi-rate mass transfer (MRMT) model that describes a linear mass transfer process where the transfer kinetics and late-time transport behavior are controlled by properties of the host medium, especially the immobile domain. The intrinsic connection between the MRMT and TTLM models helps to estimate the main time-nonlocal parameters in the TTLM model (which are the time scale index, the capacity coefficient, and the truncation parameter) either semi-analytically or empirically from the measurable aquifer properties. Further applications show that the TTLM model captures the observed solute snapshots, the breakthrough curves, and the spatial moments of plumes up
to the fourth order. Most importantly, the a priori estimation of the time-nonlocal parameters outside of any breakthrough fitting procedure provides a reliable “blind” prediction of the late-time dynamics of subdiffusion observed in a spectrum of alluvial settings. Predictability of the time-nonlocal parameters may be due to the fact that the late-time subdiffusion is not affected by the exact location of each immobile zone, but rather is controlled by the time spent in immobile blocks surrounding the pathway of solute particles. Results also show that the effective dispersion coefficient has to be fitted due to the scale effect of transport, and the mean velocity can differ from local measurements or volume averages. The link between medium heterogeneity and time-nonlocal parameters will help to improve model predictability for non-Fickian transport in alluvial settings.

Key words: Non-Fickian diffusion, Tempered model, Prediction, Alluvial setting

1 Introduction

Non-Fickian transport has been observed in hydrological processes, motivating the development of time-nonlocal transport models [36,40]. The terminology “time-nonlocal” means that the current concentration change is affected by the history of solute loading at the same location as a result, for example, of diffusion into and out of relatively immobile zones [47]. Non-Fickian transport is manifested in different ways, where the most common way is the “trapping” behavior characterized by the late arrival of solutes in aquifers or sediment in rivers [6,18,23]. Some time-nonlocal transport theories, including the continuous-time random walk (CTRW) framework reviewed by Berkowitz et al. [5] and the standard fractional-order advection-dispersion equation (fADE) model reviewed by Zhang et al. [47], can reproduce non-Fickian transport based on assumptions of the statistics of solute particle dynamics. Although multiple theories are available, there is limited knowledge of how model parameters relate to measurable features of complex aquifers.

This study explores the predictability of parameters in the state-of-the-art, fractional-derivative model for non-Fickian transport observed in heterogeneous alluvial systems. The fractional-derivative model has been found to efficiently capture the late-time tailing (“sub-diffusion”) observed in many earth surface processes [13,15,33,34,40]. Here
the terminology “sub-diffusion” refers to the retention process where 1) solute particles experience apparent trapping periods in the relatively immobile zones, and 2) the temporal evolution of the mean displacement of solute particles tends to be slower than linear [46] (which will also be shown in this study). Alluvial settings with a range of heterogeneous geology were selected in this study, because previous Monte Carlo simulations [49] and stochastic analysis of these settings [48] provided a comprehensive picture of their non-Fickian transport. 

Zhang et al. [49] showed that the shape of the late-time breakthrough curve (BTC) can be derived in part from the distribution of thicknesses of low-conductivity sediments. These previous studies provide a basis to link the parameters of a time-nonlocal transport model to measurable aquifer characteristics such as facies heterogeneity and mean velocities.

The rest of the paper is organized as follows. In Sec. 2, the time-nonlocal model proposed first by Meerschaert et al. [32] is adopted based on knowledge obtained from Monte Carlo simulations of solute transport in Zhang et al. [49]. The predictability of parameters in the resultant physical model is then explored in Sec. 3. In Sec. 4, we check the applicability and predictability of the transport model, where time-nonlocal transport parameters are connected semi-analytically or empirically to the medium heterogeneity, and particularly, the measurable spatial statistics of hydrofacies. Limitations and possible extensions of the methodology developed by this study, and the prediction of the velocity and dispersion coefficient, are discussed in Sec. 5. Conclusions are drawn in Sec. 6. Numerical solvers of the fractional-derivative model are developed in the appendix.

2 Monte Carlo simulations and time non-local transport models for non-Fickian transport in alluvial settings

We first introduce the previous Monte Carlo simulations of non-Fickian transport [49] and explore the major medium properties of complex alluvial settings in subsec. 2.1. We then discuss the time non-local transport models and develop the numerical solvers in subsec. 2.2. The late-time tailing behavior described by multiple time non-local transport models is then evaluated in subsec. 2.3, which leads to parameter prediction in Sec. 3.
In Monte Carlo simulations of passive solute transport through regional-scale alluvial settings conducted by Zhang et al. [49], the medium heterogeneity embedded in typical alluvial settings was simulated using transition-probability based indicator geostatistics called “TPROGS” [8]. Realizations represented the fine-grain dominated alluvial setting beneath the Lawrence Livermore National Laboratory (LLNL) site in Livermore, California. Steady-state groundwater flow was calculated using the USGS block-centered finite difference code “MODFLOW” [19]. The contaminant migration through the flow fields was simulated using an efficient Lagrangian solver “RWHet” [27].

Here we consider two end-members of alluvial settings built by Zhang et al. [49], with widely varying thicknesses of immobile domains (the main reason for sub-diffusion). If the TTLM model can capture transport through such a wide spectrum of immobile layers with various thicknesses, it may also capture transport through an intermediate alluvial setting. One end member considered below is a system containing 56% low-permeability floodplain deposits, representing a fine-grain dominated alluvial setting. The other contains 26% floodplain deposits (see Table 1), representing a relatively coarse-grain dominated alluvial setting. Proportions of the other hydrofacies remain unchanged (Table 1). Each end member has three scenarios with varying hydrofacies mean lengths, and each scenario contains 100 different but equally possible realizations of hydrofacies models, to account for the uncertainty of the spatial distribution of hydrofacies. The ensemble average of solute transport results obtained by the Monte Carlo simulations in Zhang et al. [49] is used in the next section for estimation of TTLM parameters from analysis of relationships between medium properties (especially layer thicknesses) and TTLM model parameters.

One realization of the hydrofacies model for each of the six scenarios is shown in Figure 1. For example, Scenario Fine-ML1 represents the fine-grain dominated scenario where the “mean length factor” (described below) is 1, and Scenario Coarse-ML0.25 denotes the coarse-grain dominated scenario with a mean length factor 0.25. In other words, if the mean length factor is \( a \), the mean length for each hydrofacies in the high-resolution hydrofacies model is \( a \) times the field measurement of mean length at the LLNL site. Variability of mean lengths is the main factor that affects the thickness distribution of...
Table 1
Hydrofacies properties for Scenario Coarse-ML1, including mean length (m) along the strike, dip, and vertical directions, respectively (denoted as $L_{\text{Strike}}$, $L_{\text{Dip}}$, and $L_{\text{Vertical}}$, respectively, and corresponding to $y$, $x$, and $z$ axes shown in Figure 1c); hydraulic conductivity (m/day); global volumetric proportion; and average Peclet number (where the Peclet number was calculated by LaBolle and Fogg [26]). The hydrofacies mean lengths and hydraulic conductivities were estimated by Carle [7].

<table>
<thead>
<tr>
<th>Hydrofacies</th>
<th>$L_{\text{Strike}}$</th>
<th>$L_{\text{Dip}}$</th>
<th>$L_{\text{Vertical}}$</th>
<th>Proportion (%)</th>
<th>$K$</th>
<th>$P_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debris Flow</td>
<td>8</td>
<td>24</td>
<td>1.1</td>
<td>7</td>
<td>0.432</td>
<td>$5.9 \times 10^3$</td>
</tr>
<tr>
<td>Floodplain</td>
<td>27</td>
<td>67</td>
<td>2.1</td>
<td>26</td>
<td>$0.432 \times 10^{-5}$</td>
<td>$5.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Levee</td>
<td>6</td>
<td>20</td>
<td>0.8</td>
<td>19</td>
<td>0.173</td>
<td>$2.0 \times 10^3$</td>
</tr>
<tr>
<td>Channel</td>
<td>10</td>
<td>50</td>
<td>1.3</td>
<td>48</td>
<td>5.184</td>
<td>$1.5 \times 10^5$</td>
</tr>
</tbody>
</table>

Fig. 1. 3-d view of realizations of hydrofacies for six alluvial settings, including Scenario Fine-ML0.5 (a), Scenario Fine-ML1 (b), Scenario Fine-ML2 (c), Scenario Coarse-ML0.25 (d), Scenario Coarse-ML1 (e), and Scenario Coarse-ML4 (f). In scenario names, “ML” stands for “MeanLength”. The overall dimensions of the simulated domain are $970 \times 405 \times 40.5$ m ($x/y/z$), with the cell sizes $10 \times 5 \times 0.5$ m (the total number of cells is 636,417 in each realization).
Properties of hydrofacies are listed in Table 1. A large permeability difference exists between floodplain hydrofacies and the non-floodplain hydrofacies. Diffusion is the controlling transport process in the relatively low-velocity blocks of floodplain hydrofacies. Advection dominates transport in non-floodplain hydrofacies where the high-permeability channel deposits tend to be interconnected in the 3-d space [14]. This strong contrast motivated Zhang et al. [44] to define each immobile block as a cluster consisting of floodplain hydrofacies. In this study we tested the assumption by comparing the previous method with an alternative approach that distinguished mobile and immobile phases using the cutoff of velocity. To do this, we calculated the velocity distribution within each facies using the output of MODFLOW. We also calculated the time-evolution of concentrations using both the hydrofacies based and the velocity-cutoff based methods. Comparison (not shown here) revealed that the predicted breakthrough curves were nearly identical and that the floodplain facies can be reasonably treated as the immobile phase. Therefore, to be consistent with previous studies [26,44], here we apply the hydrofacies-based method to distinguish between mobile and immobile phases.

The volume fractions of immobile blocks based on their thicknesses, denoted as $P(Z)$, for the six scenarios are shown in Figure 2. Here $Z$ denotes the thickness of floodplain layers, which can be classified into multiple groups [44]. The function $P(Z)$ first distributes as a power law for relatively thin floodplain layers, and then declines as fast as exponentially for thicker layers. This critical medium property significantly affects non-Fickian transport and therefore may be used to predict parameters for transport models developed below.
2.2 The temporally tempered Lévy motion model for non-Fickian transport

The multi-rate mass transfer (MRMT) model with a linear mass transfer process can be written as [17,40]

$$\frac{\partial C_T}{\partial t} + \beta \frac{\partial C_T}{\partial t} \ast g(t) = L(x)C_T,$$  \hspace{1cm} (1a)
$$\frac{\partial C_M}{\partial t} + \beta \frac{\partial C_M}{\partial t} \ast g(t) = L(x)C_M - \beta C_0(x) g(t),$$  \hspace{1cm} (1b)

where $C_T$ and $C_M$ [ML$^{-3}$] denote the concentration of solute in the total and mobile phase, respectively; $\beta$ is the capacity coefficient; the symbol “$\ast$” denotes convolution; $L(x)$ denotes the advection-dispersion operator; $g(t)$ is the memory function; and $C_0(x)$ [ML$^{-3}$] represents the concentration of contaminants injected in the mobile phase at time $t = 0$.

Transport behavior observed in alluvial aquifers [49] guides the selection of the memory function $g(t)$ in this study. After most solute mass is flushed out through the relatively high-permeability non-floodplain lithologies, the remaining solutes trapped in the low-permeability floodplain layers will diffuse out and produce macroscopic sub-diffusive transport behavior. The upper limit of thicknesses of individual floodplain layers constrains the maximum waiting time and results in an eventual transition from sub-diffusive to Fickian transport, observed as a smooth transition from power-law to exponential decline in the late-time BTC. This pre-asymptotic transport is directly linked to the exponentially truncated power-law distribution of waiting times [49]. To capture the exponentially truncated power-law distribution of waiting times for solute particles trapped in the parallel immobile phases, Meerschaert et al. [32] proposed the incomplete Gamma function

$$g(t) = \int_t^\infty e^{-\lambda \tau} \frac{\gamma^{\tau-\gamma-1}}{\Gamma(1-\gamma)} d\tau$$  \hspace{1cm} (2)

as memory function, which in Laplace domain $t \rightarrow s$ turns into $\hat{g}(s) = \frac{(\lambda+s)^\gamma - \lambda^\gamma}{s}$ where $\lambda > 0$ [T$^{-1}$] is the truncation parameter in time and $0 < \gamma < 1$ [dimensionless] is the scale index in time. Combining (1) and (2), one obtains the temporally tempered Lévy
motion (TTLM) model for transient non-Fickian diffusion [32]:

\[
\frac{\partial C_T}{\partial t} + \beta e^{-\lambda t} \frac{\partial^\gamma}{\partial t^\gamma} [e^{\lambda t} C_T] - \beta \lambda^\gamma C_T = -\frac{\partial}{\partial x} \left[ V C_T - D \frac{\partial C_T}{\partial x} \right] + \beta C_0(x) \int_0^\infty e^{-\lambda \tau} \frac{\tau^{-\gamma-1}}{\Gamma(-\gamma)} d\tau,
\]

(3a)

\[
\frac{\partial C_M}{\partial t} + \beta e^{-\lambda t} \frac{\partial^\gamma}{\partial t^\gamma} [e^{\lambda t} C_M] - \beta \lambda^\gamma C_M = -\frac{\partial}{\partial x} \left[ V C_M - D \frac{\partial C_M}{\partial x} \right],
\]

(3b)

where \( V [LT^{-1}] \) is the advective velocity; \( D [L^2T^{-1}] \) is the dispersion coefficient; \( \Gamma() \) denotes the Gamma function; and \( \frac{\partial^\gamma}{\partial t^\gamma} \) denotes the time fractional Riemann-Liouville derivative.

Note that the model (3) can also be derived directly using the integral transform and the subordination principle (not shown here), where the advection-dispersion operator \( L(x) \) can take many other forms (such as the super-dispersion term discussed in subsec. 5.1). This can generalize the TTLM model (3). It is also noteworthy that the three parameters \( \gamma, \lambda \) and \( \beta \) in model (3) define the statistics of waiting times for solute particles. To distinguish them from the remaining parameters, we describe them as “time-nonlocal” parameters.

Both an Eulerian implicit numerical method (Appendix A.1) and a fully Lagrangian method (Appendix A.2) were developed to solve the TTLM model (3). The two numerical solutions provide necessary cross verifications and they are used below.

2.3 Comparison between the MRMT and TTLM models in capturing non-Fickian transport

Here we evaluate the similarities and differences between the TTLM and the MRMT models, to obtain information for parameter prediction discussed in Sec. 3.

The TTLM model (3) (with Fickian diffusion) is a special MRMT model with the memory function (2). It is known that the MRMT model parameters relate directly to the properties of media with regular geometry [17,18]. For the case of alluvial systems considered in this study, the rate coefficient and capacity coefficient in the MRMT model relate to the volumetric proportion of floodplain blocks classified by thickness [44]. The mathematical equivalence between the MRMT model and the TTLM model,
therefore, may be applied to build the linkage between the TTLM model parameters and medium properties. In addition, many other studies have also revealed the similarities between the MRMT model and the other time-nonlocal transport models. For example, the mathematical equivalence between the MRMT and the CTRW models was evaluated by Dentz and Berkowitz [11] and Benson and Meerschaert [4]. Neuman and Tartakovsky [36] compared the stochastic average of local advection-dispersion equation, CTRW, and fADE models, and Zhang et al. [47] further explored the underlying memory kernels. Recently, Silva et al. [41] found that these time-nonlocal models are equivalent since they all describe linear mass transfer between mobile and immobile regions, and they proposed a MRMT formulation representing all the above models of non equilibrium.

2.3.1 The MRMT model

The linear, multirate transport equation can be written as [17]

\[
\frac{\partial C_M}{\partial t} + \sum_{j=1}^{n} \beta_j \left[ \alpha_j \left( C_M - C_{IM,j} \right) \right] = S(C_M),
\]

(4)

where \(C_{IM,j}\) is the solute concentration in the \(j\)-th immobile zone; \(\alpha_j [T^{-1}]\) is the rate of the first-order mass transfer between \(C_M\) and each \(C_{IM,j}\); \(\beta_j \) [dimensionless] is the capacity coefficient; \(n\) is the number of immobile zones; and \(S()\) is the linear operator representing the advective-dispersive flux and fluid sources/sinks in the mobile domain. Model (4) is another version of (1b) with the memory function expressed by individual rate/capacity coefficients.

The late-time resident concentration in the mobile phase is [18]:

\[
C_M(L, t_{\text{late}}) = t_{\text{ad}} m_0 \sum_{j=1}^{n} \beta_j \alpha_j^2 \exp(-\alpha_j t_{\text{late}}),
\]

(5)

where \(L \) [\(L\)] is the travel distance, \(t_{\text{ad}} \) [\(T\)] is the average advective residence time, and \(m_0 \) [\(M TL^{-3}\)] is the zeroth temporal moment of the breakthrough curve. Here we approximate \(C_M(L, t_{\text{late}})\) for an alluvial system with a given distribution of floodplain layers. For diffusion-limited floodplain layers, the corresponding rate coeffi-
cient in (5) can be approximated by [44]

\[ \alpha_j = \frac{D^*}{Z_j^2}, \]  

(6)

where \( D^* \) is the molecular diffusion coefficient, and \( Z_j \) denotes the thickness of the \( j \)-th class of immobile block. \( \beta_j \) in (5) can be approximated by [44]

\[ \beta_j = \left( \frac{V_{im}}{V_{im}} \right)_j \beta_{tot}, \]  

(7)

where \((V_{im})_j\) and \(V_{im}\) are the volume of the \( j \)-th immobile block and the total immobile domain, respectively; and \( \beta_{tot} \) denotes the total capacity coefficient.

To derive the analytical solution for (5), we assume that the volume fraction of the immobile blocks classified by its thickness decreases as a power-law function

\[ P(Z_j) = A (Z_j)^m, \]  

(8)

where \( A \) is a positive constant, \( Z_j = j \), and the power-law exponent \( m < 0 \).

Inserting (6), (7), and (8) into (5), we obtain

\[
C_M(L, t_{late}) = m_0 t_{ad} \sum_{j=1}^{n} \frac{Z_j P(Z_j)}{\Sigma[Z_j P(Z_j)]} \beta_{tot} \left[ \frac{D^*}{(Z_j)^2} \right]^2 \exp \left[ -\frac{D^*}{(Z_j)^2} t_{late} \right] \\
\approx m_0 t_{ad} A \beta_{tot} (D^*)^{(m+2)/2} \Gamma \left( \frac{2+m}{2} \right) \left( t_{late} \right)^{\frac{m-2}{2}} \exp \left( -t_{late} \frac{D^*}{Z_n^2} \right),
\]  

(9)

where \( Z_n \) denotes the largest thickness. At a late time

\[ t_{late} \ll \frac{(Z_n)^2}{D^*}, \]  

(10)

(9) reveals that the mobile-phase concentration declines as power law:

\[ C_M(L, t_{late}) \propto \left( t_{late} \right)^{\frac{m-2}{2}}. \]  

(11)

In contrast, when the time is long enough for the particle to diffuse from the thickest floodplain block, the BTC late-time tail will transition from power law to exponential.
We calculate the late-time concentration (5), which is the summation of exponential functions, by assuming a power-law $P(Z_j)$ expressed by (8) (example 1 shown in Figure 3a,c) and an exponentially truncated power law $P(Z_j)$ (example 2 shown in Figure 3b,d). The second example characterizes the typical $P(Z_j)$ observed for the hydrofacies model [49] (see for example, Figure 2). For example 1, Figure 3c shows that the power-law slope of the BTC (denoted as $S_{BTC}$) is related to the power-law exponent $m$ in $P(Z_j)$ by: $S_{BTC} = -1 + m/2$, confirming the above derivation (11). In addition, the BTC transition time (from power-law to exponential) can be approximated by the maximum diffusive time $t(Z_{max}) = (Z_{max})^2/D^* = (Z_n)^2/D^*$, confirming (10).

For example 2 where $P(Z_j)$ declines as fast as exponential for the large thicknesses (Figure 3b), the transition time might not be approximated by the maximum diffusive time (Figure 3d). In this case, the actual transition occurs much earlier (Figure 3d), since the contribution of the thick immobile layers to the late-time concentration decreases much faster than that for a power-law $P(Z_j)$. We find that the diffusive time corresponding to the average thickness (denoted as $t(Z_{average})$) might be used as an empirical value to approximate the transition time, as shown by the blue vertical line in Figure 3d.

2.3.2 The TTLM model

Here we explore the late-time behavior of the BTC for transport governed by the TTLM model (3) with the memory function $g$ defined by (2). According to Haggerty et al. [18], the mobile concentration at a late time can be approximated by the memory function:

$$C_M(x, t) \approx -t_{ad} m_0 \frac{\partial g(t)}{\partial t},$$

which is valid for a pulse injection into the mobile phase with zero initial concentration [18]. Inserting (2) into (12), we obtain the approximation:

$$C_M(x, t) \propto t_{ad} m_0 \frac{\gamma}{\Gamma(1-\gamma)} t^{-1-\gamma} \exp(-t\lambda).$$

At a time

$$t \ll 1/\lambda,$$

the power-law exponent in the first term on the RHS of (13) dominates, leading to a
Fig. 3. Demonstration of the MRMT late-time approximation (5) with a power-law $P(Z_j)$ (8) ((a) and (c)), and a partially power-law $P(Z_j)$ ((b) and (d)). Here $j = 1, 2, \cdots, 36$. The dotted line in (c) and (d) denotes the power-law trend of the concentration. The vertical dashed line denotes the diffusive time corresponding to the specific immobile block with a certain thickness. In the legend in (c) and (d), $Z_{\text{max}} = Z_{36}$ denotes the maximum thickness, and $Z_{\text{average}} = Z_{18}$ denotes the average thickness.

The power-law decline of mobile concentration:

$$C_M(x, t) \propto t^{-1-\gamma}.$$  \hspace{1cm} (15)

When the time is large $t \gg 1/\lambda$, (13) is dominated by the exponential term, leading to a fast decline of mobile mass.

In the next section we predict parameters in the TTLM model (3) by comparing the late-time concentrations obtained in subsec. 2.3.1 and subsec. 2.3.2.
3 Prediction of model parameters

3.1 Prediction of the scale index $\gamma$ as a function of the slope of $P(Z)$

Numerical experiments show that the time scale index $\gamma$ controls the power-law slope of the concentration profile (Figures 4a and 5a). An instantaneous point source is injected at the origin $x = 0$, with the initial condition $C_T(x, t = 0) = 0$ and the boundary condition $C_T(x = \pm \infty, t) = 0$. For the resident concentration profile in the total phase, the power-law slope is $-\gamma$ if the truncation parameter $\lambda$ is small; while for the flux concentration or BTC, the power-law slope is $-1 - \gamma$ (see (15)). This conclusion is consistent with that of [47] for the standard time fADE (with $\lambda = 0$). The consistency is expected because the TTLM model reduces to the standard time fADE if $\lambda \to 0$.

As discussed above (subsec. 2.1), the volumetric fraction of floodplain blocks classified by their thicknesses distributes firstly as a power law for relatively thin layers, and then transitions to exponential for thicker layers (as shown by Figure 2). Comparing the two concentrations (15) and (11), we find that $\gamma$ relates to the power-law slope of $P(Z)$ (denoted as $m$) by the formula

\[ \gamma = -\frac{m}{2}. \]
Fig. 5. The concentrations for the TTLM equation (3a) (black circles, representing the resident concentration) and Eq. (3b) (grey crosses, transformed flux concentration) simulated by the Lagrangian approach developed in Appendix A.2. Parameters are: $\gamma = 0.5$, $\beta = 0.1$, $V = 1$, $D = 0.1$, and the control plane is at $x = 5$. The truncation parameter $\lambda$ is $10^{-5}$ (a), $10^{-4}$ (b), $10^{-3}$ (c), $10^{-2}$ (d), $10^{-1}$ (e), and $10^{0}$ (f). The dashed line is the solution of the 2nd-order ADE. The black and grey solid lines are the solution of (3a) and (3b) with $\lambda = 0$, respectively. In (a), the red curve shows the range of solution for the TTLM model for the total phase (3a) (due to the variation of $\lambda$), and the blue curve shows the range of solution for the TTLM model for the mobile phase (3b).

If the thickness of fine-grained deposits has a wide distribution (such as in a system dominated by fine-grained materials, and/or in a system with a relatively large mean thickness of hydrofacies), the power-law portion of $P(Z)$ or the power-law MRMT concentration (9) may be sufficiently defined to provide a convenient estimate of $\gamma$. On the other hand, the estimation of $\gamma$ for the alluvial setting (represented by the hydrofacies model) with only thin layers can have greater uncertainty, due to the uncertainty in
estimating \(m\). In the latter case, a relatively large \(\lambda\) is needed to account for the short power-law tail in the BTC. We will evaluate the general applicability of (16) in Sec. 4.

It is noteworthy that several other studies also estimated model parameters in the multirate mass transfer approach, which is a generalization of the TTLM model. For example, Willmann et al. [42] conducted 2-d numerical transport experiments and found that the slope of the BTC was mainly influenced by the connectivity of the hydraulic conductivity. This finding supports the above estimation of \(\gamma\), which is related to the vertical distribution of floodplain hydrofacies. Hollenbeck et al. [21] also fitted the piece-wise linear distribution of rate coefficients using the flux concentration observed from column transport experiments, showing the potential linkage between the BTC and mass transfer parameters.

### 3.2 Prediction of the truncation parameter \(\lambda\) as a function of immobile zone thickness and molecular diffusion

The truncation parameter \(\lambda\) captures the rate of transition for pre-asymptotic transport, as shown by the time scale (14) and numerical examples in Figure 5. When the time \(t > 1/\lambda\), the late-time concentration \(C_M\) transitions from power-law to exponential. For example, for a very small \(\lambda \leq 10^{-5}\) (Figure 5a), the concentrations for solute in both the mobile and the total phase decline as power-law in most of the modeling period (the total modeling time is \(10^4\)). Conversely, when \(\lambda \geq 10^{-1}\), there is no power-law tail for arrival times larger than \(1/\lambda\) (Figure 5e,f).

Analysis of the MRMT model in subsec. 2.3.1 shows that the transition from power law to exponential occurs at a time for the solute particle to exit the immobile block (where the molecular diffusion dominates, due to the small velocity in the low-permeability block). Zhang and Meerschaert [48] approximated the truncation parameter \(\lambda\) by a specific rate coefficient (see also the definition (6)):

\[
\lambda = \frac{D^*}{Z^*}^2, \tag{17}
\]

where \(Z^*\) is the effective thickness of the fine-grained layer corresponding to the slope transition period of BTC, and \(D^*\) is the molecular diffusion coefficient. Here the “slope
transition period” represents the time period in which the late-time BTC transitions from power-law to exponential, as shown in Figure 3c. If \( P(Z) \) distributes as a power-law for all thicknesses (such as the one assumed in equation (8)), \( Z^* \) is approximately equal to the largest thickness (\( Z_n \) in equation (8)) of immobile layers (by comparing equation (14) and equation (10)).

The actual \( P(Z) \) considered in this study however declines faster than power-law for large thickness \( Z \) (Figure 2). Hence \( Z^* \) should be smaller than \( Z_n \). Analysis in subsec. 2.3.1 and the empirical conclusion in [48] suggest that \( Z^* \) might be simply approximated by:

\[
Z^* \approx \frac{Z_{\text{min}} + Z_{\text{max}}}{2},
\]

where \( Z_{\text{min}} \) and \( Z_{\text{max}} \) are the minimum and the maximum thickness of the fine-grained layers, respectively. In the following we will test the applicability of (17) and (18) using a wide range of alluvial settings, to extend the work in Zhang and Meerschaert [48].

### 3.3 Prediction of the capacity coefficient \( \beta \)

Capacity coefficient \( \beta \) distinguishes the status of solute particles by dividing the real time \( t \) into a motion period and a subsequent immobile period, and assigns the mass ratio of solute particles in immobile and mobile phases. Hence \( \beta \) may not only reflect the property of immobile blocks, but also relate to the properties of high-permeability deposits. When \( \beta \) increases, more particles are trapped in the immobile phase, increasing the late-time concentration. The corresponding concentration profile shifts forward in time, while the slope of the concentration profile remains unchanged in a log-log plot (Figure 4b). \( \beta \) also controls the skewness of tracer snapshots (here “snapshot” is the concentration profile in space at a given time). For instance, when \( \beta \) increases, a greater number of particles is delayed behind the mean displacement, increasing the skewness of the plume.

Here we first define a dimensionless capacity coefficient \( \beta_0 \) as a time ratio, as suggested by Benson and Meerschaert [4]:

\[
\beta_0 \approx \frac{t_{\text{immobile}}}{t_{\text{mobile}}},
\]
where $t_{\text{immobile}}$ is the mean residence time for particles in fine-grained layers

$$t_{\text{immobile}} \approx \frac{1}{n} \sum_{i=1}^{n} \left[ \frac{Z_{i}^{2}}{D_{i}} P(Z_{i}) \right], \quad (20)$$

and $t_{\text{mobile}}$ represents the mean advective time that can be approximated empirically by

$$t_{\text{mobile}} \approx \frac{L_{r} R^{1/2} U_{\text{mobile}}}{V^{*}}, \quad (21)$$

where $V^{*}$ is the mean advective velocity, $L_{r}$ is the reference travel distance for $V^{*}$ to reach relative stability, $R$ denotes the factor of mean length (where the factor is 1 for the measured mean length, or “ML1” as shown in Figure 1), and $U_{\text{mobile}}$ represents the volumetric proportion of coarse-grained materials in the aquifer.

The dimensionless capacity coefficient $\beta_{0}$ can then be converted to the actual $\beta$. As defined by previous studies (such as [17,18]), the capacity coefficient is the ratio of total contaminant mass in the immobile zone to the mass in the mobile zone at equilibrium. The TTLM model (3b) defines an asymptotic mobile mass $1/(1 + \beta \gamma^{\lambda - 1})$, and the corresponding immobile mass is $\beta \gamma^{\lambda - 1}/(1 + \beta \gamma^{\lambda - 1})$. This analytical solution will be cross verified in the next section using Monte Carlo simulations. The mass ratio between immobile and mobile phases at equilibrium defined by model (3) therefore is $\beta \gamma^{\lambda - 1}$, which should also be $\beta_{0}$. Therefore, we obtain the following conversion:

$$\beta = \frac{\beta_{0}}{\gamma^{\lambda - 1}}. \quad (22)$$

Equations (19) to (22) relate $\beta$ empirically to measurable aquifer properties. This information can be used in combination with, or as an alternative to, estimation of $\beta$ from concentration data, which was previously the only feasible approach [47]. On the RHS of (21), the term $L_{r}/V^{*}$ represents an approximation of mean advective time and the remaining term adjusts the approximation given further information about facies mean lengths and proportions. For the reference hydrofacies models in this study with properties of the LLNL site, extensive numerical tests show that the mean advective velocity $V^{*}$ remains relatively stable at a travel distance larger than 100 m [44]. Therefore we select the reference length scale $L_{r} \approx 100$ m. For other alluvial sites, $L_{r}$ likely will need to be re-calculated. The Monte Carlo simulations in [49] show that, if the mean length or the proportion of high-permeability deposits is
larger, the solute particles originating from high-permeability deposits (which can be part of preferential flow paths) tend to remain in the same material for a longer time, resulting in less trapping (or a smaller $\beta$). The time $t_{mobile}$ therefore may increase with an increase of the hydrofacies mean length. The square root taken for $R$ is to account for the nonlinear influence of the mean length factor on the mass exchange during solute transport [49]. Applicability of the empirical formula (21) will be checked extensively in Sec. 4.

### 3.4 Prediction of the velocity $V$ and dispersion coefficient $D$

The remaining parameters in (3) are the velocity, $V$, and dispersion coefficient, $D$. They may depend on hydraulic factors and therefore may not be estimated reliably given only information about low-permeability deposits. To quantify the possible discrepancy between the predicted $V$ and $D$ and the best-fit equivalents, we test two different estimates of $V$. The first is the arithmetic mean velocity $V_{Ari}$, which can be calculated using Darcy’s equation ($V_{Ari} = K_{Ari} \bar{J}/\phi$) given the arithmetic mean of hydraulic conductivity ($K_{Ari}$, obtained from the hydrofacies models), the general gradient of hydraulic head ($\bar{J}$), and the effective porosity ($\phi$) [49]. In the flow model, general head boundary conditions were used to simulate inflow and outflow through the two lateral boundaries of the model, and the other boundaries were specified as no-flow conditions [49]. The second estimation is the velocity at the solute source location, denoted as $V_{Mod}$, which was calculated by MODFLOW in the groundwater flow model. This can be regarded as analogous to a field measurement of groundwater velocity using, for example, a colloidal borescope.

Finally, we estimate $D$ based on the scale of discretization of representative elementary volumes in the flow model. For the case of coarse-grain dominated alluvial system (such as Scenario Coarse-ML1), the longitudinal dispersivity $\alpha_L$ is assumed to be 10% of the cell length, resulting in an empirical $D \approx V \alpha_L$ ($\alpha_L = 1$ m) (here the molecular diffusion is orders of magnitudes smaller than $V \alpha_L$ and hence can be neglected). When the content of fine-grained materials increases in the medium, Monte Carlo simulations of solute transport reveal that the longitudinal dispersion is enhanced [49]. Previous research [29] also showed that, with a decrease of the volumetric proportion of high-permeability hydrofacies, the preferential path for both flow and transport...
Table 2
Predicted parameters used in the TTLM equation (3), including the scale index $\gamma$, the truncation parameter $\lambda$, the capacity coefficient $\beta$, velocity $V$, and dispersivity $\alpha_L$. The subscript “Ari” and “Mod” of $\beta$ denotes the capacity coefficient corresponding to the arithmetic mean of velocity ($V_{Ari}$) and the simulated velocity using MODFLOW ($V_{Mod}$), respectively.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$\gamma$ [-]</th>
<th>$\lambda$ [yr$^{-1}$]</th>
<th>$\beta_{Ari}$ [yr$\gamma^{-1}$]</th>
<th>$\beta_{Mod}$</th>
<th>$V_{Ari}$ [m/yr]</th>
<th>$V_{Mod}$</th>
<th>$\alpha_L$ [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine-ML0.5</td>
<td>0.56</td>
<td>0.00237</td>
<td>0.684</td>
<td>0.628</td>
<td>14.64</td>
<td>13.44</td>
<td>5</td>
</tr>
<tr>
<td>Fine-ML1</td>
<td>0.56</td>
<td>0.00063</td>
<td>0.380</td>
<td>0.343</td>
<td>14.64</td>
<td>13.22</td>
<td>5</td>
</tr>
<tr>
<td>Fine-ML2</td>
<td>0.56</td>
<td>0.00036</td>
<td>0.214</td>
<td>0.186</td>
<td>14.64</td>
<td>12.74</td>
<td>5</td>
</tr>
<tr>
<td>Coarse-ML0.25</td>
<td>0.69</td>
<td>0.01687</td>
<td>0.980</td>
<td>1.113</td>
<td>19.15</td>
<td>21.76</td>
<td>1</td>
</tr>
<tr>
<td>Coarse-ML1</td>
<td>0.69</td>
<td>0.00607</td>
<td>0.274</td>
<td>0.299</td>
<td>19.15</td>
<td>20.85</td>
<td>1</td>
</tr>
<tr>
<td>Coarse-ML4</td>
<td>0.69</td>
<td>0.00078</td>
<td>0.115</td>
<td>0.130</td>
<td>19.15</td>
<td>21.59</td>
<td>1</td>
</tr>
</tbody>
</table>

The proportion of floodplain deposits increases up to $\sim 2.2$ times, and we assign a dispersivity that is $2.2^2$ times larger than the one for Scenario Coarse-ML1, resulting in an approximation $\alpha_L \approx 5$ m.

Table 2 shows the estimated values for the above five parameters for both the fine- and coarse-grain dominated systems with variable mean lengths. They will be validated in the next section.

4 Application of the TTLM model to capture the preasymptotic transport simulated by the Monte Carlo approach

We apply the numerical solution of the one-dimensional TTLM model (3) to capture the solute dynamics observed in the Monte Carlo simulations [49]. The solute snapshots, breakthrough curves, and the spatial moments up to the fourth order for plumes were compared to evaluate the accuracy of parameter estimates (shown in Table 2) for the TTLM model (3).

In the following section, we first predict the snapshots using the scheme developed in Sec. 3. If the prediction does not match the observation, we explore the feasibility of the prediction method and then fit this specific parameter using the observed early-time snapshots. The obtained parameters are then used to predict the late-time snapshots,
the tracer BTCs, and plume spatial moments. The snapshot captures the spatial distribution of tracer particles at a specific time, while the BTC describes the downstream flux of tracers over time. The plume spatial moments are statistics of the plume spatial distribution. By considering all these characteristics of transport, we thoroughly evaluate the predictability of model parameters in (3).

It is noteworthy that in the Monte Carlo simulations conducted by Zhang et al. [49], absorbing boundaries were used to allow solute particles to pass through both the upgradient and downgradient boundary facies (which are perpendicular to the $x$-axis shown in Figure 1c), while the other boundaries were no-flux conditions. An instantaneous point source was injected in the mobile zone (represented by high-permeability channel facies) near the upstream boundary, while the whole domain was clear of contamination initially. Particles then move via both advection and dispersion (with an isotropic dispersivity and an effective molecular diffusivity given by [26]) through the heterogeneous alluvial settings, with the sub-grid diffusion assumed to be Fickian. Additional details of the Monte Carlo simulations can be found in [49].

The random walk solution method (see Appendix A.2) is used in this section, because 1) it can calculate both the mobile and immobile concentrations using one simulation (while the finite difference solver needs to be run twice), 2) the Lagrangian solver is computationally efficient for a small index $\gamma$ (due to the relatively longer waiting times for particles), and 3) the particle-based approach can calculate conveniently both the flux and resident concentrations.

Both the solute snapshots (see subsec. 4.1) and breakthrough curves (subsec. 4.2) are used to check thoroughly the predictability of model parameters, and hence both the resident and flux concentrations are needed. The resident concentration describes solute particles in the total phase present at some point, while the flux concentration describes particles (in the mobile state) moving irrevocably past the control plane [25,37,39]. The two concentrations can differ by orders of magnitude (see for example Figure 4) and can be related quantitatively for sub-diffusive transport [43]. To directly obtain the flux concentration using the Lagrangian solver, we counted the number of particles that move irrevocably across the downstream control plane during a unit time (such as 1 year).
4.1 Solute snapshots

We first predict the snapshots for solute particles in each phase (mobile, immobile, and total) at the sampling time $t = 10$ yr for Scenario Fine-ML1 using the parameters in Table 2. The 1-d snapshots were created by taking the ensemble average of concentrations over the transverse direction. The predicted plumes (see the dashed lines in Figure 6a) capture the major sub-diffusive behavior simulated by the random walk code, including 1) the sequestration effect near the source [49], 2) the skewed snapshots, and 3) the mass partitioning between mobile and immobile phases. In particular, the simulated plume in the mobile phase moves faster (due to the channeling of solutes in the relatively high-permeability hydrofacies [49]) than the immobile mass, generating a positively skewed snapshot for particles in the total phase.

The TTLM model prediction, however, significantly underestimates the leading plume edge in all phases (Figure 6). The predicted peak concentration for mobile solute also moves slower than the Monte Carlo average. Possible causes of these differences between observations and predictions are explored below.

To check the feasibility of estimates of the three time-nonlocal parameters $\gamma$, $\lambda$ and $\beta$, we predict the evolution of mobile mass using the TTLM model (3b). The predicted mobile mass using either capacity coefficient $\beta_{Ari}$ or $\beta_{Mod}$ (see Table 2 for the meaning of each $\beta$) generally matches the observations (Figure 6b), no matter the magnitude of velocity and dispersion coefficient. These numerical tests confirm the analysis in Sec. 3, which shows that the three time-nonlocal parameters $\gamma$, $\beta$ and $\lambda$ control the time variation of mobile mass. Velocity $V$ and dispersion coefficient $D$ do not alter the mass partitioning between mobile and immobile phases, since they do not affect the transition probability of particles between mobile and immobile phases. Therefore, the predicted values of $\gamma$, $\lambda$ and $\beta$ tend to be reliable.

We then increase $V$ to fit the observed snapshot, by keeping all the other predicted parameters unchanged. Since we assume that the longitudinal dispersivity is a constant, the dispersion coefficient $D$ increases with an increase of $V$. The fitted snapshot matches the data much better, as shown by the solid lines in Figure 6a. Here $V$ is fitted by matching the snapshot peak, and $D$ is fitted by matching the expansion of plume around the peak.
The TTLM model snapshot with a constant dispersion coefficient $D$, however, underestimates the movement of the plume front (see Figure 6c,d). Results show that the best-fit $D$ for the TTLM model is space dependent (Table 3). With $V$ and $D$ as fitting parameters, the TTLM model solutions are similar to the Monte Carlo solute snapshots in all phases (Figure 7). The best-fit velocity (denoted as $V_{Fit}$) is slightly larger than $V_{Ari}$ and $V_{Mod}$, and the best-fit dispersion coefficient (denoted as $D_{Fit}$) increases linearly with the travel distance (note that linear functions for $D_{Fit}$ in Table 3 were selected for simplicity). The space-dependent $D_{Fit}$ implies the scale-effect of transport in space, and is consistent with the Fickian motion described by the TTLM model (3) in mobile time. We will discuss in Sec. 5 the possibility to estimate the scale-effect on dispersion using Lévy motion with a constant dispersion coefficient.

Results of the TTLM model evaluations for variable mean lengths show that the TTLM method with empirically derived parameters can provide a reasonable approximation of solute spreading under a range of scales of heterogeneity. Both $V$ and $D$ are treated
Table 3
The best-fit velocity and the space-dependent dispersion coefficient for each scenario. Note that the initial point source was injected at position \(x = 115\) m.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>(V_{Fit}) [m/yr]</th>
<th>(D_{Fit}) [m(^2)/yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine-ML0.5</td>
<td>14.9</td>
<td>(D(x) = 65 + 0.30(x - 115))</td>
</tr>
<tr>
<td>Fine-ML1</td>
<td>16.8</td>
<td>(D(x) = 70 + 0.35(x - 115))</td>
</tr>
<tr>
<td>Fine-ML2</td>
<td>16.5</td>
<td>(D(x) = 80 + 0.20(x - 115))</td>
</tr>
<tr>
<td>Coarse-ML0.25</td>
<td>12.8</td>
<td>(D(x) = 40 + 0.14(x - 115))</td>
</tr>
<tr>
<td>Coarse-ML1</td>
<td>21.9</td>
<td>(D(x) = 10 + 0.001(x - 115))</td>
</tr>
<tr>
<td>Coarse-ML4</td>
<td>21.5</td>
<td>(D(x) = 21.5 + 0.0001(x - 115))</td>
</tr>
</tbody>
</table>

as fitting parameters, as above. Figure 8 shows the snapshot for Scenario Fine-ML0.5 and Scenario Fine-ML2. With an increase of mean length of hydrofacies, more mass remains in the mobile phase (probably due to the thicker preferential flow paths), and the mobile plume separates from the immobile plume. The two effects can be captured by decreasing the capacity coefficient \(\beta\) in the TTLM model, as shown by (21).

Figure 9 shows the snapshot for Scenario Coarse-ML0.25 and Scenario Coarse-ML4.
Fig. 8. The Monte Carlo simulated snapshots (symbols) versus solutions of the TTLM model (3) (solid lines) for Scenario Fine-ML0.5 (the left column) and Scenario Fine-ML2 (the right column). The snapshot is at time 10 yrs ((a) and (c)) and 50 yrs ((b) and (d)). Note that the first snapshot (at 10 yrs) was used for parameter fit, and then the best-fit parameters were used to predict the other snapshot.

Similar to the behavior observed for the fine-grain dominated system, here the skewness of solute snapshots decreases with an increase of hydrofacies mean lengths (i.e., the skewness decreases from positive to negative). The decrease of skewness corresponds to a decrease of the capacity coefficient (as shown in Table 2) in the TTLM model. This is consistent with equation (19) for \( \beta \), which predicts that \( \beta \) decreases with an increase of \( R \), the hydrofacies mean length factor.

Solute transport in Scenario Coarse-ML4 is captured well using the TTLM model, even when all parameters are predicted directly from hydrogeological characteristics (Figure 9). Therefore, for the coarse-grain dominated alluvial system with thick and spatially connected hydrofacies, it is possible to predict directly the solute transport using the method developed above. The interconnected, high-permeability hydrofacies consist of preferential flow paths that may last for a relatively long distance, due to the dominant coarse-grained deposits. Solute particles therefore can transport for a relatively long distance along these preferential flow paths. Hence the arithmetic mean velocity is a good estimator of velocity when channel deposits are highly interconnected.

In contrast, different from the other scenarios, Scenario Coarse-ML0.25 (Figure 9) has a relatively small best-fit velocity and a relatively large best-fit dispersion coefficient (see
Fig. 9. The Monte Carlo simulated snapshots (symbols) versus solutions of the TTLM model (3) (solid lines) for Scenario Coarse-ML0.25 (left column) at time 10 yrs (a) and 50 yrs (b); and for Scenario Coarse-ML4 (right column) at time 10 yrs (c) and 50 yrs (d). The first snapshot (at 10 yrs) was used for parameter fit, and then the best-fit parameters were used to predict the other snapshot.

Table 3), although the other three time-nonlocal parameters are predicted reasonably well. This discrepancy is probably due to the short mean length of hydrofacies in this specific scenario. The short mean length of channels may result in tortuous preferential flow paths for solute particles, or transmission of solutes through lower conductivity materials. A percolation analysis of the realizations showed that the channels typically percolate through the entire model domain. The lower effective velocity indicates that the solute did not migrate directly downgradient via geologically interconnected channels. Therefore, the local velocity in high-permeability deposits may be greater than the mean velocity along the solute travel route. Further test of this hypothesis and the investigation of hydrological flow paths in interconnected high-conductivity networks are needed in a future study.

4.2 Breakthrough curves

For this experiment, we predict the solute BTCs using the TTLM model (3b), where the three time-nonlocal parameters (γ, λ and β) are predicted and the two transport parameters (V and D) are fitted using the solute snapshots in Sec. 4.1. This approach
still requires parameter fitting of $V$ and $D$, so it does not allow exact prediction of all parameters.

Results show that model predictions generally match the observed BTCs (Figure 10). For alluvial systems dominated by fine-grained materials, each of the five model parameters is generally able to capture the relevant characteristic of solute transport. First, the scale index $\gamma$ predicted by (16) captures the power-law slope of BTCs, especially for scenarios with a wide distribution of $P(Z)$ (such as Scenario Fine-ML2 shown by Figure 10a). In particular, for the fine-grain dominated alluvial settings, the power-law portion of $P(Z)$ contains an exponent ($m = -1.12$, see Figure 2a) larger than that for the coarse-grain dominated alluvial settings (which is $m = -1.38$, see Figure 2b). These differences are manifested in the resulting BTCs: the late-time BTC for Scenario Fine-ML2 is slightly heavier than that of Scenario Coarse-ML4. This confirms the relationship between $m$ and $\gamma$ as predicted by equation (16).

Second, the truncation parameter $\lambda$ generally captures the transition from power-law to exponential decline for the BTC at late times. With a decrease of hydrofacies mean length, the thickness distribution $P(Z)$ shrinks, resulting in a larger $\lambda$ (based on the estimation formula (17)). A larger $\lambda$ describes an earlier transition from power-law to exponential decline for solute concentrations, as illustrated by Figure 10.

Third, the capacity coefficient $\beta$ (combined with $\gamma$ and $\lambda$) can capture the solute mass remaining in the mobile phases, since the simulated flux concentration matches the Monte Carlo observations (Figure 10). Further validations using the moment data are shown below.

Finally, the velocity obtained from the snapshots can characterize the mean drift of solute particles. The best-fit space-dependent dispersion coefficient using snapshots also generally predicts the real dispersion, expressed by both the early arrivals of BTCs and the peak concentration.

The same conclusions were found for alluvial systems dominated by coarse-grained materials, where the BTCs are not shown here for simplicity.
Fig. 10. Prediction using the TTLM model (3) (red line) of the solute breakthrough for Scenarios Fine-ML2 (a), Fine-ML1 (c), and Fine-ML0.5 (e) shown in Table 2. (b), (d), and (f) are the linear-linear plot (to show the peak) of (a), (c), and (e), respectively. The symbols represent the “real” BTC (i.e., the Monte Carlo result). The dashed line denotes the prediction without truncation (using the Fast Fourier Transform approach, see Baeumer et al. [1]). The Gaussian solution is also shown for comparison.

4.3 Plume spatial moments

Figure 11 shows the predicted spatial moments up to the fourth order for plumes in different phases. Different orders of spatial moments calculated by the TTLM model are affected by different model parameters. For example, the mobile mass decline in time is controlled by the three time-nonlocal parameters ($\gamma$, $\lambda$ and $\beta$) [48]. Therefore the combination of $\gamma$, $\lambda$ and $\beta$ can be evaluated based on the predictions of the mobile mass. The mean displacement of solute particles is controlled by the time-nonlocal...
parameters as well as one more parameter $V$, because $V$ affects the drift for all mobile particles. Therefore, after the three time-nonlocal parameters are validated using the mobile mass data, the observed mean displacement of solutes can be used to check the feasibility of the best-fit velocity (note that the velocity was fitted using the solute snapshot at a specific time, as shown in Sec. 4.1). In addition, the variance of solute plume is controlled by the time-nonlocal parameters and the velocity, and by one more (and the last) parameter, dispersion coefficient $D$. Hence the variance data can be used to check the value of $D$. After all the five model parameters are validated, the TTLM model predicts the two higher order moments, skewness and kurtosis. As shown by Figure 11, the TTLM model generally captures the trend of the observed moments up to the fourth order.

The TTLM model also characterizes non-Fickian transport behavior for all scenarios. First, the mobile mass decreases quickly at the beginning, and then gradually approaches an asymptote (Figure 11a, f). Second, the mean displacement increases slower than linear in time (Figure 11b, g), exhibiting the typical behavior of sub-diffusion. Third, the variance grows faster than linear in time (Figure 11c, h), representing the property of super-diffusion. This is due to the stretching of particle plumes downstream: the mobile particles move faster along the high-permeable, non-floodplain deposits, while the trailing tail of plumes is trapped by the relatively immobile zones in low-permeability blocks near the source [49]. Note, however, we still call the transport “sub-diffusive”, due to the apparent trapping mechanism. In the TTLM model, $\beta$ controls the quantity of particles remaining around the source, and the velocity affects the downstream stretching of particles. Figure 11 shows that the TTLM model with parameters derived from hydrogeological properties can efficiently capture this “sub-diffusive” transport behavior.

The TTLM model also accurately predicts particle transport in different phases, especially for the scenario with a large mean length for hydrofacies. For example, as shown by Figure 11g, mobile mass moves faster than its immobile counterpart. On the other hand, the immobile plume has a larger variance (Figure 11h), due to the strong effect of “sequestration” [49]. In addition, the snapshot for particles in the mobile phase has a negative skewness (Figure 11i), due to the fast motion of most solute particles along the preferential flow paths. The channeling flow also causes the positive kurtosis for mobile particles (Figure 11j). The accurate representation of solute dynamics in all phases by
Fig. 11. The predicted moments (lines) using the TTLM model (3) versus the Monte Carlo results (symbols) for Scenario Coarse-ML0.25 (left column) and Coarse-ML4 (right column). (a) and (f) - the decline of mobile mass; (b) and (g) - Mean displacement; (c) and (h) - Variance; (d) and (i) - Skewness; and (e) and (j) - Kurtosis. The dashed line in (a) and (f) represents the asymptotic mass in the mobile phase, as expressed by $1/(1 + \beta_0) = 1/(1 + \beta \gamma \lambda^{-1})$. 

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the TTLM model indicates that predictions are accurate of the three time-nonlocal model parameters from hydrogeological properties.

5 Discussion

This section discusses limitations of the prediction scheme developed above, and challenges in predicting velocity and dispersion coefficients.

5.1 Limitations of the prediction scheme

There are two major limitations of the prediction scheme for time-nonlocal transport parameters. First, real-world transport exhibits not only subdiffusion due to absorptive or diffusive mass transfer, but also superdiffusion due to fast displacement of solute particles along for example specific preferential flow paths in alluvial systems [3,47]. Here we conduct a preliminary test to check the feasibility of the above parameter predictions for mixed sub- and super-diffusion. The other motivation of this test is the scale-dependent dispersion coefficient $D(x)$: if the transport model can be improved to replace the variable $D(x)$ by a constant $D$, then is it possible to develop an efficient scheme to predict this constant $D$? Applications in Sec. 4 show that the best-fit dispersion coefficient for some scenarios increases with the travel distance. The scale-dependent transport has been efficiently captured by the space-fractional ADE model, which is a space nonlocal transport model and describes superdiffusion. Here the “space nonlocal” means that the concentration change at the current location depends on concentrations at other locations [47]. This motivates us to add the space nonlocality into the TTLM model.

If we replace Brownian motion in the mobile phase by Lévy motion, the TTLM model
Fig. 12. The modeled snapshot using the generalized TTLM model (23) (lines) versus the Monte Carlo results (symbols) for Scenario Fine-ML1 (a) and Scenario Fine-ML2 (b), respectively. In (a), the best-fit $\alpha^* = 1.82$ and $V = 16.8 \text{ m/yr}$. In (b), the best-fit $\alpha^* = 1.70$ and $V = 16.5 \text{ m/yr}$. The dispersivity remains as a constant (5 m) in the two examples.

(3) is replaced by its generalization:

$$\left[ \frac{\partial}{\partial t} + \beta e^{-\lambda t} \frac{\partial^\gamma e^{\lambda t}}{\partial t^\gamma} - \beta \lambda \gamma \right] C_T = -V \frac{\partial C_T}{\partial x} + \frac{\partial^{\alpha^*-1}}{\partial x^{\alpha^*-1}} \left[ D \frac{\partial C_T}{\partial x} \right] + \beta C_0 \int_t^\infty e^{-\lambda \tau} \frac{\tau^{-\gamma-1}}{\Gamma(-\gamma)} d\tau$$  \hspace{1cm} (23a)

$$\left[ \frac{\partial}{\partial t} + \beta e^{-\lambda t} \frac{\partial^\gamma e^{\lambda t}}{\partial t^\gamma} - \beta \lambda \gamma \right] C_M = -V \frac{\partial C_M}{\partial x} + \frac{\partial^{\alpha^*-1}}{\partial x^{\alpha^*-1}} \left[ D \frac{\partial C_M}{\partial x} \right] ,$$  \hspace{1cm} (23b)

where $1 < \alpha^* \leq 2$ is the order of the Riemann-Liouville fractional derivative in space. When $\alpha^* = 2$, (23) reduces to (3).

Figure 12 shows the applicability of the generalized TTLM model (23) in capturing the scale-dependent dispersion observed for both Scenario Fine-ML1 and Scenario Fine-ML2. Model (23) does capture the leading edge of plumes, even if a constant dispersion coefficient is used.

The above preliminary application shows that the time-nonlocal parameters remain unchanged when the TTLM model extends to super-diffusive transport. The space nonlocality may only affect the particle jump size, and it does not alter particle waiting times. Hence the time-nonlocal parameters estimated above may be still valid when the model extends to super-diffusion. In addition, the scale-dependent Brownian dispersion in space may be described by the Lévy motion with a constant dispersion coefficient.

The disadvantage of applying model (23), however, is the additional parameter $\alpha^*$ that may be difficult to predict from hydrogeological properties [47]. Further tests of model
and the predictability of $\alpha^*$ are therefore needed in a future study. 

The second limitation is that the above prediction scheme for time-nonlocal parameters is built for mobile-immobile like alluvial settings with a large permeability contrast between floodplain and non-floodplain hydrofacies. If the geologic medium has a much smaller permeability gap and does not lead to a strong diffusive mass transfer process, the above prediction is no longer valid. In this case, one may reduce the number of unknown parameters by assuming the index $\gamma \approx 1$ (i.e., without the immobile zone) and predicting only the retardation coefficient $1 + \beta$. In addition, this study considers steady-state flow and the point-source injection mode. Whether the prediction scheme is valid for transient flow and other injection conditions (including the initial source dimension and the injection modes) remain to be shown.

5.2 Challenges in predicting velocity and dispersion coefficient

The strong local variation of hydraulic conductivity and head gradient in a typical alluvial aquifer creates challenges for the determination of velocity, $V$, in the field. The sensitivity of the estimated $V$ to the sample location along the flow path remains obscure. If the flow path consists of interconnected high-permeability sediments, then the local velocity may decrease near the terminus of the preferential path. If the travel distance is much larger than the mean length of hydrofacies in a stationary medium, the effective velocity may become stable [44]. It is also noteworthy that the velocity $V$ affects the plume center ($\approx Vt/(1 + \beta \gamma \lambda^{-1})$) and variance ($\approx 2Dt/(1 + \beta \gamma \lambda^{-1}) + \beta\gamma(1 - \gamma)\lambda^{-2}V^2t/(1 + \beta \gamma \lambda^{-1})^3$) at late times [48], and hence the estimation of $V$ and $D$ affects the prediction of plume spatial distribution.

This study also implies that the best-fit velocity using the TTLM model (3) can be on the same order of $V_{Ari}$ and $V_{Mod}$. A similar conclusion was found for several field applications. For example, at the well-known MADE test site (an alluvial depositional system), the best-fit $V (=0.11 \text{ m/d})$ using the fADE model is close to the estimated velocity in the field ($0.12 \sim 0.36 \text{ m/d}$) [3]. At Cape cod, Massachusetts, the well-known natural gradient tracer test in much more homogeneous glaciofluvial deposits (where the measured hydraulic conductivity for different deposits fluctuates by one order of magnitude and the estimated natural logarithm variance of conductivity is as low as
0.26) can be interpreted by the fADE with a best-fit velocity (0.43 m/d) [47] which is in the range of field measured ground water velocity (0.39 ∼ 0.51 m/d) [16]. Therefore, the average of field measured velocities might provide an initial estimation for $V$, although we cannot predict the exact value of $V$ without curve-fitting at present.

The reason that the velocity is not as predictable as the time non-local parameters might be related to the complexities of the velocity distributions in the heterogeneous alluvial settings. Our Monte Carlo simulations show that the majority of advective transport occurs along interconnected pathway of non-floodplain hydrofacies, especially the channel deposits. The exact location and extent of the interconnected channel network vary among the realizations [44]. Therefore, even if the spatial statistics and general hydrology of the aquifer are known, there remains considerable uncertainty in the effective velocity. However, this is not a problem in predicting the late-time tail of BTC (or the time-nonlocal parameters), because the late-time tail of BTC is not strongly affected by the exact location of each immobile zone, but rather is controlled by the time spent in aquitard layers of variable thickness. We will further explore these issues in a future study.

The constant, effective dispersion coefficient $D$ is difficult to predict because of the well-known scale effect of solute transport, although the time-nonlocal term is introduced in the TTLM model (3) to account for the random waiting process in particle dynamics. A challenging question is: how much can the time-nonlocal term compensate for the scale effect “missed” by a constant $D$? Experiments are needed to address this fundamental question, before one quantifies the strong influence of medium architecture on dispersion.

6 Conclusions

This study tests the capability of a stochastic transport model with non-local parameters derived from observable aquifer characteristics in predicting solute dynamics in regional-scale alluvial systems. The interconnected aquifers and surrounding aquitards of alluvial systems result in transient sub-diffusion that can not be efficiently captured by classical Fickian-based transport models. A temporally tempered Lévy motion model is applied to predict non-Fickian solute transport. The final goal is to bridge the
gap between model parameters and measurable properties of medium heterogeneity.
The analysis conducted above leads to the following four primary conclusions.

1) The TTLM model proposed by Meerschaert et al. [32] is applicable for non-Fickian transport observed in a wide spectrum of finitely-correlated alluvial systems. The model characterizes the exponentially truncated Lévy process in time and logically extends the standard time-fractional ADE model by capturing the upper truncated power-law distribution for the particle waiting times. The finite thickness of diffusion-limited layers in alluvial settings, which is the main cause of pre-asymptotic transport, results in an exponentially truncated waiting time distribution for solute particles visiting those layers.

2) Semi-analytical or empirical predictions can be built for the three time-nonlocal parameters in the TTLM model, including the scale index $\gamma$, capacity coefficient $\beta$ and truncation parameter $\lambda$ that control the time for particles spent in the immobile phase. The space-independent parameters $\gamma$ and $\lambda$ can be estimated given the volume fraction of low-permeability deposits classified by thickness, $P(Z)$. In field studies, $P(Z)$ can potentially be estimated from detailed well logs, outcrops, or geophysical surveys that characterize the dimensions of the low-conductivity layers. This provides a practical way to link specific model parameters directly to medium heterogeneity, and hence may help to limit the uncertainty of the fractional-derivative models in simulating solute transport through complex alluvial settings.

3) The effective velocity and dispersion coefficient in the TTLM model (3) could not be predicted accurately based on measurable hydrofacies properties. Numerical tests show that when the medium is dominated by fine-grained deposits, the best-fit velocity $V$ can be slightly larger than the arithmetic mean of local velocities, due probably to the enhanced channeling effect of flow in high-permeability hydrofacies surrounded by the pervasive, relatively low-permeability hydrofacies. The corresponding dispersion coefficient $D$ increases with the travel distance, probably due to the scale effect of transport. Only for the coarse-grain dominated alluvial systems with interconnected hydrofacies, is $V$ close to the arithmetic mean velocity. Dispersion coefficient in this specific case can also be treated as a constant. How to accurately predict $V$ and $D$ for a general alluvial system remains unresolved. It is noteworthy that, even if we can not predict $V$ and $D$ directly from aquifer properties, we can still approximate the power-
law slope and the general shape of the BTC because these properties are controlled by the time-nonlocal, predictable parameters.

4) The detailed comparison between the MRMT model and the TTLM model helps to predict the parameters used in the TTLM model. Note, however, that we select the TTLM model in this study and suggest it for future applications, because it contains fewer parameters than most other time-nonlocal transport models, and it can be extended conveniently to capture the space-nonlocal transport process.
This appendix describes numerical methods to approximate the generalized TTLM model (23). Numerical approaches are implemented because there is no analytical solution. Both Eulerian and Lagrangian methods are developed, for cross verification.

### A.1 Eulerian solution

The TTLM model (23b) can be discretized using the implicit finite difference scheme:

\[
\frac{C_i^{n+1} - C_i^n}{\Delta t} + \frac{\beta e^{-\lambda t_n+k}}{(\Delta t)^\gamma} \sum_{k=0}^{k=n+1} \left[ f_k e^{\lambda t_n-(k-1)} C_i^{n-(k-1)} \right] - \beta \lambda C_i^{n+1} = -V \frac{C_i^{n+1}}{\Delta x} \sum_{k=i}^{i+1} \left[ D_j \frac{C_j^{n+1} - C_j^{n+1}}{\Delta x} \right],
\]

where \( f_k \) and \( g_k \) denote the Grünwald weight for the \( \gamma \)-order and \( (\alpha^*-1) \)-order fractional derivative, respectively; and \( \Delta t \) and \( \Delta x \) are the step size in time and space, respectively.

Repeating (A.1) for each node, one can get the final equations:

\[
[F] C^{n+1} = C^n + \Delta t S^{n+1},
\]

where \([F]\) is a \((K+1) \times (K+1)\) coefficient matrix; \( C^{n+1}, C^n \), and \( S^{n+1} \) are \((K+1)\) vectors; and \( K + 1 \) denotes the total number of nodes in space.

The entry in \([F]\) is:

\[
F_{i,j} = \begin{cases} 
0, & \text{when } j > i + 1 \\
-\frac{\Delta t}{(\Delta x)^{\alpha}} D_i g_0, & \text{when } j = i + 1 \\
1 + \frac{1}{(\Delta t)^{\gamma-1}} - \Delta t \beta \lambda + V \frac{\Delta t}{(\Delta x)^{\alpha}} D_i g_0 - \frac{\Delta t}{(\Delta x)^{\alpha}} D_i g_1, & \text{when } j = i \\
-\frac{\Delta t}{\Delta x} D_i g_1 - \frac{\Delta t}{(\Delta x)^{\alpha}} D_i g_2, & \text{when } j = i - 1 \\
-\frac{\Delta t}{(\Delta x)^{\alpha}} D_j g_i - \frac{\Delta t}{(\Delta x)^{\alpha}} D_j g_{i-j}, & \text{when } j < i - 1 
\end{cases}
\]
where $F_{0,0} = 1; F_{0,j} = 0$ for $j = 1, \ldots, K; F_{K,K} = 1; F_{K,K-1} = -1; \text{and } F_{K,j} = 0$ for $j = 0, \ldots, K - 2$.

The Greschgorin theorem [22] is used here to explore the stability of the above finite difference scheme. The eigenvalues of the matrix $[F]$ are in the disks centered at $F_{i,i}$ with radius $r_i = \sum_{k=0, k\neq i}^{K} F_{i,k}$. Given the entry in $[F]$ listed above, we find that

\[ F_{i,i} - r_i = 1 + \beta \left( \frac{1}{(\Delta t)^{\gamma-1}} - \Delta t \beta \lambda^\gamma \right). \quad (A.3) \]

If the time step is small enough
\[ \Delta t < \frac{1}{\lambda}, \quad (A.4) \]
we have
\[ F_{i,i} - r_i > 1. \quad (A.5) \]

On the other hand, we find that
\[ F_{i,i} + r_i = 1 + \beta \left( \frac{1}{(\Delta t)^{\gamma-1}} - \Delta t \beta \lambda^\gamma + 2V \frac{\Delta t}{\Delta x} + 2D_i \frac{\Delta t}{(\Delta x)^{\alpha^*}} g_0 - 2D_{i-1} \frac{\Delta t}{(\Delta x)^{\alpha^*}} g_1 \right). \quad (A.6) \]

In (A.6), the Grünwald weight $g_0 = 1$ and $g_1 = -(\alpha^* - 1) < 0$. Hence if the inequality (A.4) is valid, we always have
\[ F_{i,i} + r_i > 1. \quad (A.7) \]

(A.5) and (A.7) show that the magnitude of eigenvalues of $[F]$ are equal or larger than 1. Hence the spectral radius of the inverse matrix $[F]^{-1}$ is equal to or less than 1, and any error in $C^{n+1}$ is not magnified. Therefore the above finite difference scheme is conditionally stable, with the stability criterion of (A.4).

A similar finite difference scheme can be built for the TTLM model (23a) for the total (mobile plus immobile) phase.

A.2 Lagrangian solution

The Lagrangian approach tracks random-walking particles whose dynamics are governed by the Langevin version of the TTLM model (23). The following two-step algo-
rithm describes the displacement and the subsequent rest for each particle:

\[ X(t_{\text{now}} + dt) = X(t_{\text{now}}) + Vdt + D^{1/\alpha^*}dL_{\alpha^*}(dt) + \Theta \left| \frac{\partial D}{\partial x} \right|^{1/(\alpha^*-1)}dL_{\alpha^*-1}(dt), \quad (A.8a) \]

\[ t_{\text{next}} = t_{\text{now}} + dt + \omega, \quad (A.8b) \]

where the sign function \( \Theta = 1 \) if \( \frac{\partial D}{\partial x} > 0 \); \( \Theta = -1 \) if \( \frac{\partial D}{\partial x} < 0 \); and \( \Theta = 0 \) if \( \frac{\partial D}{\partial x} = 0 \). \( dL_{\alpha^*}(dt) \) and \( dL_{\alpha^*-1}(dt) \) denote random noises underlying an \( \alpha^* \)-order and \( (\alpha^*-1) \)-order Lévy motion, respectively. The \( dt + \omega \) term denotes the total time for the particle to finish one jump and the following rest, where \( dt \) denotes the operational time and \( \omega \) is the tempered Lévy stable random variable. \( \omega \) can be approximated using the exponential rejection method \[2\].

Numerical random walk methods for the solution of the MRMT or CTRW equations were also developed previously. For example, Dentz et al. \[12\] calculated the CTRW model using a two-step random walk in space and time, where the jump in space or time contains a drift and a random increment (see their equations (13) and (14)). Le Borgne and Gouze \[28\] considered a time increment stochastically drawn from a waiting time distribution (see their equation (8)). Here the discrete Langevin equation (A.8) is slightly different because it considers also super-diffusion in space which can be extended to a vector process with non-orthogonal dispersion \[45\].

It is noteworthy that the term \( dt + \omega \) is the waiting time process discussed in \[45\]. Given the operational time \( dt \), the corresponding real time \( t_{\text{next}} \) can be calculated by (A.8b), which is a Markov process. Since \( 0 < \gamma < 1 \), \( \omega \) is always positive and \( t_{\text{next}} \) increases monotonically, resulting in a computationally efficient solver.

When \( \alpha^* = 2 \) (i.e., the diffusion is Fickian), the jump size (A.8a) reduces to the Markov process used for Fickian diffusion with drift (see for example, \[27\])

\[ X(t_{\text{now}} + dt) = X(t_{\text{now}}) + \left[ V + \Theta \left| \frac{\partial D}{\partial x} \right| \right] dt + \varpi \sqrt{2Ddt}, \quad (A.9) \]

where \( \varpi \) is a normally distributed random variable with zero mean and unit variance.

The above Eulerian and Lagrangian solvers have been tested and compared extensively. One example is shown in Figure A.1, where the concentration in the immobile phase
Fig. A.1. Numerical solution of the generalized TTLM model (23) for solute snapshots ((a) and (c), at time $t = 50$) and concentrations ((b) and (d)) using the Lagrangian method (symbols) versus the implicit Eulerian finite difference method (lines). In the case shown in (a) and (b), the parameters are: $\gamma = 0.5$, $\beta = 0.05$, $\lambda = 1 \times 10^{-5}$, $\alpha^* = 1.9$, $V = 1$, and $D(x) = 0.1 + 0.02x$. In (c) and (d), model parameters are: $\gamma = 0.6$, $\beta = 0.02$, $\lambda = 1 \times 10^{-3}$, $\alpha^* = 1.7$, $V = 2$, and $D(x) = 0.2 + 0.05x$. In all cases, the instantaneous point source is located at $x = 50$, and the control plane (for (b) and (d)) is located at $x = 60$.

is simply the difference between the total and the mobile concentrations.

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