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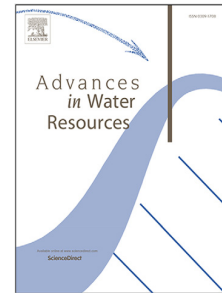
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# Upscaled models for time-varying solute transport: Transient spatial-Markov dynamics

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June 14, 2022

## Abstract

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Correlated velocity models (CVMs) have proven themselves to be effective tools for describing a wide range of solute transport behaviors in heterogeneous porous media. In particular, spatial Markov models (SMMs) are a class of CVMs where subsequent Lagrangian velocities along transport trajectories depend only on the current velocity, and not on past history. Such models provide a powerful tool for modeling transport in terms of a limited number of flow properties, such as the Eulerian point distribution of (flow) velocities, tortuosity, and the spatial scale of persistence of velocities. However, to date, all SMM modeling frameworks and applications have assumed that the underlying flow is steady-state. In this work, we extend SMMs to the case of time-varying flows. We propose, compare, and validate alternative numerical implementations, and we determine conditions for validity and efficiency based on standard physical quantities used to describe flow and transport at the Darcy scale. The models require additional information relative to a steady-state velocity SMM and we discuss the conditions under which this extra burden is warranted. We also provide clear, deterministic tests for the validity of the transient SMM, termed the “slow variation” and “fast propagation” criteria, which offer clear guidance on when transient, upscaled models are reasonable to employ. Our work forms the basis of a new framework allowing for the application of efficient upscaled models of transport to realistic transient flow conditions.

## 1 Introduction

The general aim of upscaled models of solute transport in porous media is to capture the impacts of inhomogeneities without explicitly representing the mechanisms that drive transport and/or their spatiotemporal variability (Dentz et al., 2020; Sund et al., 2019). The philosophy behind upscaled methods revolves around the notion that the computational and data-support burdens imposed by distributed models incur significant computational costs and lend sufficient uncertainty to predictions such that distributed models are not necessarily practical in every circumstance. A reduced-complexity strategy can be advantageous in many such cases. One of the promising upscaled transport frameworks is that of the continuous time random walk (CTRW), where the transition times between steps are modeled as a random variable (Berkowitz et al., 2006; Scher and Lax, 1973; Scher and Montroll, 1975). The model for the spatial increments and associated transition times distinguishes different flavors of CTRWs. A contemporary group of methods that have demonstrated broad applicability are correlated velocity models (CVMs), which in particular employ a fixed-length spatial step discretization.

In the conceptual model behind a CVM, travel times between adjacent steps in a CTRW are not independent and identically distributed events, due to correlations in the velocity field. Consider a Lagrangian particle moving through a natural system whose velocity is sampled at fixed spatial increments along its streamline. Natural media are often characterized by well-defined characteristic lengths, such as the mean lengths of hydrofacies (Carle and Fogg, 1996; Lee et al., 2007; Weissmann et al., 1999), and this means that a Lagrangian particle moving quickly along a preferential flow path is more likely to continue moving quickly than it is to abruptly slow down, though both options are possibilities. As the distance between sample locations increases, the Lagrangian (i.e., particle trajectory) velocity correlations decay proportionate to the spatial scales of the geological formations (Sherman et al., 2020), and the transitions eventually become uncorrelated. Models of the transition time to complete the “next” step in the random walk can leverage these correlations by conditioning the transition time based on the most recent step. This is precisely what is done in a Spatial Markov Model (SMM) (Dentz et al., 2016; Le Borgne et al., 2008a,b), where transitions are conditioned on the “previous” step only. An SMM can be parameterized in terms of a small number of properties with clear physical meaning, such as Eulerian velocity statistics, tortuosity, and spatial correlation lengths of Lagrangian velocities, which are related to the characteristic spatial scales of the hydrogeology (Aquino and Le Borgne, 2021; Dentz et al., 2016; Le Borgne et al., 2008). Although SMMs are Markovian in terms of the number of steps taken by a particle, and therefore in space due to the fixed

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4 49 spatial increments, the resulting temporal dynamics may ultimately be non-Markovian as a result of  
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6 50 broadly-distributed waiting times (De Anna et al., 2013; Holzner et al., 2015; Kang et al., 2014; Meyer  
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8 51 and Saggini, 2016; Meyer and Tchelepi, 2010). The flexibility of the SMM allows complex transport  
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10 52 phenomena to be modeled within its framework, resulting in significant conceptual and computational  
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12 53 simplifications when compared to other CTRWs that otherwise require explicit modeling of nonlocal  
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14 54 transport mechanisms, i.e., arbitrarily far particle jumps or dependency on long-term trajectory his-  
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16 55 tory (Berkowitz et al., 2006; Klages et al., 2008; Meerschaert and Sikorskii, 2012; Metzler and Klafter,  
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18 56 2004). Applications of SMMs to date have been diverse with compelling results obtained across a  
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20 57 diverse spectrum of situations (Bolster et al., 2014; Comolli et al., 2019; Dentz et al., 2020; Hakoun  
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22 58 et al., 2019; Kang et al., 2011; Puyguiraud et al., 2019a,b, 2021; Sherman et al., 2017, 2019; Sund  
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24 59 et al., 2015a,b, 2017; Wright et al., 2019). However, one of the limitations of all SMM applications to  
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26 60 date is that the transitions have been exclusively assumed to be stationary in both space and time,  
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28 61 even in the case of multi-continuum formulations (Engdahl and Bolster, 2020; Kim and Kang, 2020).

27 62 The assumption of spatial stationarity often makes sense in the context of the linkages between  
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29 63 SMM transitions and hydrogeologic correlations, and many studies have shown that stationary up-  
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31 64 scaled models are effective in certain heterogeneous media (Hakoun et al., 2019; Puyguiraud et al.,  
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33 65 2019a). Allowing for spatial non-stationarities is not a particularly difficult issue to address, at least  
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35 66 conceptually, because one could simply apply a different correlation model at different positions along  
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37 67 the path of a Lagrangian particle (Aquino and Le Borgne, 2021). These correlation changes could  
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39 68 be defined to coincide with known changes in the hydrogeology, so the only implementation barrier is  
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41 69 developing different models of correlations for the different regions and deciding on the cutoffs for each.  
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43 70 To do so may be time-consuming and require additional data, but it is not technically challenging, nor  
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45 71 is it beyond the capabilities of current SMM frameworks.

45 72 The issue of temporal non-stationarities (transience) is significantly more involved because CVM  
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47 73 formulations are based on connections between geological structure and spatial correlations. All work  
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49 74 on CVMs has employed steady-state velocity fields, and it is unclear if such correlations between  
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51 75 structure and velocity remain when the flow field varies in time. In reality, flow paths can change  
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53 76 significantly due to transience, especially when flow is driven by spatially-distributed recharge or in  
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55 77 unconfined settings (Engdahl, 2017). Transience can also impart non-uniqueness when an aggregated  
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57 78 transport metric like a breakthrough curve is used. For example, two particles entering the same  
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59 79 point of a distributed velocity field at two different times could take two different paths (drastically  
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61 80 so in the case of variably-saturated flows, Engdahl and Bolster, 2020). Similarly, different particles

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4 81 entering at different locations may ultimately have similar travel times to reach a fixed monitoring  
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6 82 point because of transient changes in the flow field. These cases, and many more, would immediately  
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8 83 invalidate assumptions of even weak stationarity (i.e., stationarity of increments), which would seem  
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10 84 to deal a crippling blow to the conceptual underpinnings of all the current CVMs. One option to deal  
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12 85 with these issues would be to relegate CVMs to cases of strict stationarity where transient effects are  
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14 86 sufficiently averaged out. However, our perspective is that doing so would be unnecessarily limiting,  
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16 87 because a more careful inspection of SMMs suggests that they can be adapted to accommodate at  
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18 88 least some transient velocity fields if some care is taken. At a minimum, an upscaled representation  
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20 89 of these transient processes should (i) be conditional to the “clock time” at which a particle entered  
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22 90 the flow field, and (ii) somehow account for the temporal changes in upscaled velocity distributions,  
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24 91 correlations, or both. As with any upscaled model, some simplifying assumptions are necessary, but  
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26 92 in this case we will show that conditions for validity and numerical efficiency can be posed in terms  
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28 93 of the typical physical parameters used to describe flow and transport in porous media at the Darcy  
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30 94 scale.

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32 95 The central questions addressed in this article are how to generalize (correlated) CTRWs to the  
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34 96 case of transient velocities, and what conditions are necessary for these generalizations to be valid  
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36 97 and practical. The motivation is to preserve the theoretical and computational benefits of SMMs  
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38 98 when the underlying flow field is time-dependent. Several options of varying complexity are evaluated  
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40 99 to accomplish this goal, and we consider their benefits and pitfalls in the context of analytic and  
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42 100 numerically-defined transient velocity fields. We start by reviewing the basic concepts of the SMM and  
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44 101 assessing its limitations regarding transient flow fields. Three approaches to accommodate transience  
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46 102 are then developed, and we show that two of these are sufficiently robust for general applications.  
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48 103 Specific criteria are developed for the validity of the transient SMM. The approach requires no further  
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50 104 specific assumptions about the underlying flow field, but we focus here on flow through porous media at  
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52 105 the Darcy (aquifer) scale. We validate our results against numerical simulations using both analytical  
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54 106 and realistic flow fields where transience is induced by time-varying (periodic) boundary conditions. In  
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56 107 the interest of compactness, the concepts and examples are demonstrated using a Bernoulli relaxation  
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58 108 model for the Markov velocity process (Dentz et al., 2016), so we close with a discussion of how the  
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60 109 approach can be generalized to other forms of transient CVMs. Collectively, the results advance the  
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62 110 capabilities of CVMs to include transience and offer clear guidance regarding when these models would  
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64 111 be appropriate and accurate.  
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## 2 Spatial-Markov model

SMMs are one of many CVMs that conceptualize (advective) transport in terms of Lagrangian particle trajectories, whereby a solute mass is discretized onto the particles (Sherman et al., 2020). Trajectories are usually modeled as a succession of steps of fixed length  $\Delta s$  along the streamlines of a flow and each step has a constant velocity, but the velocities may change as the particle completes successive steps. The basic concept is that the transition time (i.e., the step length divided by the velocity) distribution accounts for the heterogeneity in a flow field without explicitly modeling it, such that transport follows a stochastic-convective ensemble along streamlines. The step length corresponds to a choice of discretization of Lagrangian particle trajectories and the description converges to a continuum process in the limit of small  $\Delta s \rightarrow 0$  (i.e., becomes independent of the discretization when it is sufficiently fine, as is expected of a properly-discretized model). Particle positions after  $k$  steps along a streamline (particle path) are denoted  $X_k$  with the corresponding times  $T_k$  to complete the  $k$ th step obey the stochastic recursion relations (Dentz et al., 2016)

$$X_{k+1} = X_k + \frac{\Delta s}{\chi}, \quad T_{k+1} = T_k + \frac{\Delta s}{V_k}, \quad (1)$$

where  $V_k$  is the velocity magnitude during the  $k$ th step, which is constant throughout the step. Typically, the tortuosity  $\chi$  is approximated by the average tortuosity, which is computed as the average of the Eulerian velocity magnitude divided by the average of its projection along the mean flow direction (Koponen et al., 1996),

$$\chi = \frac{\bar{v}}{\langle \mathbf{v} \cdot \hat{\mathbf{x}} \rangle}. \quad (2)$$

Here,  $\mathbf{v}$  is the Eulerian velocity vector,  $\hat{\mathbf{x}}$  is the unit vector along the mean flow direction, and  $\langle \cdot \rangle$  denotes the average over space. The numerator represents the average of the Eulerian velocity magnitude,  $\bar{v} = \langle |\mathbf{v}| \rangle$ , so that  $\chi \geq 1$ . The initial time and position for each particle are often taken as  $T_0 = 0$  and  $X_0 = 0$ , respectively (though nonzero positions and times are permissible), and the initial velocities  $V_0$  are distributed according to the initial condition at this time.

The key ingredient of a spatial-Markov model is that the velocities  $V_k$ , seen as a function of  $k$ , form a Markov chain. The Markov property means that the probability of the next step having velocity  $V_{k+1}$  is conditional only on the most recent step's velocity  $V_k$ , and not on past history through earlier velocities. Under strict stationarity of the underlying flow field, the corresponding transition probabilities, given the current velocity, are constant in both space and time. Discretizing velocities

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4 into classes, such that class  $i$  comprises velocities between  $b_i$  and  $b_{i+1}$  and has width  $\Delta v_i = b_{i+1} - b_i$ , the  
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6 midpoint velocity  $v_i = (b_{i+1} + b_i)/2$  is associated with class  $i$ . The velocity process is then characterized  
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8 by the probabilities  $r_{ij}$  of transitioning to class  $i$  given that the current velocity is in class  $j$ .

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10 In order for the velocities to correspond to a spatial-Markov process, the probability of transitioning  
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12 to a different class must be proportional to the step length  $\Delta s$ , so that, for a given velocity, the spatial  
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14 rate of transition (transition probability per unit distance) is constant and the transition probability  
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16 decays exponentially with the step length (Van Kampen, 1992). The overall persistence of velocities is  
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18 characterized by the correlation length  $\ell_c$  of velocity magnitudes along streamlines, which at the Darcy  
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20 scale is typically of the same order as the scale of spatial variability of permeability (Hakoun et al.,  
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22 2019). Thus, taking into account that  $\sum_i r_{ij} = 1$  for all classes  $j$  to conserve probability (a transition  
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24 from any given velocity class  $j$  must end at *some* velocity class  $i$ ), we write, for a small spatial step  
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26  $\Delta s$  compared to the correlation length  $\ell_c$  (Aquino and Le Borgne, 2021),

$$r_{ij} = \frac{\Delta s}{\ell_c} \beta_{ij} (1 - \delta_{ij}) + \left[ 1 - \frac{\Delta s}{\ell_c} (1 - \beta_{ii}) \right] \delta_{ij}, \quad (3)$$

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29 where the dimensionless  $\beta_{ij}$  encode the velocity-dependence of the transition probabilities and  $\delta_{ij}$  is  
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31 a Kronecker delta. Thus, the term proportional to  $(1 - \delta_{ij})$  denotes the probability of changing to a  
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33 different velocity class, whereas the term proportional to  $\delta_{ij}$  denotes the probability of remaining in  
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35 the same velocity class. As shown in Aquino and Le Borgne (2021), the corresponding dynamics result  
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37 in a well-defined spatial-Markov process in the continuum limit of fine step discretization  $\Delta s \rightarrow 0$ ,  
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39 so long as the velocity class discretization associated with a given  $\Delta s$  is chosen such that the time  
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41 increments  $\Delta s/v_i \rightarrow 0$  for all classes  $i$  as  $\Delta s \rightarrow 0$ .

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43 The full transition matrix of an SMM is an  $N \times N$  matrix, where  $N$  is the number of velocity bins.  
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45 This can be difficult to parameterize in practice, so we shall instead adopt an analytical model based  
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47 on a discretized Bernoulli relaxation process for the velocities (Aquino and Le Borgne, 2021; Dentz  
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49 et al., 2016; Sherman et al., 2020). We expect this approach to provide good results for quantities  
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51 such as breakthrough curves at distances larger than a few correlation lengths (Hakoun et al., 2019;  
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53 Puyguiraud et al., 2019a). Under this process, particle velocities persist on the scale of the correlation  
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55 length  $\ell_c$ . When a particle changes to a different velocity class in a given step, the probability of  
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57 the new velocity being in class  $i$  is independent of the current velocity class  $j$ , and it is given by a  
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59 prescribed equilibrium probability  $p_i^\infty$ . In this sense, the Bernoulli process may be seen as the simplest  
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61 Markov process that relaxes to a prescribed equilibrium distribution over a given characteristic scale.  
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4 This also provides a direct link to SMM parameterizations based on Gaussian Copulas (Massoudieh  
5 and Dentz, 2020). Assuming that the probability of transition per unit length is constant and equal to  
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168 This also provides a direct link to SMM parameterizations based on Gaussian Copulas (Massoudieh  
169 and Dentz, 2020). Assuming that the probability of transition per unit length is constant and equal to  
170  $1/\ell_c$  implies that the probability of persistence is exponential (Feller, 2008; Van Kampen, 1992), and  
171 the transition probabilities are given by (Dentz et al., 2016)

$$r_{ij} = e^{-\Delta s/\ell_c} \delta_{ij} + (1 - e^{-\Delta s/\ell_c}) p_i^\infty. \quad (4)$$

172 Expanding in Taylor series for small  $\Delta s/\ell_c \ll 1$  and comparing to Eq. (3), we obtain

$$\beta_{ij} = p_i^\infty, \quad (5)$$

173 independent of the current velocity class  $j$  as expected.

174 The probability  $p_i^\infty$  must be defined in terms of flow properties in order for the Bernoulli process to  
175 relax to the correct velocity distribution for a given transport problem. To this end, we introduce the  
176 Eulerian velocity probability density function (PDF)  $p_E$ , defined such that  $p_E(v) dv$  is the probability  
177 of finding a velocity in the infinitesimal vicinity  $dv$  of  $v$  at a uniformly-randomly chosen spatial location.  
178 In other words, the Eulerian velocity PDF represents the point velocity statistics of the underlying flow  
179 field, in terms of the spatial probability of occurrence. Note that the Eulerian mean velocity, which  
180 was introduced above as a spatial average, can also be computed from the Eulerian velocity PDF as  
181  $\bar{v} = \int_0^\infty dv v p_E(v)$ . The equilibrium distribution of the Bernoulli process represents the distribution  
182 of velocities measured at a given downstream distance far from injection. Under the assumptions of  
183 flow incompressibility and ergodicity (*i.e.* velocity statistics sampled in time along a sufficiently long  
184 trajectory are the same as across the spatial domain), the corresponding equilibrium velocity PDF,  
185 called the s-Lagrangian velocity PDF in some works, is the flux-weighted Eulerian PDF (Dentz et al.,  
186 2016; Puyguiraud et al., 2019a),

$$p_F(v) = \frac{v p_E(v)}{\bar{v}}. \quad (6)$$

187 In the discretized description,  $p_i^\infty$  is the probability associated with the discretized velocity class  $i$ ,

$$p_i^\infty = \int_{b_i}^{b_{i+1}} dv p_F(v) \approx \Delta v_i p_F(v_i), \quad (7)$$

188 where the approximation holds for small velocity classes,  $\Delta v_i/\bar{v} \ll 1$ . The Bernoulli process is thus  
189 fully parameterized given knowledge of the Lagrangian (*i.e.*, along streamlines) correlation length  $\ell_c$

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4 and the Eulerian velocity PDF  $p_E(v)$ .  
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### 191 **3 Non-stationary spatial-Markov model**

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11 192 Consider now how to generalize the previous description to situations where the underlying flow field  
12 depends on time. Specifically, we seek a spatial-Markov model that is (statistically) non-stationary  
13 193 in time, in order to reflect transience (i.e., time dependence) of the underlying flow field. In a real,  
14 194 distributed transport system, the local velocity of a Lagrangian particle depends on position and time,  
15 195 which change along particle trajectories; the particle transport paths may be changing as time passes  
16 196 and thus may not coincide with paths along instantaneous flow streamlines. A robust upscaled repre-  
17 197 sentation of general transport dynamics is hopeless, because this scenario implies that in general the  
18 198 position and transition time changes cannot be decoupled. This means that an SMM is not applicable  
19 199 unless some simplifying assumptions are made. Otherwise, the required three-dimensional random walk  
20 200 may have complexity comparable to a distributed model, defeating the purpose of upscaled modeling.  
21 201

22  
23 202 Conceptually, particle velocities in the upscaled model could be considered to change according to  
24 203 two mechanisms that represent the changes in a physical transport system: (i) As in the classical SMM,  
25 204 a particle moves according to the local velocity and then samples a new velocity at a different, nearby  
26 205 point in space; and (ii) The local velocity at a particle's position changes due to the time-dependent  
27 206 nature of the flow. In general, these two processes cannot be fully decoupled since they could be  
28 207 happening simultaneously, but under certain conditions an upscaled description remains possible. A  
29 208 critical evaluation reveals two criteria under which an SMM should remain valid and practical: (a)  
30 209 Slow (temporal) variation of velocities, and (b) Fast (spatial) propagation of velocity changes. Slow  
31 210 variation means that the temporal change in the flow distribution throughout the medium is sufficiently  
32 211 slow that many spatial transitions typically occur before appreciable changes in the local velocities.  
33 212 Fast propagation means that when substantial changes in the velocity field do occur, they act quickly  
34 213 throughout the spatial domain compared to transport processes, so that all changes in the velocity  
35 214 PDF can be safely approximated as synchronous, or instantaneous, throughout the domain. The latter  
36 215 has been a common assumption in many studies of transient transport behaviors (see Engdahl et al.,  
37 216 2016), suggesting it could also be adopted for SMM applications.

38  
39 217 Even under these assumptions, the Eulerian velocity PDF representing spatial flow statistics still  
40 218 needs to be updated over time to reflect the transient changes. The remainder of this section is  
41 219 concerned with how, and how often, to do so, and the assumptions associated with these decisions.  
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220 In particular, the underlying Eulerian velocity PDF must be considered as transient in all of the  
221 specific cases analyzed below. The most practical approaches to achieving this consist in adopting  
222 parameterized PDFs where some or all of the parameters can be made functions of time. This important  
223 issue will be revisited in Section 5. For now, we merely posit that the transient Eulerian velocity PDF  
224  $p_E(v; t)$ , describing point velocity statistics at each time  $t$ , is known, and we discuss three different  
225 candidates for implementing a discretized transient SMM.

### 226 3.1 Naïve explicit

227 The simplest version of a transient SMM is one where the velocity PDF is updated only at steps where  
228 velocity transitions occur. This “Naïve explicit” (NEX) scheme is still described by the recursion  
229 relations (1). The key difference is that the transition probabilities  $r_{ij}(t)$  now depend on the current  
230 “clock time” of the random walker through the coefficients  $\beta_{ij}(t)$ , see Eq. (3). At each transition,  
231 the Eulerian velocity PDF is updated to  $p_E(v; T_k)$ , and the corresponding transition probabilities  
232  $r_{ij}(T_k)$  are calculated before determining the new velocity. Note that in the specific case of a Bernoulli  
233 random walk, particle velocities only change with a probability given by  $\exp(-\Delta s/\ell_c)$ , independent of  
234 the current velocity, but otherwise remain the same as in the previous step (see Eq. (4)); thus, in this  
235 case, the velocity PDF is only updated to accommodate transient changes when a Bernoulli-model  
236 change in velocity would occur. Thus, for a Bernoulli random walk, transience in-between transitions  
237 is effectively ignored.

238 The simplicity of this approach is appealing, but it suffers from significant limitations because it  
239 makes no attempt to identify when it is actually necessary to account for transient changes. As we  
240 will see, this means that it does not converge to the same solution as the more involved discretization  
241 schemes proposed below in the continuum limit of fine discretization  $\Delta s \rightarrow 0$ . When the flow field  
242 changes very slowly (in the sense of the slow-variation criterion developed in detail in what follows),  
243 the NEX model may provide sufficient accuracy in practice, but if the timescales of transience impart  
244 fluctuations faster than the travel times, which should occur often at low velocities, significant errors  
245 will accumulate because important transient changes are ignored. The necessary conditions for this  
246 NEX model to provide a realistic approximation may not be practical in many real-world situations.  
247 We nonetheless include it here for its conceptual simplicity and to highlight the role of the more subtle  
248 procedures developed for the following, more involved discretization schemes.

### 3.2 Turning point explicit

The problem with the primitive NEX model is that it is entirely oblivious to the rate at which the flow field changes. If the flow field changes quickly, many velocity updates are necessary in, potentially, a short time compared to standard SMM velocity transitions, especially for particles moving at low velocities. Thus, our goal is to find an approach where the time and number of velocity PDF updates are dictated by the magnitude of the temporal changes in the velocity PDF. Before continuing, recall that particle velocities in a transient SMM may change due to two mechanisms: (i) As before, a particle moves according to the local velocity, and samples a new velocity at a different, nearby point in space; and (ii) The local velocity at a particle's position changes due to the time-dependent nature of the flow.

In the context of a transient field, mechanism (i) requires a rule to determine the transition probabilities  $r_{ij}(t)$  for times  $t$  over each time range between velocity changes. In turn, mechanism (ii) requires a rule to determine velocity transitions due directly to the change in the underlying flow field. First, we determine the time range characterizing appreciable velocity changes. Knowledge of the time-dependent Eulerian PDF  $p_E(v; t)$ , as a function of velocity  $v$  for each time  $t$ , implies knowledge of the mean Eulerian velocity as a function of time,

$$\bar{v}(t) = \int_0^\infty dv p_E(v; t)v. \quad (8)$$

Over a given time interval, which we call a variation window  $\Delta t_v$ , the difference in the average particle displacement associated with the change in mean velocity can be quantified through

$$\Delta s_v = |\bar{v}(t + \Delta t_v) - \bar{v}(t)|\Delta t_v. \quad (9)$$

The quantity  $\Delta s_v$  may be interpreted as the approximate error in the average particle displacement that would arise from not taking the mean velocity variability into account. The error in the usual discretized spatial-Markov description, associated with mechanism (i), is on the order of the discretization step length  $\Delta s$ . Thus, in order to obtain an error of the same order associated with discretizing mechanism (ii), we choose  $\Delta t_v$  such that  $\Delta s_v = a\Delta s$ , where  $a \leq 1$  is a free parameter controlling the maximum step size under transience, and as such the magnitude of allowable errors. Note that this will in general correspond to a time-dependent variation window  $\Delta t_v(t)$ .

For given values of  $a$  and  $\Delta s$ , Eq. (9) can be solved numerically for  $\Delta t_v$ . The procedure leads to a

series of turning points  $T_{v,k'}$  where variation of the Eulerian flow field is to be taken into account; for this reason, we call this approach the “Turning Point Explicit” (TPE) method. Specifically, we have

$$T_{v,k'+1} = T_{v,k'} + \Delta t_{v,k'}, \quad T_{v,0} = T_0 = 0, \quad (10)$$

where  $\Delta t_{v,k'} = \Delta t_v(T_{v,k'})$  is the variation window associated with the last turning point. Note that many transition times  $T_k$  associated with mechanism-(i) transitions are expected to occur between two turning points when the slow-variation condition (a) is met, as discussed in more detail below. A straightforward numerical procedure to determine the variation windows and associated turning points is described in Appendix A.

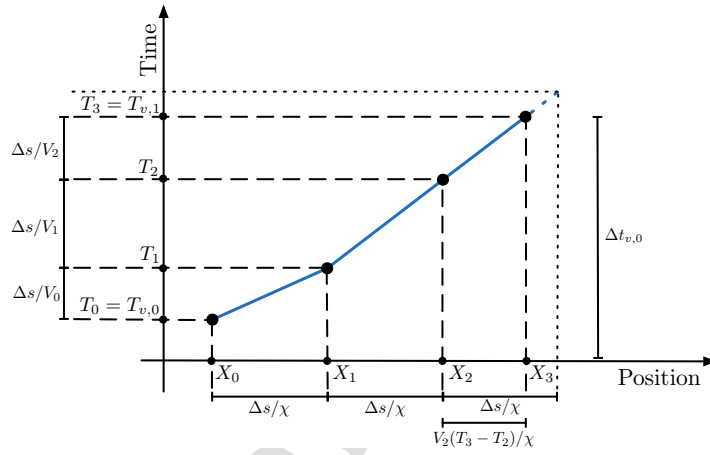


Figure 1: Illustration of the algorithm for mechanism (i), representing spatial-Markov transitions. As explained in detail in the text, starting at time  $T_{v,0} = T_0$  and position  $X_0$ , the variation window  $\Delta t_{v,0}$  is first computed based on mean flow velocity variability. The Markov transition times  $\Delta s/V_i$  associated with steps of length  $\Delta s/\chi$  are then computed, until the turning point time  $T_{v,1} = T_{v,0} + \Delta t_{v,0}$  is reached. The portion of the last step corresponding to times exceeding  $T_{v,1}$ , represented by the dashed lines, is discarded, leading to the solid blue trajectory. Mechanism (ii) is then employed to find the new velocity at the new turning point, the Markov transition probabilities are updated according to the transient Eulerian PDF evaluated at  $T_{v,1}$ , and the algorithm is repeated.

We now formalize mechanism (i). Starting at the time  $T_{v,k'}$  of the last flow-variation transition, determine the next variation window  $\Delta t_{v,k'}$ . Then, employ Eq. (3) for the transition probabilities  $r_{ij}(t) = r_{ij}(T_{v,k'})$ , together with the transition coefficients  $\beta_{ij}(t) = \beta_{ij}(T_{v,k'})$ , which depend on the choice of spatial-Markov process. The transition probabilities remain constant throughout the variation window. Next, update particle positions and times according to Eq. (1). However, when during some step  $k$  a particle’s time would exceed the next turning point time  $T_{v,k'+1}$  associated velocity variation

(Eq. (10)), the new time and position are determined according to

$$X_{k+1} = X_k + V_k \frac{T_{k+1} - T_k}{\chi}, \quad T_{k+1} = T_{v,k'+1}, \quad (11)$$

in order to account for the partial completion of the step. Note that the remainder of the last transition distance and duration are discarded. Having determined that the next Markovian velocity transition has not occurred by time  $T_{k+1}$ , we know the velocity remains constant and equal to  $V_k$  during the partial step. The turning point corresponding to the next Markovian change in velocity can simply be recomputed in the next iteration without further assumptions due to the lack of memory of Markov processes (see, e.g., Van Kampen, 1992). The algorithm for mechanism (i) is illustrated in Fig. 1. This procedure is to be applied to all particles, followed by mechanism (ii), described below, and then repeated. Note that the NEX scheme proceeds similarly regarding the turning point times  $T_k$  and positions  $X_k$ , but does not require explicit variation windows. Rather, the position increments are always  $\Delta s/\chi$ , and the underlying transition probabilities are updated only when a velocity transition to a different class occurs.

Next, we turn to mechanism (ii), which corresponds to determining the new velocity at the flow-variation turning point times  $T_{v,k'}$ . Consider the transition probabilities of Eq. (3). Under a change in the flow field, these may change through the correlation length  $\ell_c$  and/or through the velocity-dependent coefficients  $\beta_{ij}$ . In order to set up mechanism (ii) in a simple and physically-reasonable manner, we assume that the flow structure remains unchanged, maintaining the correlation length  $\ell_c$  and the tortuosity  $\chi$  constant, but the Eulerian velocity PDF may change in time, keeping its functional form but changing its mean through a rescaling. As familiar examples, this is the case at the pore scale when the underlying velocity field corresponds to Stokes flow, and at the Darcy scale when the hydraulic conductivity structure remains the same but the average head gradient driving the flow is rescaled. Once a transition due to velocity variation happens, at some transition time which we again name  $T_k$  (now with  $k \geq 1$ ) for convenience, the local flow velocity at the particle's position is likely to have changed appreciably. To take this into account, mechanism (ii) consists of rescaling the particle's previous velocity according to the change in mean velocity,

$$V_{k+1} = \frac{\bar{v}(T_{v,k'+1})}{\bar{v}(T_{v,k'})} V_k, \quad (12)$$

or the corresponding class velocity in the discretized picture. This choice corresponds to assuming that the change in the velocity statistics can be approximated by an overall rescaling of the point

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4 velocities, in line with the assumptions discussed above. This mechanism is applied to all particles,  
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6 and the procedures described for mechanisms (i) and (ii) are then repeated. Note that, at the begin of  
7  
8 procedure (i), the Markov transition probabilities are recomputed according to the velocity distribution  
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10 at the new turning point time.

11 The correlation length and tortuosity are determined by the flow structure but can change in a  
12  
13 given medium with an unchanging structure, for example due to the formation of preferential flow  
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15 paths. While the mechanism (ii) rule can be applied to a case where the flow structure also varies, its  
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17 physical significance is more difficult to justify. A more complex transition rule may be necessary in  
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19 such cases, which we do not discuss further here.

### 21 3.3 Fully-implicit model

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23  
24 So far we have considered one method that only updates transition probabilities each time a velocity  
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26 change takes place (and not at turning points where velocity remains the same), and one that auto-  
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28 matically “detects” when updates are needed, which, in the process, may cause the step sizes to change  
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30 (i.e., TPE). Another possibility is one where the spatial step size is chosen and fixed, but transient  
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32 changes are always accommodated, no matter how big or small the transient fluctuation(s) may be.  
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34 In practice, the concept of a variation window introduced for TPE subtly implies that, for a given  
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36 finite step size  $\Delta s$ , the changes of the velocity PDF during a step are small enough that stochastic  
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38 variations compensate for any inaccuracies imposed by the use of a constant velocity. In other words,  
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40 the “true” velocity might be slightly higher/lower over any given step, but the average remains repre-  
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42 sentative. An alternative interpretation of this nuanced point is that it assumes that small changes to  
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44 the *probability* associated with a given velocity are insignificant inside an appropriately-sized variation  
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46 window. Transposing this argument, one could instead assume that small changes to a velocity have  
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48 an insignificant impact on its probability over the time of the transition, which leads us to the third  
49  
50 strategy.

51 The key assumption for the following approach is that the cumulative probability associated with  
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53 a particle velocity,

$$P(v) = \int_0^v dv p_E(v), \quad (13)$$

54  
55 does not change during a spatial step, or that a particular particle’s velocity *rank* on the cumulative  
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57 density function (CDF) remains constant over any given step. This is similar to the assumption made  
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59 under the TPE method, where changes in the underlying flow field were modeled as a constant rescaling  
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4 of the velocity PDF due to change in the mean velocity. For example, at  $t = 0$ , perhaps  $v = 0.1$  has  
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6 cumulative probability  $P(v) = 0.8$  (20% of velocities above 0.1), but at  $t = 1$  the overall flow increases  
7  
8 such that  $v = 0.15$  now corresponds to  $P(v) = 0.8$  (20% of velocities above 0.15); in other words, a  
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10 particle that begins moving with  $P(v) = 0.8$  holds this rank throughout a step even as the velocity  
11  
12 associated with this rank evolves.

13 Discretizing velocities in terms of rank, and denoting the velocity of a random walker conditional  
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15 to a particular probability value (or rank) as  $v_p(t)$ , where  $p$  denotes the associated rank class, we can  
16  
17 consider the trajectory of a particle along the SMM path as an equation of motion for each step. Since  
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19 within a transition the particle velocity is allowed to change but the rank remains fixed, each step in  
20  
21 the 1d random walk is described by the ordinary differential equation (ODE)

$$\frac{dX_p(t)}{dt} = \frac{v_p(t)}{\chi}, \quad (14)$$

22  
23 where  $X_p(t)$  is the downstream position, and  $v_p(t)$  is a time-dependent function that describes the  
24  
25 transient velocity as a function of clock time for a given probability rank class,  $p$ . For a step of known  
26  
27 length  $\Delta s$ , this separable ODE has the general solution  
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31

$$\Delta s = \int_{T_k}^{T_{k+1}} dt v_p(t), \quad (15)$$

32  
33 where  $\Delta s = \chi[X_p(T_{k+1}) - X_p(T_k)]$  is the imposed displacement along particle paths,  $T_k$  is the clock  
34  
35 time at the beginning of the step, and  $T_{k+1}$  is the unknown final time. Thus, particle positions in  
36  
37 terms of step number  $k$  remain given by  $X_{k+1} = X_k + \Delta s/\chi$ , but transition times are determined  
38  
39 according to an implicit equation.  
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43 Given a function for  $v_p(t)$ , the left-hand side of (15) is known and the right-hand side will be a  
44  
45 function of  $T_{k+1}$  only, the unknown time when the step is finished, to be found via an implicit solution.  
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47 The resulting equation will likely be nonlinear, but the solution of (15) for the final time,  $T_{k+1}$ , gives an  
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49 exact solution when  $v_p(t)$  may be approximated analytically, subject to the simplifying assumptions.  
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51 We term this approach the ‘‘Fully-implicit model’’, since it requires the solution of an implicit (possibly  
52  
53 nonlinear) equation for every particle in the random walk at every step. Note that this approach is  
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55 an exact expression for the travel time when  $v_p(t)$  is known analytically, with the single assumption  
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57 that the probability associated with the velocities is constant for the duration of the step. Once a  
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59 step  $k$  is completed, a new probability rank class may be determined analogously to before, according  
60  
61 to the transition probabilities (3) associated with the step (*i.e.*, via a transition matrix or analytical  
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4 Markov process). The Eulerian velocity PDF is made a function of clock time, and the transitions  
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6 probabilities are computed according to its form at the beginning of the step,  $p_E(v; T_k)$ , as for the  
7  
8 previous methods.

9  
10 Consider Fig. 1 for the turning points and variation windows of the TPE scheme. Like the NEX  
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12 scheme, the fully-implicit method, as well as the approximations developed below, does not require  
13  
14 the computation of variation windows, and the position increments are always  $\Delta s/\chi$ . Unlike NEX,  
15  
16 however, transient changes are reflected in the transition probabilities at every step, and not only  
17  
18 when velocity changes occur. Furthermore, as already discussed, velocity variability of a particle due  
19  
20 to the transient changes within a transition can be captured, in which case the time increments are  
21  
22 obtained implicitly via Eq. (15) rather than given directly by  $\Delta s/V_k$ . The stationary SMM case  
23  
24 is easily recovered by defining, within step  $k$ ,  $v_p(t) = V_{p,k}$ , where  $V_{p,k}$  is constant within the step.  
25  
26 Then,  $\Delta s = V_{p,k}(T_{k+1} - T_k)$ , and we conclude that the transition time is  $T_{k+1} - T_k = \Delta s/V_{p,k}$ , as  
27  
28 expected. Next, consider a simple example of transience by assuming a linear increase in velocity  
29  
30 over time:  $v_p(t) = V_{p,k} + \alpha(t - T_k)$ , where  $\alpha$  is a constant growth rate. This gives the quadratic  
31  
32  $\Delta s = \alpha(T_{k+1} - T_k)^2/2 + V_{p,k}(T_{k+1} - T_k)$ , which has one real-valued, positive solution for the transit  
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34 time,  $T_{k+1} - T_k = (\sqrt{1 + 2\alpha\Delta s/V_{p,k}^2} - 1)V_{p,k}/\alpha$ . Note that this reduces to the previous case when  
35  
36 the growth rate or step size are sufficiently small such that  $2\alpha\Delta s/V_{p,k}^2 \ll 1$ . A similar technique can  
37  
38 in principle be employed for any integrable function that defines  $v_p(t)$ , but we reiterate that solutions  
39  
40 will likely need to be approximated using a nonlinear solver.

### 390 3.3.1 Fully-Transient explicit approximation

41  
42 The fully-implicit scheme has the advantage of accounting for all the changes in  $v_p(t)$  when the latter  
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44 is known, but it should be evident that an implicit nonlinear solution for every particle at every step  
45  
46 will be computationally demanding. The most obvious simplification is to use the velocity from the  
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48 beginning of the time step in an explicit, first-order scheme that always updates the PDF for transience,  
49  
50 so we abbreviate this Fully-Transient Explicit approximation as FTE.

51  
52 A single evaluation of the velocity is used for every step, so that transient changes *during* the step  
53  
54 are strictly ignored. The FTE then proceeds according to the recursion relations (1), with the velocities  
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56  $V_k$  selected according to (3), computed according to an Eulerian velocity PDF that is a function of  
57  
58 clock time, updated as  $p_E(v; T_k)$  at each particle step as before. The advantage of this approach is  
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60 speed and simplicity but, like the NEX scheme, the cost is that it makes no attempt to account for  
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62 transient changes during a spatial step. However, the velocity associated with each rank is updated at

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4 every step, whereas the NEX scheme only accounts for changes in the transition probabilities when a  
5 transition leads to a *change in velocity class*, so TPE will naturally have advantages from an accuracy  
6 standpoint. Note that NEX and FTE can differ significantly under the Bernoulli relaxation model,  
7 because the probability of remaining in the same velocity class may be significant. Unlike the NEX  
8 scheme, for which velocity changes occur on the order of the correlation length  $\ell_c$ , FTE accounts for  
9 velocity changes within a step length  $\Delta s$ . Thus, the accuracy in capturing the transient field increases  
10 when the spatial discretization is refined, leading to appropriate convergence of FTE. For a given  $\Delta s$ ,  
11 the accuracy will be dependent on the nature of the transient signal, and significant errors should be  
12 expected anytime the velocity changes are large relative to the magnitude of the transition time and/or  
13 spatial steps.  
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### 22 3.3.2 Runge-Kutta 3 integration

23 Additional accuracy for an explicit approximation of the fully-implicit scheme can be obtained by  
24 adding more evaluations of the velocity distribution to create a Runge-Kutta predictor-corrector  
25 scheme. The velocity rank (cumulative probability) is required to be constant during each spatial  
26 step, since the velocity will be evaluated at multiple times for the “predictor” steps, but the associated  
27 velocity distributions being evaluated may be any arbitrary transient PDF that is defined as a function  
28 of time. This goes beyond the NEX and FTE schemes by accounting for transient changes *during* each  
29 step of the SMM, but avoids solving a nonlinear equation as is typically required for the fully-implicit  
30 scheme.  
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39 A good balance of accuracy and numerical cost is provided by the standard 3rd-order Runge-Kutta  
40 (RK3) scheme (Pozrikidis et al., 1998). For the trajectory of a temporally non-stationary random  
41 walker during step  $k$  and for a given rank  $p$ , the time at the end of the step,  $T_{k+1}$ , is computed  
42 according to  
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$$50 \quad t^* = T_k + \frac{\Delta s}{2v_p(T_k)}, \quad (16a)$$

$$51 \quad t^{**} = T_k + \Delta s \left[ \frac{2}{v_p(t^*)} - \frac{1}{v_p(T_k)} \right], \quad (16b)$$

$$52 \quad T_{k+1} = T_k + \frac{\Delta s}{6} \left[ \frac{1}{v_p(T_k)} + \frac{4}{v(t^*)} + \frac{1}{v(t^{**})} \right], \quad (16c)$$

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58 where  $t^*$  and  $t^{**}$  are the first and second predictor estimates of the time to complete the step. As before,  
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4 the new velocity at the end of each step  $k$  is computed according to the transition probabilities (3)  
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6 associated with the step, obtained based on the time-dependent Eulerian PDF  $p_E(v; T_k)$  updated at  
7  
8 the beginning of the step.

9  
10 We reiterate that the rank (probability) of the velocity is assumed constant throughout the spatial  
11  
12 step but that the value associated with each predicted transition time can change; note that the  
13  
14 assumption of constant rank is also necessary in other stochastic Runge-Kutta schemes (Engdahl and  
15  
16 Aquino, 2018; Honeycutt, 1992). The three evaluations of the transient velocity lead to an accuracy of  
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18 the scheme scaling as  $\mathcal{O}(\Delta s^3)$ ; note that this is the accuracy of the *estimated transition time*  $T_{k+1} - T_k$ ,  
19  
20 and not the overall accuracy of a simulated breakthrough curve. We found that this RK3 scheme gives  
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22 accuracy comparable to a direct, implicit solution of (15), while providing a computationally-efficient  
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24 approach (but note that this may not hold when the velocity changes are not smooth and slowly-  
25  
26 varying). As such, the fully-implicit solution is omitted below for the sake of brevity.

## 27 4 Applicability conditions

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30 The four different explicit methods described above (NEX, TPE, FTE, and RK3) each have slightly  
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32 different assumptions and conceptual models, but some general criteria must be met by the flow field  
33  
34 for these methods to provide reasonable approximations of transport in a computationally-efficient  
35  
36 manner. We posited in Section 3 that a transient SMM should be valid and efficient under (a) slow  
37  
38 variation of the velocity, and/or (b) fast propagation of transient changes to the velocity field. Each  
39  
40 of these merits some additional discussion in the context of Darcy-scale flow in aquifers.

### 41 4.1 Physical mechanics of the flow

42  
43 Consider a section of a confined aquifer that has a well defined mean flow direction along which  
44  
45 the head decreases. As long as the source of any transience is imposed outside the section under  
46  
47 consideration (i.e. changes in recharge are applied some distance upstream of the section in question),  
48  
49 we may quantify the impacts of those changes simply in terms of time-varying heads observed at each  
50  
51 end (longitudinally) of the section and ignore the specific cause(s) of the transience. The impacts  
52  
53 of the head changes at the boundaries on the velocity distribution within the aquifer depend on the  
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55 heterogeneity of the various properties in the domain, but generally what matters is how much of the  
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57 field is affected and how quickly.

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59 Consider what happens in the case where a pressure pulse rapidly propagates through the aquifer.

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455 Assuming the hydraulic conductivity structure of the medium remains unchanged, and no source/sink  
456 terms, changes in flow velocity across the medium are due to variations in head that reflect the under-  
457 lying hydraulic conductivity field. The piezometric head,  $h$ , obeys

$$S_s \frac{\partial h}{\partial t} = \nabla \cdot \mathbf{K} \nabla h, \quad (17)$$

458 where  $S_s$  [1/L] is the specific storage and  $\mathbf{K}$  is the hydraulic conductivity tensor [L/T], subject  
459 to appropriate boundary and initial conditions (Charbeneau, 2006). Assuming constant  $S_s$  (spatial  
460 variation produces an advective-type term), this is a diffusion equation for  $h$ , with the role of the  
461 diffusion coefficient played by the hydraulic diffusivity [L<sup>2</sup>/T]

$$D_H = \frac{\mathbf{K}}{S_s}. \quad (18)$$

462 Hereafter, we assume for simplicity a locally-isotropic  $\mathbf{K}$  field, so that it is sufficient to consider the  
463 scalar (diagonal) values  $K$  and  $D_H$ . The conductivity  $K$  can vary spatially, so it is convenient to  
464 consider an average value for  $D_H$  that realistically homogenizes spatial heterogeneities,  $D_H^*$ , which  
465 could be computed, e.g., as a geometric (power) mean over  $K(x, y, z)$  (Charbeneau, 2006). The  
466 timescale associated with the propagation of head perturbations across a distance  $\ell$ , and associated  
467 flow variations, is then the diffusive timescale  $\tau_H = \ell^2 / (2D_H^*)$ .

468 Over a given longitudinal length scale of interest,  $\ell$ , the timescale associated with (advective)  
469 transport can be estimated as  $\tau_A = \ell / \bar{v}$ . The fast-propagation condition (b) can now be translated  
470 as the requirement that flow variations must propagate much faster than solute transport,  $\tau_H \ll \tau_A$ ,  
471 corresponding to

$$\ell \ll \frac{2D_H^*}{\bar{v}}. \quad (19)$$

472 We have assumed that the main limiting factor is the propagation along the longitudinal direction,  
473 but a similar criterion could be developed that includes any propagation speed contributions from the  
474 lateral components.

475 We take  $\ell$  equal to the length of the domain of interest. In that case, if condition (19) holds,  
476 the perturbation may be assumed to travel instantaneously across the domain, or that all velocities  
477 change instantly when a head change is applied at the boundaries. For large domains, this criterion  
478 could be relaxed by estimating  $\ell$  according to the characteristic size of the solute plume through its  
479 longitudinal dispersion  $\sigma_x^2$ , such that  $\ell \sim \sigma_x$ . In this case, the perturbation can be assumed to cross the

entire plume instantaneously, but it may be necessary to delay the change in transition probabilities according to the time it takes the perturbation to reach the plume.

Finally, note that the Darcy equation itself does not dictate the velocity and it is assumed that the average local flow velocity is proportional to the local hydraulic conductivity  $K$  and the porosity. Since  $K$  typically exhibits much broader variability than specific storage, low hydraulic diffusivity  $D_H$  is commonly associated with low flow velocities, so that velocity in the lower- $D_H$  regions is expected to be slower than the mean value, and conversely for the higher- $D_H$  regions. Thus, we expect that employing an appropriate average, such as  $D_H^*$ , in Eq. (19) will usually lead to a reasonable estimate of the applicability of the fast propagation criteria, but factors like connectivity and extreme degrees of heterogeneity could impact this criterion.

## 4.2 Slow-variation criterion

As long as the velocity changes propagate across the domain sufficiently fast, the TPE and RK3 methods will provide good approximations of the transient PDF. However, it is advantageous from a computational standpoint if Eulerian velocities across the domain change sufficiently slowly in time that many transitions occur within a variation window  $\Delta t_v$ . In order to estimate  $\Delta t_v$  in terms of the variability in the mean velocity, consider the limit of small  $\Delta s$ , under which  $\Delta t_v$  is expected to be small. Then, Taylor expansion of Eq. (9) yields

$$\Delta s_v \approx \left| \frac{d\bar{v}}{dt} \right| \Delta t_v^2, \quad (20)$$

and, solving for  $\Delta t_v$ ,

$$\Delta t_v \approx \sqrt{\frac{a\Delta s}{|d\bar{v}/dt|}}. \quad (21)$$

Note that the Taylor expansion leading to this result is inaccurate near local temporal extrema of the mean velocity, where  $|d\bar{v}/dt| = 0$ , which is why we employ the more robust numerical procedure described in Appendix A to compute  $\Delta t_v$ . However, this approximation provides a useful estimate of the role of flow variability. The number of mechanism (i) transitions within  $\Delta t_v$  is of order  $\bar{v}\Delta t_v/\Delta s$ , which we wish to be large. We thus obtain for the slow-variation condition (a):

$$\left| \frac{d\bar{v}}{dt} \right| \ll \frac{a^2\bar{v}^2}{\Delta s}. \quad (22)$$

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4 In particular, for the spatial-Markov description to adequately resolve transport, we need  $\Delta s \lesssim \ell_c$ ,  
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6 and we must have  $a \leq 1$ . Thus, the minimal requirement for condition (a) to be met may be expressed  
7  
8 as

$$\left| \frac{d\bar{v}}{dt} \right| \ll \frac{\bar{v}^2}{\ell_c}. \quad (23)$$

9  
10 This is a time-dependent criterion, and the procedure may remain practical even if it does not hold  
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12 for certain times. If this constraint holds, Eq. (22) may be used to choose  
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$$\frac{a^2 \bar{v}^2}{|d\bar{v}/dt|} < \Delta s < \ell_c, \quad (24)$$

15  
16 in order to ensure the method is both accurate and efficient. In practice,  $\Delta s$  can be chosen as the mini-  
17  
18 mum of given multiples of the left and right terms in the inequality, e.g.,  $\Delta s = \min\{5\bar{v}^2/(|d\bar{v}/dt|), \ell_c/10\}$ .  
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20 Note also that  $\Delta s$  may be chosen adaptively, according to the temporal variation of the mean velocity,  
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22 or constant according to a specific value such as the maximum or average of  $\bar{v}^2/|d\bar{v}/dt|$  over the times  
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24 of interest.  
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28 Combining the slow-variation condition, Eq. (23), and the fast-propagation condition, Eq. (19), we  
29  
30 obtain  
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$$\sqrt{\ell_c \left| \frac{d\bar{v}}{dt} \right|} \ll \bar{v} \ll \frac{2D_H^*}{\ell}. \quad (25)$$

32  
33 Given the spatial mean  $\bar{v}(t)$  of the underlying flow field as a function of time, this result represents the  
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35 conditions for practical applicability (accuracy and efficiency) of the transient spatial-Markov model,  
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37 in terms of the velocity correlation length  $\ell_c$ , the longitudinal scale of interest  $\ell$ , and the (average)  
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39 hydraulic diffusivity  $D_H^*$ .  
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## 44 5 Examples and cross-comparison

45  
46 Existing analytical models for transport under transient velocities assume spatially-uniform flow fields (see  
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48 Engdahl et al., 2016), and there are no closed-form analytical solutions for the transient, hetero-  
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50 geneous velocity fields that would lead to correlated transport. Accordingly, this section provides  
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52 cross-comparison of the different transient SMM models under varying degrees of transience. We  
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54 first compare the behavior of the four methods using a simplified analytical flow field, before mov-  
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56 ing on to numerical validation against direct simulations based on numerically-computed, spatially-  
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58 heterogeneous velocity fields. We exclusively consider the Bernoulli process SMM hereafter. Recall  
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60 that the Bernoulli SMM admits a minimal parameterization in terms of the Eulerian velocity PDF  
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4 and a velocity correlation length, providing a simple and parsimonious model. Nonetheless, any SMM  
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6 transition mechanisms could be employed with minor modifications involving only the model's param-  
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8 eterization (see Sherman et al., 2020). Under the present choice, the coefficients  $\beta_{ij}(t)$ , which fully  
9  
10 characterize the transition probabilities  $r_{ij}(t)$  through Eq. (3), are obtained from the Eulerian PDF of  
11  
12 point velocity magnitude statistics at a given time through Eq. (7). To further simplify the demon-  
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14 strations, we also adopt a gamma PDF of Eulerian velocities with various prescribed time-dependent  
15  
16 mean velocities  $\bar{v}(t)$ ,

$$p_E(v; t) = \left[ \frac{\theta v}{\bar{v}(t)} \right]^\theta \frac{e^{-\theta v/\bar{v}(t)}}{v\Gamma(\theta)}, \quad (26)$$

17  
18 where  $\Gamma(\cdot)$  is the gamma function. This type of PDF combines low-velocity power-law behavior (with  
19  
20 scaling  $v^{\theta-1}$ ,  $\theta > 0$ ) with an exponential cutoff at high velocities. These features control long-term  
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22 tailing of the resulting transit time distributions due to retention in low velocity zones as well as  
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24 mean transit times, which in turn control key transport features such as mean plume displacement  
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26 and longitudinal dispersion (Aquino and Le Borgne, 2021; Dentz et al., 2016). The gamma PDF has  
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28 been employed to model Eulerian velocity PDFs in porous media both at the pore and the Darcy  
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30 scales (Alim et al., 2017; Aquino and Le Borgne, 2021; Dentz et al., 2016; Holzner et al., 2015). The  
31  
32 corresponding flux-weighted Eulerian (or s-Lagrangian) PDF, Eq. (6), is again gamma,

$$p_F(v; t) = \left[ \frac{\theta v}{\bar{v}(t)} \right]^\theta \frac{e^{-\theta v/\bar{v}(t)}}{\bar{v}(t)\Gamma(\theta)}, \quad (27)$$

33  
34 with the same exponential cutoff and a low-velocity dependency  $\propto v^\theta$ . Alternative parameterizations  
35  
36 of the gamma PDF, along with fitting procedures, are discussed in Appendix B.

### 37 38 39 40 41 42 43 **5.1 Analytically-defined velocities**

44  
45 The analytical cross-validation exercise assumes that *i*) a gamma distribution of velocities exists within  
46  
47 the domain, and *ii*) the Eulerian mean velocity is described by a periodic function of the form

$$\bar{v}(t) = v_0 \left[ 1 + \eta \sin \left( \frac{2\pi(t + t_0)}{\tau} \right) \right], \quad (28)$$

48  
49 where  $v_0 [L/T]$  is a long-term mean velocity,  $\eta [-]$  scales the magnitude of the velocity fluctuation  
50  
51 (subject to  $0 < \eta < 1$  so velocities remain positive),  $\tau [T]$  is the period of the transient cycle, and  $t_0$   
52  
53  $[T]$  is a temporal shift. The corresponding transient gamma distribution for the SMM is then given  
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59 by (27).  
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552 The example problem is defined by a domain length  $L = 100 [L]$ , tortuosity  $\chi = 1$  for simplicity,  
553 velocity correlation length  $\ell_c = 10 [L]$ , gamma PDF exponent  $\theta = 5$ , long-term average velocity  
554  $v_0 = 0.04 [L/T]$ , and temporal shift  $t_0 = 0$ . The four approaches (NEX, TPE, FTE, and RK3)  
555 are assessed under different  $\tau$  and  $\eta$  combinations (Figure 2), and then at different discretizations to  
556 demonstrate convergence (Figure 3). Any number of parameter combinations could be used, but our  
557 goal is to demonstrate how transience impacts the model relative to a steady-state approximation. In  
558 each case, we provide comparison to a stationary SMM, which is obtained by setting  $\bar{v}(t) = v_0$  and  
559  $\eta = 0$ . We choose  $\Delta s = 1$ , so a random walker crosses a velocity correlation length in  $\ell_c/\Delta s = 10$  steps  
560 and the full domain in  $L/\Delta s = 100$  steps. We use 5000 random walkers; higher particle numbers did not  
561 have a significant impact on the results since we focus on mean behaviors, not on capturing tailing. The  
562 (cumulative) breakthrough curves (BTCs) at the downstream domain boundary for different parameter  
563 combinations of low/high magnitude ( $\eta$ ) and small/large period ( $\tau$ ) of transience are shown in Fig. 2,  
564 with specific values shown in each panel. The time scales of transience were defined in terms of the  
565 average velocity ( $v_0$ ) and domain length ( $L$ ), corresponding to the typical time for a particle to cross  
566 the domain. In all of these plots, the FTE curve is under the RK3 curve at this scale, and both are  
567 usually close to the TPE curve. Only the NEX and SS (steady-state) curves are visibly distinct from  
568 the other transient models at all times.

569 An observation that can be made from Fig. 2 is that there are some cases where TPE differs from  
570 RK3. The reason for this is the parameter  $\Delta s_v = a\Delta s$  in the TPE model; a value of  $a$  must be specified,  
571 which controls the magnitude of the “allowable” errors. Fig. 2 used  $a = 0.5$ , and this can be reduced  
572 to increase accuracy, at the cost of requiring more steps. Given sufficiently small  $a$ , and thus  $\Delta s_v$ ,  
573 the TPE and RK3 results are essentially identical if the spatial discretization  $\Delta s/\ell_c$  is also sufficiently  
574 small. This is shown via a convergence analysis in Fig. 3 with  $a = 0.1$ , where TPE, FTE, and RK3  
575 all exhibit nearly identical mean travel times as  $\Delta s/\ell_c$  is decreased (i.e., the number of steps needed  
576 to cross a correlation length is increased, so that all relevant structure in the flow field is resolved).  
577 Similar behaviors can be found for any fixed level of the BTC, but we only show convergence of the  
578 median arrival time for brevity.

## 579 5.2 Spatially-heterogeneous flow field

580 Our final example considers flow in a 2d, heterogeneous flow field subjected to transient boundary  
581 conditions. Here we simulate transport explicitly using fully-resolved Lagrangian random walk particle  
582 tracking (RWPT), and then compare the result to the proposed, upscaled, transient SMM schemes.



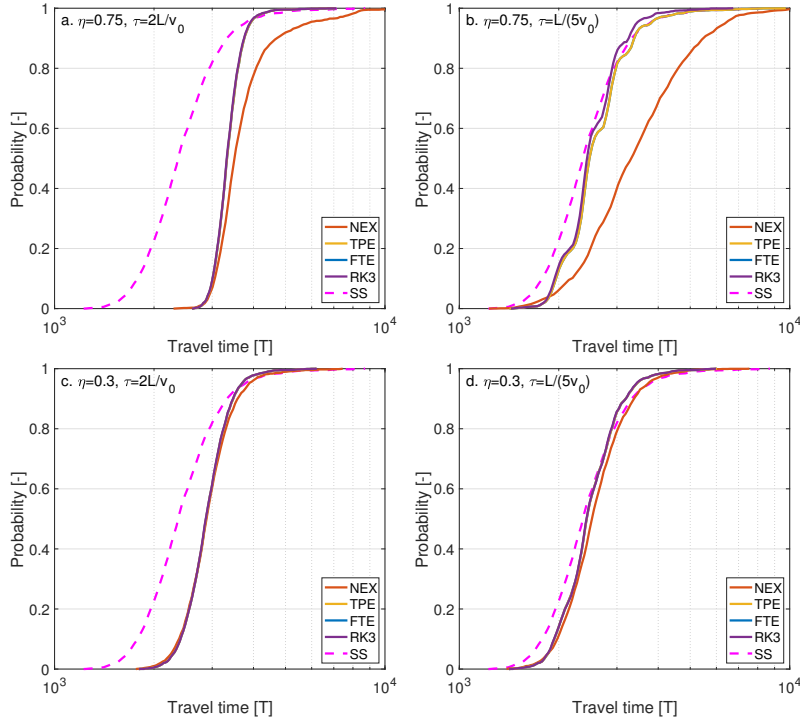


Figure 2: Comparison of the transient SMM models to a steady-state (SS) approximation for different magnitudes and periods of transient velocity changes. Small fluctuations with long periods may not require transient corrections, but it should be clear that as the frequency and magnitude of transient deviations increase the transient models depart significantly from the SS curve. Note also that three of the methods (TPE, FTE, RK3) generally agree with each other, whereas NEX is only reasonable under low-magnitude transience (small  $\eta$ ).

583 The flow domain was defined to have a length  $L = 100$  along the mean flow direction  $[L]$  and an  
 584 aspect ratio of 2 : 1 (length to width). The hydraulic conductivity tensor was locally isotropic, and the  
 585 scalar conductivity  $K$  in the domain was a log-normal multi-Gaussian random field with major and  
 586 minor correlation length scales of  $\lambda_1 = 10 [L]$  and  $\lambda_2 = 6 [L]$ , a geometric mean of  $K_* = 0.2 [L/T]$ ,  
 587 and unit variance of the log- $K$  field. The specific storage and porosity were taken to be spatially  
 588 constant and given by  $S_s = 1.0 \times 10^{-5} [1/L]$  and  $\phi = 0.3$ . A longitudinal spreading scenario was  
 589 created by assigning zero-flux boundaries at the extents of the minor axes and Dirichlet boundaries  
 590 at the ends of the major axes. The transient head changes were applied at the upstream boundary  
 591 according to a periodic sine function that varied the gradient across the domain from 2% to 4% with  
 592 a period of  $\tau = 4000 [T]$ . This fluctuation and parameter definitions satisfy the fast propagation and  
 593 slow variation criteria, and are also representative of the kinds of fluctuations one can expect in real,

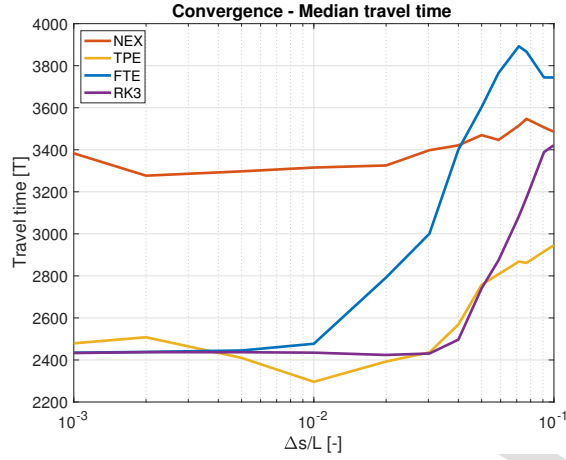


Figure 3: Convergence test of the proposed methods. As  $\Delta s$  is decreased, all but the NEX scheme approach the same mean behavior showing that they are solving the same system. TPE, FTE, and RK3 all converge to the same result for sufficiently refined discretizations, though they have different computational costs and assumptions.

594 undeveloped aquifers (Engdahl, 2017; McCallum and Shanafield, 2016).

595 The transient groundwater flow equation was solved using 2nd-order implicit finite differences and  
 596 the domain was uniformly discretized into square cells of size  $\Delta x = \Delta y = 1$  [L]. A snapshot of the  
 597 velocity field, head contours, and streamlines is shown in Fig. 4. The time step of the transient model  
 598 was  $\Delta t = 1$  [T] and flow and transport were solved sequentially at each time step using an operator-  
 599 splitting scheme. The reference, fully-resolved, RWPT transport simulation used a flux-weighted initial  
 600 condition of  $10^5$  particles released at  $x = 5$  and tracked forward over time to  $x = 95$  (corresponding to  
 601 a length  $L = 90$  for transport) to avoid any potential boundary impacts. Standard advective particle  
 602 tracking methods were used, integrated in time with a 2nd-order Runge-Kutta scheme.

603 A gamma distribution was fit to the Eulerian velocity PDF at each time step of the transient  
 604 flow simulation to simplify the parameterization of the SMM. The error of the fitted to the simulated  
 605 distribution was computed to confirm that the simplified model was reasonable. Root mean squared  
 606 relative errors of the fitted CDFs were small ( $\approx 0.011$  over all times) and the worst linear correlation  
 607 coefficient across all fits in time was  $\rho = 0.991$ ; this shows the gamma PDF is a good approximation  
 608 for this flow field, although it is not exact. Further, the Eulerian PDF was well described by Eq. (26)  
 609 with fixed  $\theta = 4.14$ , and the effect of transient changes at the boundary on the transient mean velocity  
 610 were modeled well by (28), with  $v_0 = 2.06 \times 10^{-2}$  [L/T],  $\eta = 0.33$ ,  $\tau = 4000$  [T], and  $t_0 = -\tau/2$ . A  
 611 comparison of the simulated and fitted transient velocity PDFs for 4 times is shown in Fig. 5. The time

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612 scale of the transient changes,  $\tau$ , was identical to that of the prescribed head changes, providing more  
613 evidence that the fast propagation assumption is valid in this case. In addition, the average gradient  
614 was 3%, so the  $\eta = 0.33$  factor represents a fluctuation of  $\pm 1\%$ . This value matches the specified range  
615 of a 2% to 4% gradient and shows that the transient velocity model can be inferred from the transient  
616 boundaries.

617 The correlation length was estimated based on the multi-Gaussian field as  $\ell_c = \lambda_1 = 10 [L]$ . The  
618 upscaled Bernoulli SMM uses  $\Delta s = 1 [L]$ , corresponding to  $\ell_c/\Delta s = 10$  and 90 steps to traverse  
619 the domain of transport, and tortuosity  $\chi = 1.12$ , which was computed directly from the flow field.  
620 An ensemble of 5000 random walkers were used for the SMM and the resulting BTCs for all four  
621 proposed transient SMM explicit schemes are shown in Fig. 6a, along with a steady-state SMM and  
622 the simulated BTC for comparison. The blue bars represent the (distributed, 2d) reference simulation.  
623 All data is binned according to the bars shown for the resolved simulations to make the comparison  
624 clearer; the value of each bar applies at its mid-point along the horizontal axis. The PDFs for the two  
625 best methods (TPE and RK3) are also shown in Fig. 6b, along with the steady-state simulation SS  
626 and the reference RWPT model; the main difference is that RK3 captures some of the secondary peak  
627 in the falling limb of the BTC. Note that, for the TPE method,  $\Delta s_v = a\Delta s$  with  $a = 1$  was used as for  
628 the analytical examples. As before, use of sufficiently small  $a$  and  $\Delta s$  would lead to similar results for  
629 TPE and RK3, at the cost of increased computational expense, but either of these schemes provides a  
630 good upscaled approximation of the simulated BTC.

631 The similarity of the different SMM approximations to the simulated BTC was assessed using root  
632 mean square error (RMSE) and the Hellinger distance (HD) metric (Hellinger, 1909), both applied to  
633 the PDF of travel times for the upscaled SMM simulations. The HD metric quantifies the overlap or  
634 similarity between the different PDFs, relative to the RWPT simulation. Values close to zero indicate  
635 strong similarity and values near one indicate high degrees of difference; smaller values mean better  
636 reproduction of the target distribution. Bianchi Janetti et al. (2020) used the HD metric to assess  
637 the performance of a trajectory-based SMM, demonstrating its utility in assessing SMMs. The RMSE  
638 and HD values are shown in Table 1 and demonstrate quantitatively that the transient versions all  
639 out-perform the steady-state SMM. The approximations of the fully-implicit model (see Section 3.3,  
640 FTE and RK3) offer a slight advantage but smaller values of  $\Delta s_v = a\Delta s$  (through using smaller values  
641 of the free parameter  $a$ ) would increase the accuracy of TPE to a similar extent. In any case, all the  
642 transient SMMs are considered overall good approximations. It is worth noting that the magnitude of  
643 the transient changes in this example are not as severe as some of those seen in Section 5.1, but there

Model	SS	NEX	TPE	FTE	RK3
HD	$1.01 \times 10^{-1}$	$9.63 \times 10^{-2}$	$7.94 \times 10^{-2}$	$5.50 \times 10^{-2}$	$5.52 \times 10^{-2}$
RMSE	$1.53 \times 10^{-2}$	$1.20 \times 10^{-2}$	$1.21 \times 10^{-2}$	$6.46 \times 10^{-3}$	$6.81 \times 10^{-3}$

Table 1: Hellinger distance (HD) metric and RMSE for the different SMM approximations of the simulated BTC. All transient SMM models show better performance than the steady-state model.

are clear departures from the steady-state model. This flow field is weakly heterogeneous due to its low log-K variance, so a higher degree of heterogeneity and greater contrast in the  $K$  field would likely lead to more significant departures. Whether or not these departures are significant enough to justify a fully-transient upscaled model leads directly into our discussion.

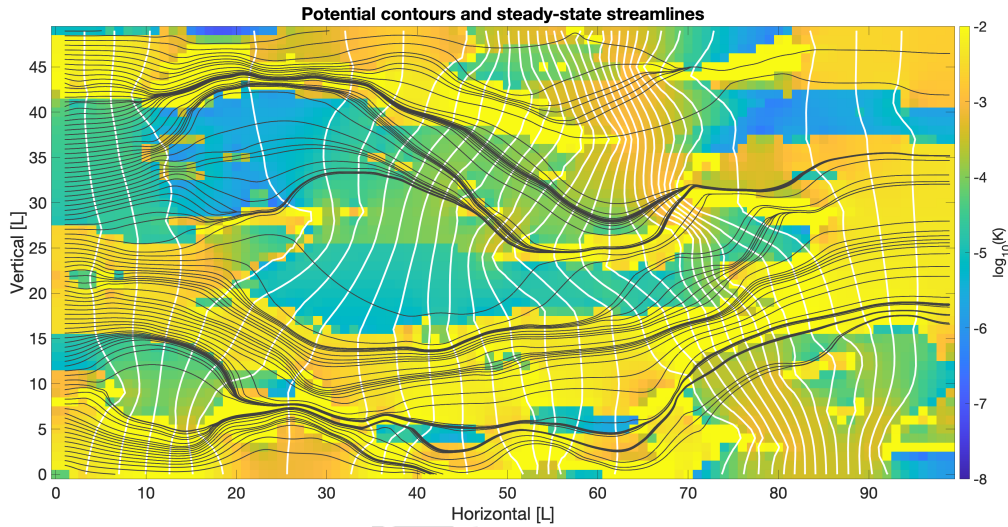


Figure 4: Heterogeneous, 2d flow field used for the transient model evaluation. White solid lines are contours of the potential field, black lines are the streamlines from the steady-state simulation, and the colors represent the base-10 logarithm of the velocity magnitude. The hydraulic conductivity field was generated using a hierarchical combination of transition probability geostatistics and stochastic multi-Gaussian fields.

## 6 Discussion and conclusions

The main purpose of this manuscript has been to determine if transient versions of spatial Markov models can be developed, and in this we have been successful. The heterogeneous velocity field example (Figure 4) with a time-dependent Dirichlet boundary condition verifies that transient SMM schemes can offer good upscaled approximations of key quantities such as breakthrough curves. As clearly seen in Fig. 6b, the proposed RK3 scheme most accurately captured the BTC, in particular regarding both

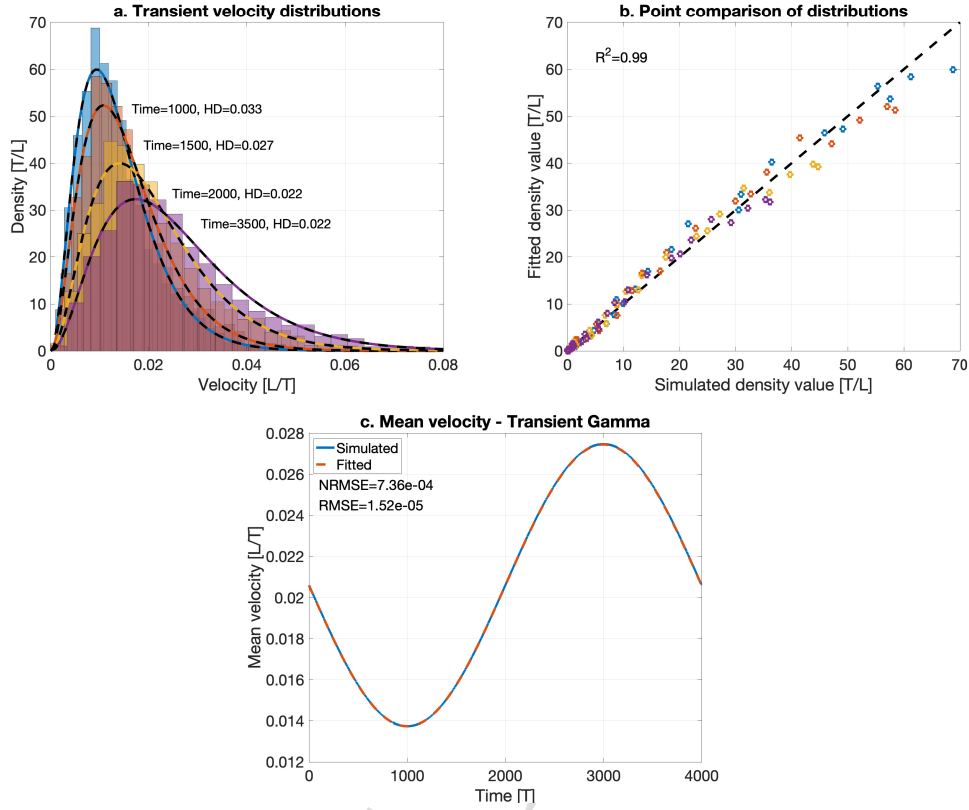


Figure 5: a. Simulated (bars) and fitted (lines) transient velocity PDFs in the 2d simulation domain for four times spanning the range of the transient cycle. HD denotes the Hellinger distance. b. Point-wise comparison of the fitted transient gamma distributions in panel (a) versus their simulated values. c. Comparison of the simulated and fitted mean velocity for the example flow field for one period of the transient cycle. Root mean squared (RMSE), normalized root mean squared errors (NRMSE),  $R^2$ , and HD confirm the accuracy and effectiveness of this functional approximation.

654 the maximum and transient-induced secondary peak. Nonetheless, both the TPE and RK3 methods  
 655 offer accuracy for a reasonable increase in computational cost over stationary SMMs, and both TPE  
 656 and FTE converge to the same answer as RK3 when the spatial step is sufficiently refined (see Fig. 3).

657 However, there is one major concern that cannot be overlooked, which is not unique to this study.  
 658 A key question regarding practical application of any upscaled model is, can the model parameters  
 659 be inferred reliably? In this case, the bare-minimum required elements for the transient SMMs are:  
 660 i) the correlation length scale for the Bernoulli relaxation process, ii) a reference Lagrangian velocity  
 661 distribution, and iii) a model for how that distribution changes over time. Each of these is considered  
 662 independently in the following paragraphs.

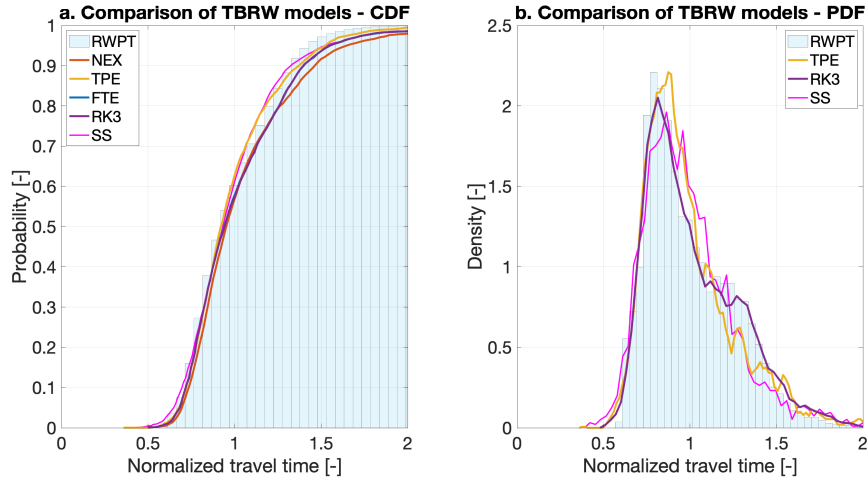


Figure 6: Comparison of the BTCs computed from the (fully-resolved) RWPT-based and (upscaled) transient SMM simulations. This example uses a small, but realistic, transient forcing that might be expected in natural aquifers. The advantage of the transient model is evident in the PDF plot, where the small secondary peak in the RWPT-BTC is captured by the RK3 scheme but completely missed by the steady-state (SS) approximation. As discussed in detail in the text, better results for the different transient methods can be obtained by further refining the discretization.

663 The first item is the model for the SMM transitions. We have assumed the spatial Markov correla-  
 664 tions do not vary over time. There are strong connections between geological structure and the spatial  
 665 correlations (Sherman et al., 2020), and geological structures generally change on time scales orders  
 666 of magnitude larger than solute transport, so modeling the correlations does not represent a unique  
 667 or undue burden to the transient random walk. Furthermore, if a full SMM transition matrix (e.g  
 668 Engdahl and Bolster, 2020) was used instead of a Bernoulli relaxation process there are only a few  
 669 more operational issues to consider. One is whether the initial and final bins change simultaneously  
 670 as the Lagrangian velocity PDF evolves; we see no reason they would not evolve jointly, particularly  
 671 since the model would become intractable if they did not. Another concern is whether the bounds  
 672 on the individual velocity bins should evolve over time. The development of the fully-implicit scheme  
 673 (Section 3.3) required that small changes in velocity cannot significantly impact the velocity rank, so  
 674 the extension of this for broader validity is that slow changes to the velocity field cannot change the  
 675 ranks of the distribution; this is merely another way of looking at the slow-variation criterion (23).  
 676 In the absence of a strong transient boundary, our view is that a “shock” to the system would be  
 677 necessary to invalidate the assumption of stable velocity ranks, such as abruptly turning on a large  
 678 pumping well. If this were the case, the slow variation criterion would clearly be violated, negating

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4 679 the benefits of application of the upscaled model in the first place. Aside from these, we see no obvi-  
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6 680 ous additional considerations necessary to adopt a full SMM transition matrix instead of a Bernoulli  
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8 681 relaxation process.

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10 682 The second item to consider is how to obtain the reference Lagrangian velocity distribution. This  
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12 683 is arguably the most important yet difficult component to obtain. The best one could be expected to  
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14 684 do is to use a data-driven, geostatistical description of the expected hydraulic conductivity field that  
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16 685 is subjected to the anticipated boundary conditions for flow and transport. Evaluating this expected  
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18 686 distribution might require methods like a stochastic Monte-Carlo ensemble, but each realization would  
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20 687 be steady-state and so the ensemble should run quite fast. From these, the expected behaviors of the  
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22 688 reference velocity distribution can be obtained, or any other threshold value (such as percentiles) to  
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24 689 assess the uncertainty range, and the slow variation and fast propagation criteria (25) could easily be  
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26 690 assessed at the same time. The resulting velocity distributions could then be used in a transient SMM  
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28 691 in lieu of a large ensemble of transient Monte-Carlo simulations, which would surely offer large compu-  
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30 692 tational savings. We consider this a reasonable compromise, but it must be noted that uncertainties in  
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32 693 the geostatistical description, including unresolved heterogeneities or non-stationarities, will propagate  
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34 694 into the upscaled model as will uncertainties in the boundary conditions. It is also possible to estimate  
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36 695 SMM model parameters from breakthrough curves alone (see Sherman et al., 2017), though doing so  
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38 696 in aquifers would be hampered by incomplete sampling or recovery of a tracer. Estimating the velocity  
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40 697 PDF remains challenging but methods exist by which it can be reasonably approximated, which is all  
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42 698 one should expect when using an upscaled model.

43  
44 699 The third item is the model for how the reference velocity distribution changes over time. The  
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46 700 model for changes is at least “plausibly obtainable” because of the fast propagation criteria. The  
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48 701 key point is that if (19) is satisfied then the relative changes at the boundaries of the flow field  
49  
50 702 can be used to approximate the changes in the velocity PDF. Engdahl (2017) considered a system  
51  
52 703 where combinations of transient Dirichlet boundaries were used at the ends of a confined, longitudinal  
53  
54 704 domain where transport was simulated using the fully transient velocity fields. The results showed  
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56 705 strong correlation between the transient forcing and the velocity fluctuations, meaning that relative  
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58 706 changes in the mean can be inferred, hence our definition of (28). Long-term shifts in the mean may  
59  
60 707 also be accommodated (e.g Massoudieh, 2013), which can quickly overwhelm higher frequency impacts  
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62 708 on the mean. So, depending on the time scales of transport, it may be more important to capture  
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64 709 long-term trends, which can be accurately inferred from observation well data, though models would  
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710 be needed for forecasting. Some inaccuracies are inevitable, but as long as the estimated transient

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4 signal is representative of a system's overall changes, reasonable results can be expected. Our example  
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6 from Section 5.2 illustrates this idea: the fitted model for the velocity transience was based solely on  
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8 the transience at the boundaries, and the model performed well.

9  
10 Upscaled models should not strive to be perfect reproductions of transport behaviors, as this  
11  
12 would invalidate their purpose of being large-scale approximations through over-fitting. The goal  
13  
14 of the transient Spatial Markov models proposed herein is to balance the complexities of transient  
15  
16 velocity fields with the simplicity of upscaled models using a framework that leverages recent advances  
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18 in correlated velocity models. The main point of this discussion is that our definitions of the slow  
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20 variation and fast propagation criteria (25) provide all the necessary evaluation criteria to assess the  
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22 validity and usefulness of the proposed models for a given scenario. There is a need for site-specific  
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24 data in order to evaluate those criteria, and the decision to use transient upscaled models likely comes  
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26 down to the subjective question of sufficient data abundance: is there enough data to confidently build  
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28 the desired model? To this we can offer no new insights because every case is unique. We can say  
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30 that the data requirements for transient SMMs falls between those of steady-state SMMs and spatially  
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32 explicit, distributed models. There are benefits to accuracy (Section 5) relative to the former, and  
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34 clear advantages of speed relative to the latter, but ultimately the data dictate which models should  
35  
36 be used for a given purpose.

## 37 A Numerical determination of the flow variation window

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39 In this appendix, we describe a straightforward numerical approach to obtain the variation window  
40  
41  $\Delta t_v$  according to Eq. (9). Note that more sophisticated root-finding techniques could also be employed.

42  
43 In order to sequentially determine the  $\Delta t_{v,k'}$  associated with each of the turning point times  $T_{v,k'}$ ,  
44  
45 see Eq. (10), we consider a time resolution for step  $k'$  given by

$$46 \Delta t_{k'} = \frac{\Delta s_v}{\bar{v}(T_{v,k'})} = \frac{a\Delta s}{\bar{v}(T_{v,k'})}. \quad (29)$$

47  
48 This resolution represents the time necessary to cross the spatial variation threshold  $\Delta s_v = a\Delta s$  of  
49  
50 Eq. (9) at the current mean velocity. We expect this choice to provide a good compromise between  
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52 speed and accuracy, especially when the slow-variation condition (a) is met (see Section 3), but note  
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54 that a finer or coarser resolution could be employed. The variation window  $\Delta t_{v,k'} = n_{k'}\Delta t_{k'}$  is then  
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56 determined in terms of the number  $n_{k'}$  of time-resolution steps required to exceed the allowed variation  
57  
58



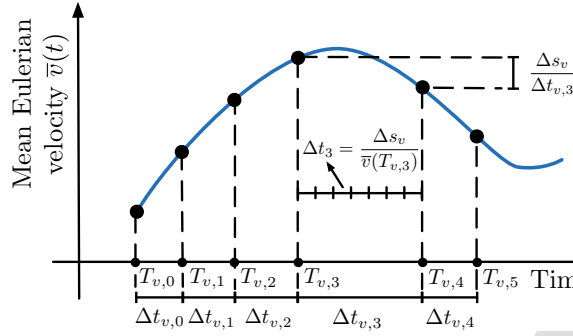


Figure 7: Illustration of the algorithm to determine the variation windows  $\Delta t_{v,k'}$  associated with temporal variation of the Eulerian mean velocity. The variation windows  $\Delta t_{v,k'} = T_{v,k'+1} - T_{v,k'}$  determine the turning point times  $T_{v,k'}$ , starting at  $T_{v,0} = T_0$ , at which flow velocity variations are taken into account. Each  $\Delta t_{v,k'}$  is determined so that the mean velocity variation  $\Delta v_{k'} = |\bar{v}(T_{v,k'} + \Delta t_{v,k'}) - \bar{v}(T_{v,k'})|$  is such that  $\Delta v_{k'} \Delta t_{v,k'} = \Delta s_v$ , where  $\Delta s_v$  is related to the spatial-Markov step size by a factor  $a \leq 1$ ,  $\Delta s_v = a \Delta s$ . In order to determine these variation windows numerically, we consider a step-dependent maximum resolution  $\Delta t_{k'} = \Delta s_v / \bar{v}(T_{v,k'})$ , as illustrated for  $\Delta t_{v,3}$ . Then,  $\Delta t_{v,k'}$  is approximated the smallest integer multiple of  $\Delta t_{k'}$  such that  $\Delta v_{k'} \Delta t_{v,k'}$  exceeds  $\Delta s_v$ .

738  $\Delta s_v$ . Numerically,  $n_{k'}$  can be computed as the smallest integer  $n$  such that

$$|\bar{v}(T_{v,k'} + n \Delta t_{k'}) - \bar{v}(T_{v,k'})| n \Delta t_{k'} > \Delta s_v. \quad (30)$$

739 In the simplest implementation, the value of the mean velocity over time is scanned sequentially,  
 740 at a temporal resolution of  $\Delta t_{k'}$ , until the prescribed tolerance  $\Delta s_v$  is exceeded. This procedure is  
 741 illustrated in Fig. 7.

## 742 B Parameterization and fitting of the gamma velocity PDF

743 The gamma PDF is typically parameterized in terms of a shape parameter  $\alpha$  and a rate parameter  $\xi$ ,  
 744 defined such that

$$p_{\Gamma}(x; \alpha, \xi) = \frac{\xi^{\alpha}}{\Gamma(\alpha)} x^{\alpha-1} e^{-\xi x}, \quad (31)$$

745 where, for a random variable with this distribution,  $p_{\Gamma}(x; \alpha, \xi) dx$  is the probability of a value in the  
 746 infinitesimal vicinity  $dx$  of  $x$ . This PDF can be fit to velocity data directly by applying a standard  
 747 minimum-square criterion to determine  $\alpha$  and  $\xi$ .

748 In the present application, where the Eulerian velocities are taken to be gamma-distributed, it is  
 749 convenient to choose a parameterization that emphasizes features that are key to solute transport.

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4 The scale parameter  $\alpha$  controls the tailing properties at low velocities, which control the large-time  
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6 750 tailing of transit times and thus the late-time dispersion behavior (Aquino and Le Borgne, 2021; Dentz  
7  
8 751 et al., 2016). Thus, we choose to keep  $\theta = \alpha$  as a parameter. On the other hand, the mean  $\alpha/\xi$  of the  
9  
10 752 gamma distribution has a clear physical meaning in our context: it represents the spatial average of  
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12 753 the velocity at a given time. Thus, we parameterize our Eulerian velocity PDF by setting  $\xi = \alpha/\bar{v}(t)$ ,  
13  
14 754 i.e.,

$$15 \quad p_E(v; t) = p_\Gamma \left[ v; \alpha, \frac{\alpha}{\bar{v}(t)} \right], \quad (32)$$

16  
17 755 which corresponds to Eq. (26). To fit this form to velocity data at a given time, we fit  $\alpha$  to the  
18  
19 756 low-velocity behavior of the data PDF, and set  $\bar{v}(t)$  to the spatial mean of the data.

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21 757 Alternatively, we could enforce the correct average velocity  $\bar{v}(t) = \alpha/\xi$  and velocity variance  $\sigma_v^2 =$   
22  
23 758  $\alpha/\xi^2$ , which can be achieved by setting

$$24 \quad p_E(v; t) = p_\Gamma \left[ v; \frac{\bar{v}^2(t)}{\sigma_v^2(t)}, \frac{\bar{v}(t)}{\sigma_v^2(t)} \right]. \quad (33)$$

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29 759 To fit this form, we would simply set the mean and variance according to the data.

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31 760 These three parameterizations are formally equivalent. If the true Eulerian velocity distribution  
32  
33 761 were gamma, the three fitting procedures would also be equivalent. However, if the latter are applied  
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35 762 to arbitrary data, they may produce different results, as they focus on constraining different quantities  
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37 763 given the two degrees of freedom (independent parameters) that characterize a gamma distribution.  
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39 764 The first aims to provide the “overall best” fit for the PDF itself, while the second enforces the correct  
40  
41 765 mean velocity and large transit time (low velocity) tailing, and in turn the third captures mean velocity  
42  
43 766 and velocity variance exactly.

## 44 45 46 767 **C Implementing the flux-weighted CDF**

47  
48 768 Flux-weighting of the gamma PDF in Eq. (31) corresponds to multiplication by  $v/\bar{v}$ , from which we  
49  
50 769 can obtain the associated cumulative distribution function by integration:

$$51 \quad P_\Gamma(v; \alpha, \xi) = \frac{1}{\bar{v}\Gamma(\alpha)} \int_0^v (\xi v')^\alpha e^{-\xi v'} dv',$$

$$52 \quad = \frac{\gamma(\alpha + 1, \xi v)}{\bar{v}\Gamma(\alpha)}, \quad (34)$$

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4 where  $\gamma(\cdot, \cdot)$  is the lower incomplete gamma function. Recalling that  $\xi = \alpha/\bar{v}$ , we obtain  
5  
6

$$P_L(v; t) = P_T[v, \alpha, \alpha/\bar{v}(t)] = \frac{\gamma[\alpha + 1, \alpha v/\bar{v}(t)]}{\bar{v}(t)\Gamma(\alpha)}. \quad (35)$$

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10 This form of the flux-weighted CDF allows standard, well-known functions to be used to approximate  
11  
12 the SMM numerically.  
13  
14

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Highlights

Transient versions of the spatial Markov model are developed

Each flavor has tradeoffs in simplicity and robustness suited to different cases

Robust validity criteria to assess model applicability are derived

Journal Pre-proof



**Author statement**

**Engdahl** - Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Writing - Review & Editing, Visualization

**Aquino** - Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Writing - Review & Editing, Visualization

Journal Pre-proof

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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