



Perspective on theories of non-Fickian transport in heterogeneous media

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ABSTRACT

Subsurface fluid flow and solute transport take place in a multiscale heterogeneous environment. Neither these phenomena nor their host environment can be observed or described with certainty at all scales and locations of relevance. The resulting ambiguity has led to alternative conceptualizations of flow and transport and multiple ways of addressing their scale and space–time dependencies. We focus our attention on four approaches that give rise to nonlocal representations of advective and dispersive transport of nonreactive tracers in randomly heterogeneous porous or fractured continua. We compare these approaches theoretically on the basis of their underlying premises and the mathematical forms of the corresponding nonlocal advective–dispersive terms. One of the four approaches describes transport at some reference support scale by a classical (Fickian) advection–dispersion equation (ADE) in which velocity is a spatially (and possibly temporally) correlated random field. The randomness of the velocity, which is given by Darcy's law, stems from random fluctuations in hydraulic conductivity (and advective porosity though this is often disregarded). Averaging the stochastic ADE over an ensemble of velocity fields results in a space–time–nonlocal representation of mean advective–dispersive flux, an approach we designate as stnADE. A closely related space–time–nonlocal representation of ensemble mean transport is obtained upon averaging the motion of solute particles through a random velocity field within a Lagrangian framework, an approach we designate stnL. The concept of continuous time random walk (CTRW) yields a representation of advective–dispersive flux that is nonlocal in time but local in space. Closely related to the latter are forms of ADE entailing fractional derivatives (fADE) which leads to representations of advective–dispersive flux that are nonlocal in space but local in time; nonlocality in time arises in the context of multirate mass transfer models, which we exclude from consideration in this paper. We describe briefly each of these four nonlocal approaches and offer a perspective on their differences, commonalities, and relative merits as analytical and predictive tools.

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1. Introduction

Transport of nonreactive (passive) tracers through porous media has been traditionally described by a deterministic advection–dispersion equation (ADE) based on analogy to Fick's laws of diffusion [5]. Nonreactive tracer transport that is not adequately described by an ADE is therefore said to be non-Fickian. In the special case of Fickian transport at a uniform velocity far from sources or boundaries, a slug of tracer evolves into a Gaussian plume with a variance that grows linearly with time. Correspondingly, in the special case where mean-uniform flow takes place through a heterogeneous porous or fractured continuum, non-Fickian behavior manifests itself through deviations of the mean concentration profile from a Gaussian shape and/or a nonlinear growth rate of a plume's mean squared displacement. Such behavior (especially but not only when the growth rate is a power-law) is com-

monly referred to as anomalous transport [53]. The purpose of our paper is to provide a perspective on some modern theories of non-Fickian transport in heterogeneous porous media in velocity fields that are either uniform or nonuniform in the mean. We start by recalling briefly the fundamental tenets of traditional Fickian transport.

1.1. Classical ADE

The macroscopic description of tracer fate and migration in a uniform porous medium by means of an ADE rests on an assumed analogy to Fick's laws of diffusive transport. Analogy to Fick's first law posits that macroscopic tracer mass flux $\mathbf{J}(\mathbf{x}, t)$ through a fluid-saturated pore space, at any "point" \mathbf{x} within a fictitious continuum representing the fluid–solid mixture at time t , can be expressed as $\mathbf{J} = \mathbf{J}_{adv} + \mathbf{J}_{dir} + \mathbf{J}_{dis}$, where $\mathbf{J}_{adv}(\mathbf{x}, t)$ is advective mass flux attributed to the macroscopic fluid velocity $\mathbf{v}(\mathbf{x}, t)$ through the pore space (Darcy flux divided by a scalar advective, sometimes called effective or kinematic, porosity), $\mathbf{J}_{dir}(\mathbf{x}, t)$ is mass flux due to molecular diffusion across the saturated pore space, and $\mathbf{J}_{dis}(\mathbf{x}, t)$ is dispersive

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mass flux attributed to random deviations of fluid velocities within this pore space from their macroscopic value \mathbf{v} . The analogy further posits that

$$\mathbf{J}_{\text{adv}} = \mathbf{v}c, \quad \mathbf{J}_{\text{dif}} = -D_m \nabla c, \quad \mathbf{J}_{\text{dis}} = -\mathbf{D}_d \nabla c, \quad (1)$$

where $c(\mathbf{x}, t)$ is macroscopic concentration (solute mass per unit saturated pore space), D_m is an effective molecular diffusion coefficient (smaller than that in pure fluid due to the obstruction of molecular paths by solids), and $\mathbf{D}_d(\mathbf{x}, t)$ is a dispersion tensor (typically expressed as $\mathbf{D}_d = \lambda \mathbf{v}$, where v is the magnitude of \mathbf{v} and λ is a dispersivity tensor whose principal components are considered to be properties of the medium, parallel and normal to \mathbf{v}). Analogy to Fick's second law posits that solute mass in the saturated pore space is conserved at the macro-scale. In the absence of sinks or sources, this yields a mass balance equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{J}_{\text{adv}} + \mathbf{J}_{\text{dif}} + \mathbf{J}_{\text{dis}}). \quad (2)$$

Substituting (1) into (2) yields the advection–dispersion equation (ADE)

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + \nabla \cdot [(D_m \mathbf{I} + \mathbf{D}_d) \nabla c], \quad (3)$$

where \mathbf{I} is the identity tensor.

1.2. Non-Fickian behavior

The classical ADE (3) often fails to predict observed behavior of solute in the subsurface. Non-Fickian transport behavior has been observed both in the laboratory [78,79,47,13,58] and in the field [68,80,48,32,77,92]. The common feature of these and other experiments is heterogeneity of porous media. Similar non-Fickian behavior has been attributed to heterogeneity of ambient environments in areas as diverse as virus migration in cells [75], protein dynamics [89], transport of lipid granules in the cytoplasm of living yeast cells [85], fluctuations of stocks on financial markets [69], and animal movement in heterogeneous landscapes [39]. Mean non-Fickian behavior has likewise been observed and analyzed in turbulent dispersion (e.g. [43,44,72,31,45]).

To understand the failure of the ADE to model transport in heterogeneous media, it is important to recall that traditionally (1)–(3) have been considered to be deterministic. This required one to assume that all quantities entering into the ADE are defined on a representative elementary volume (REV) large enough to render their space–time variations sufficiently slow to be described deterministically [5]. In dealing with heterogeneous media it is common to consider smaller support volumes (designated here by ω) which, though large enough to be ascribed (directly or indirectly) measurable macroscopic properties, do not represent REV's, as explained in greater detail in [64,63]. Instead, quantities defined on the scale of ω vary rapidly enough to justify treating them as random functions of space and/or time over a fictitious macroscopic continuum. When this is the case, the ADE becomes stochastic. The most common (numerical Monte Carlo) method of solving a stochastic ADE is to generate numerous random realizations of the underlying velocity field, solve the ADE numerically for each field and average the results over all realizations. The results are summarized in terms of multivariate (due to the space–time dependence of \mathbf{v} and c) sample statistics such as frequency histograms and sample moments (most commonly mean, variance, auto- and cross-covariance). As the number of realizations increases the sample statistics converge (if all is well) to their theoretical stochastic or ensemble statistics.

It has been demonstrated theoretically [20,15,42,65,94,61,91,22] and computationally [37,57,56] that even if transport in

each random realization is governed by the ADE, the ensemble mean deterministic transport through randomly heterogeneous media is generally non-Fickian.

Though the above stochastic theories of transport in porous media are closely related to those underlying turbulent diffusion, there are two fundamental differences between them: (a) the first takes place at small and the second at large Reynolds numbers, and (b) porous flow velocities depend in a known way on medium hydraulic properties coupled with externally imposed head conditions while turbulent velocities fluctuate randomly in space–time. It follows that whereas uncertainty about turbulent velocities is aleatory (controlled by chance), uncertainty about velocities in a porous medium is epistemic (due to incomplete knowledge of medium properties and imposed heads) and hence reducible through conditioning on hydrogeologic data (e.g. [81]). Whereas the aleatory nature of turbulent velocities may justify treating them as being space–time stationary and perhaps even Gaussian, conditioning coupled with the imposition of (at least partially) known forcings (initial conditions, boundary conditions and sources) render porous flow velocities nonstationary and generally non-Gaussian (e.g. [57,56]). We therefore consider it essential that stochastic theories of flow and transport in porous media be capable of accounting for nonstationary and non-Gaussian behaviors in bounded domains subject to realistic forcings and descriptions of site geology (for the latter see [88,71,46] and references therein), though not all presently do so.

In a stationary mean-uniform velocity field, non-Fickian transport manifests itself through an early (pre-asymptotic) linear increase in longitudinal and transverse dispersivities with mean travel distance (or, equivalently, time). Tracer experiments of Peaudecerf and Sauty [68] provided the first documented field evidence that an individual plume may spread at variable rates over long periods of time. That the same can happen over a much longer period of at least 600 days in a mildly heterogeneous geologic medium is vividly demonstrated by the celebrated tracer experiment at Borden, Ontario, Canada [48,80]. Whereas longitudinal dispersivity (parallel to the mean velocity) eventually stabilizes at a constant “Fickian” asymptote, the transverse dispersivity first reaches a peak and then either decreases to zero or stabilizes at a constant value below the peak, depending on the model. Dentz et al. [26,27] have demonstrated numerically and Attinger et al. [3] have proven analytically that whereas in two dimensions the transverse dispersivity tends asymptotically to small laboratory-scale values, in three dimensions it stabilizes at much larger field-scale values. Whereas the two-dimensional behavior is consistent with second-order perturbation theories (e.g. [20,15,21]), the three-dimensional behavior agrees more closely with a quasilinear theory based on Corrsin's conjecture [65,94].

Non-Fickian pre-asymptotic behavior is explained by the fact that as a plume grows, it gradually encounters (samples) heterogeneities on larger and larger scales. In a statistically homogeneous medium, asymptotic Fickian behavior may eventually be reached due to the limited range of these scales. Yet when one juxtaposes apparent longitudinal dispersivities, determined in the laboratory and in the field for a variety of porous and fractured media on the basis of Fickian models that consider medium properties to be spatially uniform (and thus provide no resolution of the way in which these properties vary in space), their values increase consistently with the scale of observation (plume mean travel distance or travel time) at a rate that is faster than linear [60]. This persistent, supralinear dispersivity scale effect has been interpreted [60,59,30] to imply that the juxtaposed media represent a hierarchy of log permeability fields which behave jointly as a random fractal. When one juxtaposes apparent longitudinal dispersivities determined on the basis of Fickian models that do resolve some larger-scale spatial variations in medium properties, one finds

[62,64] that the rate of dispersivity increase with observation scale diminishes.

In the presence of boundaries and/or under conditioning on measurements, the velocity field becomes nonstationary. Though this requires a nonlocal representation of mean transport (see below), localization is sometimes possible as an approximation. Corresponding analyses [57,56] demonstrate that boundaries tend to increase the rate at which longitudinal and transverse dispersivities vary with mean travel distance (or, equivalently, time) and conditioning tends to decrease it. An asymptotic Fickian regime fails to develop, as the dispersivities vary continuously with mean travel distance and the plume remains non-Gaussian.

1.3. Nonlocal representations

Despite some examples to the contrary (e.g. [62,25]), non-Fickian transport in heterogeneous porous media generally manifests itself through nonlocal mean behavior represented by integro-differential equations or (where such exist) their fractional derivative equivalents. Since subsurface fluid flow and solute transport take place in a multiscale heterogeneous environment, neither these phenomena nor their host environment can be observed or described with certainty at all scales and locations of relevance. The resulting ambiguity allows for alternative conceptualizations of flow and transport and multiple ways of addressing their scale and space–time dependencies.

In this paper, we focus on four conceptualizations and representations of nonlocal mean transport of nonreactive tracers that have gained some prominence in the hydrologic literature over the last two decades: a space–time–nonlocal representation based on the assumption of advective–dispersive behavior at a reference support scale [42,61,91,57,56] which we designate stnADE; a space–time–nonlocal representation based on a Lagrangian representation of particle motions in a stationary random velocity field [18,16] which we denote by stnL; a time–nonlocal representation of mean particle transport on a discrete lattice having arbitrarily small cell sizes based on a continuous time random walk (CTRW) concept (e.g. [55,73,8]); and space–fractional representations of advection and dispersion (fADE) [50,7,6,93] that are nonlocal in space but local (except in the case of multirate mass transfer) in time.

We describe briefly each of these four nonlocal approaches and offer a perspective on their differences, commonalities, and relative merits as analytical and predictive tools. We compare these approaches theoretically on the basis of their underlying premises with emphasis on the mathematical forms of the corresponding nonlocal advection and dispersion terms. We omit from our discussion other models of non-Fickian transport (see [17]). Some of these, such as models based on spatial averaging (e.g. [70]) and homogenization (e.g. [4]), generally aim at obtaining localized forms of advective–dispersive flux. Others, such as multirate mass transfer [35] and delayed diffusion [28] models, can be related to the four approaches analyzed in this paper [24,28].

2. Stochastic ADE representation of non-Fickian transport

The most recent and general representation of mean space–time nonlocality based on stochastic ADE is that of Morales-Casique et al. [57,56]. This explicit (integro-differential) representation of mean space–time–nonlocality, which we designate stnADE, is a generalization of the Eulerian–Lagrangian representation [67]. It admits time varying as well as nonstationary velocities fields due to the effects of sources, boundaries and conditioning on measured values of support-scale parameters and/or state variables. The approach is based on the premise that Darcian and Fickian behaviors occur on some local support scale ω centered about point \mathbf{x} , i.e.,

that transport on scale ω can be accurately described by the ADE (5) below. The local dispersion coefficient \mathbf{D}_d is assumed to be constant and deterministic, and the advective velocity \mathbf{v} is modeled as a space–time nonstationary random field satisfying a stochastic flow equation:

$$\nabla \cdot \mathbf{v} = f(\mathbf{x}, t), \quad (4)$$

where $f(\mathbf{x}, t)$ is an ω -scale random fluid source (and/or accumulation term involving the time derivative of head) normalized by advective porosity, which is treated as a constant scalar. The statistics of f , including its joint moments with \mathbf{v} , are taken to be known. These moments are determined by solving the stochastic flow equation (4) subject to appropriate (generally random) initial and boundary conditions, conditioned on measurements of hydraulic conductivity and advective porosity and/or hydraulic head and flux on support ω . Methods to compute them include forward and inverse conditional Monte Carlo simulation or the solution of corresponding recursive conditional moment equations [82,83,34,38,90].

2.1. Stochastic ADE

Allowing for the presence of (uncertain) random sources/sinks $g(\mathbf{x}, t)$, the concentration of a nonreactive solute in a domain Ω bounded by Γ is governed locally by the advection–dispersion equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + \nabla \cdot (\mathbf{D}_d \nabla c) + g, \quad \mathbf{x} \in \Omega \quad (5)$$

subject to initial and boundary conditions

$$c(\mathbf{x}, 0) = C_0(\mathbf{x}), \quad \mathbf{x} \in \Omega, \quad (6a)$$

$$c(\mathbf{x}, t) = C_D(\mathbf{x}, t), \quad \mathbf{x} \in \Gamma_1, \quad (6b)$$

$$-\mathbf{D}_d \nabla c(\mathbf{x}, t) \cdot \mathbf{n}(\mathbf{x}) = W(\mathbf{x}, t), \quad \mathbf{x} \in \Gamma_2, \quad (6c)$$

$$[\mathbf{v}(\mathbf{x}, t)c(\mathbf{x}, t) - \mathbf{D}_d \nabla c(\mathbf{x}, t)] \cdot \mathbf{n}(\mathbf{x}) = P(\mathbf{x}, t), \quad \mathbf{x} \in \Gamma_3, \quad (6d)$$

where C_D is a random concentration prescribed on boundary segment Γ_1 , W is a random dispersive flux normal to boundary segment Γ_2 , P is a random advective–dispersive flux prescribed on boundary segment Γ_3 , and \mathbf{n} is an outward unit normal to any segment of $\Gamma = \Gamma_1 \cup \Gamma_2 \cup \Gamma_3$. All quantities are defined on the scale ω . Though the theory does not require it, for simplicity and without loss of generality all forcing terms g , C_0 , C_D , W , P are taken to be prescribed in a manner that renders them statistically independent of \mathbf{v} and each other. Treating the solute source g as being statistically independent of the velocity field is justified when tracer is introduced into groundwater without materially perturbing \mathbf{v} and f , as by spreading contaminants on the soil surface without impacting infiltration rates, or introducing a tracer into an active well without affecting its flow rate. Taking initial and boundary terms to be statistically independent of the velocity field, as represented by \mathbf{v} and f , is justified when the solute acts as a tracer so that it does not impact fluid density, and when it is sampled at some reference time $t = 0$ and at the boundaries without materially perturbing the velocity field (by remote sensing as in the case of radioactive tracers, or by extracting minute volumes of fluid by means of solution samplers).

Eqs. (6) allow for proper representation of inflow, outflow and no-flow boundary conditions. Although conditions at outflow boundaries are generally unknown, they must nevertheless be prescribed for a solution to exist when \mathbf{D}_d is nonzero; the effect of such boundaries on upstream concentration diminishes with increasing Péclet number [33,67]. For convenience, it is common to set $W = 0$ at outflow boundaries, thereby neglecting dispersion and assuming that resident concentration is continuous across the outlet [23,56]. Another option is to approximate concentration gradients along outflow boundaries numerically by their values at nearby upstream grid nodes [12].

2.2. Mean transport equations

Random functions $a(\mathbf{x}, t)$ are expressed as

$$a(\mathbf{x}, t) = \langle a(\mathbf{x}, t) \rangle_c + a'(\mathbf{x}, t), \quad \langle a'(\mathbf{x}, t) \rangle_c \equiv 0, \quad (7)$$

where $\langle \cdot \rangle_c$ designates ensemble mean (statistical expectation) conditioned on measurements (as implied by the subscript; for simplicity and without loss of generality, the authors do not condition forcing terms and therefore drop the subscript from their moments) and primed quantities are zero-mean random fluctuations about the mean. The former are viewed as unbiased predictors of their random counterparts, and the latter as the associated prediction errors, all defined on the scale ω (without upscaling of any kind). In the theoretical limit of full conditioning the prediction error $a'(\mathbf{x}, t)$ tends to zero and the predictor $\langle a(\mathbf{x}, t) \rangle_c$ approaches the true value $a(\mathbf{x}, t)$ regardless of ergodicity (which is therefore not required for the approach to be valid). Decomposing all random functions in (5) according to (7) and taking conditional ensemble mean (which, for all forcing terms, reduces to the unconditional mean) leads to

$$\frac{\partial \langle c \rangle_c}{\partial t} = -\nabla \cdot (\langle \mathbf{v} \rangle_c \langle c \rangle_c) + \nabla \cdot (\mathbf{D}_d \nabla \langle c \rangle_c + \mathbf{Q}_c) + \langle g \rangle, \quad \mathbf{x} \in \Omega, \quad (8)$$

where $\mathbf{Q}_c(\mathbf{x}, t) = \langle \mathbf{v}'(\mathbf{x}, t) c'(\mathbf{x}, t) \rangle_c$ is the conditional dispersive flux. In a similar manner one obtains from (6) the initial and boundary conditions for (8)

$$\langle c(\mathbf{x}, 0) \rangle_c = \langle C_0(\mathbf{x}) \rangle, \quad \mathbf{x} \in \Omega, \quad (9a)$$

$$\langle c(\mathbf{x}, t) \rangle_c = \langle C_D(\mathbf{x}, t) \rangle, \quad \mathbf{x} \in \Gamma_1, \quad (9b)$$

$$-\mathbf{D}_d \nabla \langle c(\mathbf{x}, t) \rangle_c \cdot \mathbf{n}(\mathbf{x}) = \langle W(\mathbf{x}, t) \rangle, \quad \mathbf{x} \in \Gamma_2, \quad (9c)$$

$$[\langle \mathbf{v}(\mathbf{x}, t) \rangle_c \langle c(\mathbf{x}, t) \rangle_c - \mathbf{D}_d \nabla \langle c(\mathbf{x}, t) \rangle_c + \mathbf{Q}_c(\mathbf{x}, t)] \cdot \mathbf{n}(\mathbf{x}) = \langle P(\mathbf{x}, t) \rangle, \quad \mathbf{x} \in \Gamma_3. \quad (9d)$$

The dispersive flux \mathbf{Q}_c is given exactly by the implicit expression

$$\begin{aligned} \mathbf{Q}_c(\mathbf{x}, t) = & \int_0^t \int_{\Omega} \alpha_c(\mathbf{x}, t; \mathbf{y}, \tau) \nabla_{\mathbf{y}} \cdot \mathbf{Q}_c(\mathbf{x}, t; \mathbf{y}, \tau) d\mathbf{y} d\tau \\ & - \int_0^t \int_{\Omega} \beta_c(\mathbf{x}, t; \mathbf{y}, \tau) \nabla_{\mathbf{y}} \langle c(\mathbf{y}, \tau) \rangle_c d\mathbf{y} d\tau \\ & - \int_0^t \int_{\Omega} \gamma_c(\mathbf{x}, t; \mathbf{y}, \tau) \langle c(\mathbf{y}, \tau) \rangle_c d\mathbf{y} d\tau \\ & - \int_0^t \int_{\Gamma_3} \alpha_c(\mathbf{x}, t; \mathbf{y}, \tau) \mathbf{Q}_c^T(\mathbf{x}, t; \mathbf{y}, \tau) \mathbf{n}(\mathbf{y}) d\mathbf{y} d\tau \\ & + \int_0^t \int_{\Gamma_3} \beta_c(\mathbf{x}, t; \mathbf{y}, \tau) \langle c(\mathbf{y}, \tau) \rangle_c \mathbf{n}(\mathbf{y}) d\mathbf{y} d\tau \end{aligned} \quad (10)$$

with kernels

$$\alpha_c(\mathbf{x}, t; \mathbf{y}, \tau) = \langle G(\mathbf{x}, t; \mathbf{y}, \tau) \mathbf{v}'(\mathbf{x}, t) \rangle_c, \quad (11a)$$

$$\beta_c(\mathbf{x}, t; \mathbf{y}, \tau) = \langle G(\mathbf{x}, t; \mathbf{y}, \tau) \mathbf{v}'(\mathbf{x}, t) \mathbf{v}'^T(\mathbf{y}, \tau) \rangle_c, \quad (11b)$$

$$\gamma_c(\mathbf{x}, t; \mathbf{y}, \tau) = \langle G(\mathbf{x}, t; \mathbf{y}, \tau) \mathbf{v}'(\mathbf{x}, t) f'(\mathbf{y}, \tau) \rangle_c. \quad (11c)$$

The random Green's function $G(\mathbf{x}, t; \mathbf{y}, \tau)$ satisfies a stochastic advection–dispersion equation subject to zero initial and boundary conditions. Since G depends on boundary configuration but not on boundary values, the same holds true for \mathbf{Q}_c (as long as one considers $g, C_0, C_D, W,$ and P to be statistically independent of \mathbf{v}). The vectors α_c and γ_c , and the tensor β_c constitute nonlocal parameters which depend on the flow field but not on transport-related forcing terms. They are however conditioned on measurements, as is the mean velocity $\langle \mathbf{v} \rangle_c$ in (8) and (9), and thus inherently nonunique (in that they depend on the quantity and quality of available data; whereas conditioning on hydraulic conductivity measurements is relatively straightforward [56], conditioning on hydraulic heads and fluxes [38] or solute concentrations and mass fluxes can in principle be accomplished by inversion). The parameter β_c represents

dispersive flux due to an instantaneous point source of unit solute mass that is located at (\mathbf{y}, τ) and is normalized by the advective porosity.

The authors [57,56] also provide explicit expressions for the conditional covariance of concentration, as well as the conditional ensemble mean and covariance of solute flux. It is important to emphasize that the only modeling assumption on which (8)–(11) rest is the validity of the advection–dispersion equation on some local scale of measurement ω ; there are no other theoretical restrictions or limitations. The upside of this generality is the rigorous establishment of space–time nonlocality in a compact mathematical form as the manifestation of mean behavior resulting from spatio-temporal dependencies (including correlations) between velocity fluctuations and thereby between randomly heterogeneous parameters (permeability, advective porosity) that control it. The downside is the fact that (8)–(11) are not closed. Kernels (11) contain unknown moments, whose evaluation (closure) requires additional assumptions and/or approximations. The most common method of closure is to restrict the analysis to mildly heterogeneous media or well-conditioned systems in which σ_Y , the standard deviation of log hydraulic conductivity $Y = \ln K$, is relatively small. For steady-state flow this assumption has been used [57,56] to solve (8)–(11) via an iterative perturbation expansion in powers of σ_Y . Non-perturbative approximations, which include two-point (also known as Corrsin's conjecture) [61] and four-point [29] closures, require the velocity field \mathbf{v} to be Gaussian. This requirement is seldom fulfilled in subsurface hydrology where \mathbf{v} is given as a solution of the flow equation (4).

2.3. Stationary velocity fields

To reduce the coupled system of integro-differential equations (8) and (10) to a single nonlocal transport equation, it is necessary to impose a series of physical restrictions. If the velocity field \mathbf{v} is space–time stationary, ensemble moments of the Greens function depend only on space and time increments (see Appendix A in [29] for a proof), e.g. on $\langle G(\mathbf{x} - \mathbf{y}, t - \tau) \rangle$. Additionally, the integrals containing $\alpha_c(\mathbf{x}, t; \mathbf{y}, \tau)$ are of sub-leading order and can be dropped from (10). For the velocity to be stationary the flow domain must be infinite $\Omega = \Omega_{\infty}$, so the boundary integrals in (10) vanish as well. As $f(\mathbf{x}, t)$ in (4) is linear in the velocity, both β_c and γ_c in (11) depend only on space and time increments, rendering the remaining integrals in (10) space–time convolutions. Hence the mean transport equation (8) becomes

$$\begin{aligned} \frac{\partial \langle c \rangle}{\partial t} = & \nabla \cdot \left[-\langle \mathbf{v} \rangle \langle c \rangle + \int_0^t \int_{\Omega_{\infty}} \gamma(\mathbf{x} - \mathbf{y}, t - \tau) \langle c(\mathbf{y}, \tau) \rangle d\mathbf{y} d\tau + \mathbf{D}_d \nabla \langle c \rangle \right. \\ & \left. + \int_0^t \int_{\Omega_{\infty}} \beta(\mathbf{x} - \mathbf{y}, t - \tau) \nabla_{\mathbf{y}} \langle c(\mathbf{y}, \tau) \rangle d\mathbf{y} d\tau \right] + \langle g \rangle. \end{aligned} \quad (12)$$

The subscript c has been dropped because conditioning would render the velocity field nonstationary. According to (4), the stationarity of $\mathbf{v}(\mathbf{x}, t)$, specifically the requirement that $\langle \mathbf{v} \rangle$ be constant, implies that $\langle f \rangle = 0$ and $\nabla \cdot \langle \mathbf{v} \rangle = 0$. Hence, $\nabla \cdot (\langle \mathbf{v} \rangle \langle c \rangle) = \langle \mathbf{v} \rangle \cdot \nabla \langle c \rangle$.

It is worth emphasizing that the only requirement for the validity of (12) is that the advective velocity \mathbf{v} be stationary, and so that the mean (averaged) advective velocity $\langle \mathbf{v} \rangle$ be constant. This single requirement has far reaching implications. Most importantly, the flow domain has to be infinite, free of fluid sources, and no conditioning on data is possible.

3. Lagrangian model of non-Fickian transport

An equation similar in form to (12) but without the local dispersion and solute source terms can be derived on the basis of Lagrangian solute “particle” motions [18]. Let $\mathbf{X}(t)$ denote the

Lagrangian coordinate of a particle originating at $\mathbf{X}(0)$ at time $t = 0$. The particle moves with random velocity $\mathbf{v}(t) = d\mathbf{X}/dt$ and acceleration $\mathbf{a}(t) = d^2\mathbf{X}/dt^2$. In a stationary velocity field $\mathbf{v}(t)$, the probability $p(\mathbf{x}, t)$ of finding a tagged particle in the unit volume associated with the Eulerian coordinate \mathbf{x} at time t , given that it originated at $\mathbf{X}(0) = \mathbf{0}$, is governed by

$$\frac{\partial p}{\partial t} = \nabla \cdot \left[-\langle \mathbf{v} \rangle p + \int_0^t \int_{\Omega_{\infty}} \mathbf{D}_1(\mathbf{y}, t, \tau) p(\mathbf{x} - \mathbf{y}, t - \tau) d\mathbf{y} d\tau + \int_0^t \int_{\Omega_{\infty}} \mathbf{D}_2(\mathbf{y}, t, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} p(\mathbf{x} - \mathbf{y}, t - \tau) d\mathbf{y} d\tau \right]. \quad (13)$$

Kernels $\mathbf{D}_1(\mathbf{y}, t, \tau)$ and $\mathbf{D}_2(\mathbf{y}, t, \tau)$ are found as inverse Laplace–Fourier transforms of functions $\tilde{\mathbf{d}}_1(\mathbf{k}, \lambda) \Delta(\mathbf{k}, t, \tau)$ and $\tilde{\mathbf{d}}_2(\mathbf{k}, \lambda) \Delta(\mathbf{k}, t, \tau)$, respectively. Here λ is the parameter of a Laplace transform (denoted by the tilde), \mathbf{k} is the wave number of a Fourier transform (denoted by the hat), and

$$\Delta(\mathbf{k}, t, \tau) = e^{i\mathbf{k} \cdot [\mathbf{X}(t) - \mathbf{X}(t-\tau)]}, \quad (14)$$

which, for small τ , reduces to $\Delta(\mathbf{k}, t, \tau) \approx \exp(i\tau \mathbf{k} \cdot \langle \mathbf{v}(t) \rangle)$. The functions $\tilde{\mathbf{d}}_1(\mathbf{k}, \lambda)$ and $\tilde{\mathbf{d}}_2(\mathbf{k}, \lambda)$ are given by

$$\tilde{\mathbf{d}}_1(\mathbf{k}, \lambda) = \tilde{\mathbf{w}}_1(\mathbf{k}, \lambda) [1 - \lambda^{-1} \tilde{\Phi}(\mathbf{k}, \lambda)]^{-1}, \quad (15a)$$

$$\tilde{\mathbf{d}}_2(\mathbf{k}, \lambda) = \tilde{\mathbf{w}}_2(\mathbf{k}, \lambda) [1 - \lambda^{-1} \tilde{\Phi}(\mathbf{k}, \lambda)]^{-1}, \quad (15b)$$

where

$$\tilde{\Phi}(\mathbf{k}, \lambda) = i\mathbf{k}^T \tilde{\mathbf{w}}_1(\mathbf{k}, \lambda) - \mathbf{k}^T \tilde{\mathbf{w}}_2(\mathbf{k}, \lambda) \mathbf{k} \quad (15c)$$

and $\tilde{\mathbf{w}}_1(\mathbf{k}, \lambda)$ and $\tilde{\mathbf{w}}_2(\mathbf{k}, \lambda)$ are Laplace transforms of

$$\hat{\mathbf{w}}_1(\mathbf{k}, t) = -\langle \mathbf{a}'(t) e^{i\mathbf{k} \cdot [\mathbf{X}'(t) - \mathbf{X}'(0)]} \rangle, \quad (15d)$$

$$\hat{\mathbf{w}}_2(\mathbf{k}, t) = -\langle \mathbf{v}'(t) e^{i\mathbf{k} \cdot [\mathbf{X}'(t) - \mathbf{X}'(0)]} \mathbf{v}'^T(t) \rangle, \quad (15e)$$

respectively. For constant $\langle \mathbf{v} \rangle$, to second order in the magnitude of \mathbf{k} , \mathbf{D}_1 vanishes and \mathbf{D}_2 is expressible in terms of measurable lead velocity statistics.

Recalling that the probability p and the mean concentration $\langle c \rangle$ have a similar physical meaning, one can show that the stnL equation (13) is identical to the stnADE (12) without both local dispersion, $\mathbf{D}_d = \mathbf{0}$, and forcing terms (no sources/sinks and zero initial concentration), $\langle g \rangle = 0$.

4. Continuous time random walk models of non-Fickian transport

The continuous time random walk (CTRW) approach describes the random movement of solute particles in an Eulerian–Lagrangian framework. A detailed review of the approach, on which we rely below, can be found in [8].

4.1. Discrete CTRW representation

Underlying CTRW is the notion that transport takes place by the movement of discrete solute particles between discrete points or sites in space at which complete and instantaneous mixing of the solute carried by these particles takes place (particles enter a site carrying diverse concentrations but leave the site carrying a single concentration resulting from such mixing at the site). Disregarding sinks and sources, one expresses the rate at which normalized (with respect to mass) solute concentration $c(\mathbf{x}, t)$ varies with time at site \mathbf{x} , through a stochastic mass balance expression, also known as “master equation” [66,76]:

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} = - \sum_{\mathbf{y}} w(\mathbf{y}, \mathbf{x}) c(\mathbf{x}, t) + \sum_{\mathbf{y}} w(\mathbf{x}, \mathbf{y}) c(\mathbf{y}, t), \quad (16)$$

where $w(\mathbf{x}, \mathbf{y})$ is the (time-independent) transition rate at which a particle moves from site \mathbf{y} to site \mathbf{x} . The second summation represents normalized rate of solute inflow from all sites \mathbf{y} to site \mathbf{x} , and the first denotes normalized rate of outflow from site \mathbf{x} to all sites \mathbf{y} . If the transition rates form a statistically incoherent homogeneous random field, the ensemble mean concentration $\langle c(\mathbf{x}, t) \rangle$ satisfies exactly the “generalized master equation” [40]

$$\frac{\partial \langle c(\mathbf{x}, t) \rangle}{\partial t} = - \sum_{\mathbf{y}} \int_0^t \phi(\mathbf{y} - \mathbf{x}, t - \tau) \langle c(\mathbf{x}, \tau) \rangle d\tau + \sum_{\mathbf{y}} \int_0^t \phi(\mathbf{x} - \mathbf{y}, t - \tau) \langle c(\mathbf{y}, \tau) \rangle d\tau. \quad (17)$$

Here the kernel $\phi(\mathbf{z}, s)$ is defined through its Laplace transform

$$\tilde{\phi}(\mathbf{z}, \lambda) = \frac{\lambda \tilde{\psi}(\mathbf{z}, \lambda)}{1 - \tilde{\psi}_s(\lambda)}, \quad \tilde{\psi}_s(\lambda) \equiv \sum_{\mathbf{z}} \psi(\mathbf{z}, \lambda) \quad (18)$$

in terms of Laplace transforms of $\psi(\mathbf{x}, s)$, the probability rate of displacements \mathbf{z} over time intervals s , and of $\psi_s(s)$, the marginal probability rate of all such displacements.

The assumption of incoherence, which is required to derive the generalized master equation (17), means that particle transition rates corresponding to different sites or displacements lack statistical interdependence. It implies that both hydraulic/transport properties of porous media (e.g. hydraulic conductivity) and system states (e.g. hydraulic heads and fluxes) lack spatial correlations, a proposition that is rarely supported by data. That (17) and (18) do indeed reflect incoherent particle hopping rates between the sites is evidenced by the univariate nature of the probability $\psi(\mathbf{z}, s)$; to describe a coherent structure of such rates would require characterizing them by a multivariate probability function.

4.2. Continuum CTRW representation

If the kernel $\phi(\mathbf{x} - \mathbf{y}, t - \tau)$ in (17) is sharply peaked about its mean, one may confine the analysis to the limit of small displacements. This allows one to replace the discrete set of sites with a continuum by expanding $\langle c(\mathbf{y}, \tau) \rangle$ in a Taylor series about \mathbf{x}

$$\langle c(\mathbf{y}, t) \rangle = \langle c(\mathbf{x}, t) \rangle + (\mathbf{y} - \mathbf{x})^T \nabla_{\mathbf{x}} \langle c(\mathbf{x}, t) \rangle + \frac{1}{2} (\mathbf{y} - \mathbf{x})^T [\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T \langle c(\mathbf{x}, t) \rangle] (\mathbf{y} - \mathbf{x}) + \dots \quad (19)$$

Discarding terms of order higher than $O(|\mathbf{y} - \mathbf{x}|^2)$ in (19), substituting into (17), replacing the summations by integrations and recalling the assumption of statistical homogeneity, one obtains a CTRW form of a mean transport equation that is nonlocal in time

$$\frac{\partial \langle c(\mathbf{x}, t) \rangle}{\partial t} + \nabla \cdot \int_0^t [\mathbf{V}_l(t - \tau) - \mathbf{D}_l(t - \tau) \nabla] \langle c(\mathbf{x}, \tau) \rangle d\tau = 0. \quad (20)$$

The vector \mathbf{V}_l and the tensor \mathbf{D}_l are defined as

$$\mathbf{V}_l(t) = \int_{\Omega} \phi(\mathbf{x} - \mathbf{y}, t - \tau) (\mathbf{x} - \mathbf{y}) d\mathbf{y}, \quad (21a)$$

$$\mathbf{D}_l(t) = \frac{1}{2} \int_{\Omega} \phi(\mathbf{x} - \mathbf{y}, t - \tau) (\mathbf{x} - \mathbf{y}) (\mathbf{x} - \mathbf{y})^T d\mathbf{y}. \quad (21b)$$

4.3. Functional equivalence with stnADE and stnL

A functionally equivalent result can be obtained either from the simplified stnADE equation (12), which is based on statistically homogeneous advective–dispersive behavior at a reference support scale ω , or from the stnL equation (13), which is based on statistically homogeneous Lagrangian motions of solute particles. All that is required is to recognize that incoherence of particle transition rates implies incoherence of the underlying advective velocity field, which in turn implies $\langle v_i(\mathbf{x}) v_j(\mathbf{y}) \rangle \sim \delta(\mathbf{x} - \mathbf{y})$ where $\delta(\cdot)$ is the

Dirac delta function. Then the stnADE kernels in (11) are localized in space according to

$$\gamma(\mathbf{x} - \mathbf{y}, t - \tau) = [\langle \mathbf{v} \rangle \delta(t - \tau) + \mathbf{V}_l(t - \tau)] \delta(\mathbf{x} - \mathbf{y}), \quad (22a)$$

$$\beta(\mathbf{x} - \mathbf{y}, t - \tau) = [-\mathbf{D}_d \delta(t - \tau) + \mathbf{D}_l(t - \tau)] \delta(\mathbf{x} - \mathbf{y}) \quad (22b)$$

and the simplified stnADE equation (12) reduces to the CTRW equation (20) upon setting the source function $\langle g \rangle = 0$.

Since the stnL equation (13) is analogous to the simplified stnADE equation (12), its kernels localize in a similar manner and (13) likewise becomes the CTRW equation (20). These localized forms of the kernels define a one-to-one correspondence between the space–time–nonlocal stnADE and stnL models on one hand, and the time–nonlocal CTRW model on the other hand. Thus, CTRW can be viewed as a particular form of stnL which in turn constitutes a special form of stnADE.

5. Fractional advection–dispersion models of non-Fickian transport

Various representations of non-Fickian transport by ADE with fractional derivatives (fADE) have been postulated in the hydrologic literature. As pointed out in [93], the most common fADE at present is a one-dimensional form with fractional space derivatives and constant coefficients [50]:

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} + D \frac{\partial^\alpha C}{\partial x^\alpha}, \quad (23)$$

where $C(x, t)$ is said to be solute concentration, V a constant velocity, D a constant “dispersion coefficient” (having unconventional fractional dimensions) and α ($1 < \alpha \leq 2$) the order of fractional differentiation; when $\alpha = 2$ (23) reduces to the standard second-order ADE. We note that since (23) is deterministic and (as is made clear below) analogous to a special form of (12), C represents $\langle c \rangle$ or (equivalently) the probability of finding a solute particle at a particular point in space time, as discussed in e.g. [53,52]. We however retain the original notation to remain consistent with the hydrologic literature on fADE.

5.1. Relationship to CTRW

Some forms of fADE can be derived (e.g. [53]) as scaling limits of continuous time random walks (CTRW). Meerschaert et al. [52] show that the CTRW method allows determining the limit process when particle jumps have infinite variance and/or the waiting times between particle jumps have infinite mean. If particle jump sizes and waiting times are statistically independent, the first results in fractional space- and the second in fractional time derivatives. Linkage or coupling between particle jump sizes and waiting times yields fractional powers of coupled space and time differential operators. We note that waiting times represent particle trapping in multirate mass transfer models such as those associated with mobile/immobile, dual or multiple continua models of porous or fractured media. It follows that in the absence of trapping, which is the case we consider in our paper, there is no known physical mechanism that would contribute time-fractional derivatives to fADE. This explains why all fADE models we describe contain fractional derivatives in space but none in time.

In particular, it can be shown that the common fADE (23) follows directly from application of the CTRW master equation to particles executing Levy flight (e.g. [54]), a Markovian random walk process forming the analogue of Brownian motion for statistically independent and identically distributed (i.i.d.) non-Gaussian displacements characterized by a heavy-tailed distribution with infinite variance. We note that such displacements can only occur in an uncorrelated velocity field.

5.2. Various forms of fADE

Among various modifications and generalizations of the basic fADE (23) one finds a multidimensional version [92], time-fractional ADE [51,74], and the following three alternative fADE formulations [93] with spatially varying $V(x)$ and $D(x)$: a fractional flux form (FF-ADE):

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} \left[VC - D \frac{\partial^{x-1} C}{\partial x^{x-1}} \right], \quad (24a)$$

a fractional divergence form (FD-ADE)

$$\frac{\partial C}{\partial t} = -\frac{\partial VC}{\partial x} + \frac{\partial^{x-1}}{\partial x^{x-1}} \left[D \frac{\partial C}{\partial x} \right] \quad (24b)$$

and a fully fractional divergence form (FFD-ADE)

$$\frac{\partial C}{\partial t} = -\frac{\partial^{x-1} VC}{\partial x^{x-1}} + \frac{\partial^{x-1}}{\partial x^{x-1}} \left[D \frac{\partial C}{\partial x} \right]. \quad (24c)$$

Each form reduces to the standard second-order ADE when $\alpha = 2$. While (23) can be derived from CTRW, we are not aware of any specific theoretical framework that would lead formally to (24).

The three alternative formulations of fADE (24) are equivalent to the integro-differential equation [93]

$$\begin{aligned} \frac{\partial C}{\partial t} = & -\frac{\partial VC}{\partial x} + \frac{\partial}{\partial x} \int_0^t \int_{-\infty}^{\infty} \beta(x, t; y, \tau) \frac{\partial C(x-y, t-\tau)}{\partial(x-y)} dy d\tau \\ & + \frac{\partial}{\partial x} \int_0^t \int_{-\infty}^{\infty} \gamma(x, t; y, \tau) C(x-y, t-\tau) dy d\tau \end{aligned} \quad (25)$$

with the following kernels: For FF-ADE (24a)

$$\beta = \frac{D(x)\delta(\tau)H(y)}{\Gamma(2-\alpha)y^{\alpha-1}}, \quad \gamma = 0 \quad (26a)$$

for FD-ADE (24b)

$$\beta = \frac{D(x-y)\delta(\tau)H(y)}{\Gamma(2-\alpha)y^{\alpha-1}}, \quad \gamma = 0 \quad (26b)$$

and for FFD-ADE (24c)

$$\beta = \frac{D(x-y)\delta(\tau)H(y)}{\Gamma(2-\alpha)y^{\alpha-1}}, \quad \gamma = \frac{V(x-y)\delta(\tau)H(y)}{\Gamma(2-\alpha)y^{\alpha-1}}. \quad (26c)$$

Here $H(\cdot)$ is the Heaviside function, and $\Gamma(\cdot)$ is the complete Gamma function.

5.3. Functional equivalence with stnADE

Zhang et al. [93] state that each of the kernels (26) is “a special case of Neuman’s nonlocal model [61]”. This is the same as saying that with this choice of kernels the FF-ADE, FD-ADE and FFD-ADE (24) become functionally equivalent to the stnADE model (8) in an infinite domain. Yet the latter model consists of a system of integro-differential equations which cannot be reduced to either the fADE models (24) or the nonlocal transport equation (12) without a number of simplifying assumptions and corresponding physical limitations (see the discussion in Section 2). Only when velocity is space–time stationary and both forcing terms and local dispersion are absent, does the one-dimensional version of (8)–(11) reduce to the one-dimensional form of (12)

$$\begin{aligned} \frac{\partial \langle c \rangle}{\partial t} = & \frac{\partial}{\partial x} \left[-\langle \mathbf{v} \rangle \langle c \rangle + \int_0^t \int_{-\infty}^{\infty} \gamma(x-y, t-\tau) \langle c(y, \tau) \rangle dy d\tau \right. \\ & \left. + \int_0^t \int_{-\infty}^{\infty} \beta(x-y, t-\tau) \frac{\partial \langle c(y, \tau) \rangle}{\partial y} dy d\tau \right]. \end{aligned} \quad (27)$$

Whereas the fADE formulations (25)–(26) are nonlocal in space but local in time (due to the presence of $\delta(\tau)$ in each nonzero kernel), (27) is generally nonlocal in both space and time. For the two to be equivalent, it would be necessary to replace $\delta(\tau)$ with finite-support temporal kernels, i.e., to include time-fractional derivatives in the FF-ADE, FD-ADE and FFD-ADE. The equivalence would not be complete unless such coupled space–time-fractional derivative(s) could be related to a spatial (and possibly temporal) structure of the velocity field, as are the kernels in (27); the coupled space–time-fractional derivatives of Meerschaert et al. [52] arise instead from a relationship between incoherent (unstructured) particle jump sizes and waiting times. Additional conditions required for (25) and (26) and (27) to be equivalent are that the random advective velocity be independent of time and that initial concentration be zero. Finally, functional equivalence between the general stnADE formulation (8)–(11) and fADE models (25) and (26) requires that both V and D be constant, i.e., that the advective velocity be stationary in space and time. This is consistent with the observation [19] that the FF-ADE and FD-ADE, whose kernels are identical when V is constant, coincide with the one-dimensional version of the stnL (13) and, thus, the reduced one-dimensional version of the stnADE (12), as discussed in Section 3.

It follows that the FF-ADE, FD-ADE and FFD-ADE are generally not equivalent to, and less general than, the stnADE model [61], especially in its extended form [57].

6. Perspective on nonlocal representations of advective–dispersive transport

Now that we have established mathematical relationships between the four nonlocal representations of non-Fickian advective–dispersive transport (stnADE, stnL, CTRW and fADE) we are in a position to provide a perspective on their relative strengths and weaknesses. We do so by considering the assumptions that underly each approach and the ways one would or could use them to solve real-world transport problems.

Of the four nonlocal theories we compare in this paper, one (stnADE) assumes that transport on a support scale of ω in each random realization is governed by the standard second-order ADE. Consider the (admittedly rare) situation in which the ADE is mean ergodic so that averaging it in probability space (over the ensemble, as does the stnADE) is equivalent to averaging it in space. Since stnADE predicts ensemble mean transport to be nonlocal, the same would apply to space averaged transport. Hence if one analyzed observed tracer behavior deterministically using the ADE, one might conclude that the ADE does not represent adequately the observed nonlocal tracer behavior. A similar conclusion might be reached in more common nonergodic situations in which, as stnADE clearly implies, a deterministic analysis of observed transport data would generally manifest nonlocal behavior (see an extensive discussion of this in [57]). It follows that one should expect tracer experiments analyzed deterministically to exhibit non-Fickian behavior even if the underlying stochastic process is Fickian. Such deterministic manifestations of non-Fickian transport have been observed both in the laboratory [78,79,47,13,58] and in the field [68,80,48,1,11,32,77,92].

Several experimental [13,47] and numerical [49,10] investigations concluded that the underlying stochastic transport process must likewise be non-Fickian regardless of how small one takes ω to be. Such findings, which imply that non-Fickian behavior might occur in homogeneous porous media, can be explained by the presence of dead-end pores and/or recirculation zones that lead to so-called holdup dispersion [49]. Column length has been identified as another possible source of error in determination of dispersive behavior in column experiments [36,41].

In the absence of dead-end pores (a situation we consider in our paper, as noted earlier), local-scale dispersion tends to be Fickian [41]. This is because Fick's law is known to be valid on the fluid continuum scale within pore interiors, and the Taylor–Aris [84,2] Fickian analogy is known to hold on average across a set of pores connected in series. Hence, one may expect the macroscopic ADE to be valid on sufficiently small support scales ω of the kind commonly associated with random realizations of flow and transport, even if it does not apply to the much larger REV-size support scales required for deterministic analyses.

stnADE assumes that the Fickian analogy applies at some reference support scale ω and treats the corresponding advective velocity as a multivariate random field defined on a space–time continuum. The velocity field is generally nonstationary and statistically interdependent in space–time over an arbitrary range of scales. stnADE does not, in itself, say anything about the size of ω or the physical, chemical or biological phenomena that give rise to either the velocity field or the dispersion process. In this sense, stnADE is neither more nor less scientifically valid or general than are particle-based approaches such as stnL and CTRW. By taking ω to be much smaller than a laboratory setup, stnADE would predict mean nonlocal behavior on the laboratory scale just as would stnL and CTRW.

Actual applications of stnADE to date have taken advective velocity to obey Darcy's law on the scale of ω . To allow conditioning stnADE on actual measurements, ω has been selected so as to render all quantities (parameters, state variables, forcing terms) entering into the corresponding stochastic flow and transport equations measurable, or inferable from measurements, on this scale at any point in space–time (without requiring that ω constitute a representative elementary volume, or REV, in the traditional sense of this term). Doing so is not a fundamental requirement of stnADE but a choice which renders the approach operational at the cost of some underlying generality. Any attempt to render stnL, CTRW or fADE similarly operational would have to come at a comparable cost. As stnL and CTRW are presently limited to stationary fields of particle motion, they are not amenable to conditioning on measured values of quantities that control these motions. The fact that geologic media tend to be structured on a multiplicity of scales additionally imparts a corresponding degree of coherence to such motions which CTRW and fADE presently fail to capture. It thus appears that stnL, CTRW and fADE would have to be modified in major ways (the latter two more so than the first) to render them operationally competitive with stnADE. Though fADE equations (24) contain variable fractional velocities and dispersion coefficients, we are not aware of any specific theoretical framework that would lead formally to these equations, and are therefore unclear about the physical meaning of the corresponding fractional parameters. In particular, we see no way of estimating these parameters on the basis of hydraulic or any data other than by fitting the models to observed concentrations and/or solute mass fluxes.

The operational basis of stnADE is in principle much broader than that represented by Darcy and Fickian behaviors on the scale of ω . The approach can be extended to any linear or nonlinear representations of flow and transport on reference support scales at which these phenomena are experimentally observable and quantifiable. Ensemble averaging of the corresponding stochastic flow and transport equations would always be possible numerically by conditional Monte Carlo simulation or other computational means, if not formally as in (8)–(12). As stochastic variables controlling flow and transport on the scale of ω would almost always possess a coherent structure, such averaging would almost always render the corresponding state variables implicitly nonlocal in both space and time, even in the absence of a solute trapping mechanism. This has been demonstrated numerically through comparisons with stnADE solutions [56].

A major advantage of the operational ADE-based approach is that it allows one to predict not only mean behavior conditional on real data but also higher-order statistical moments representing deviations from the mean. For example, stnADE has allowed deriving space–time–nonlocal equations for the conditional covariance of concentrations and corresponding explicit expressions for the conditional second moments of solute flux [57,56]. No comparable higher-moment equations have been developed to date on the basis of stnL, CTRW or fADE.

As already mentioned, solving stnADE (or stnL) equations requires a suitable closure scheme. Current perturbative methods of solution (e.g. [57]) are limited to mildly variable or well-conditioned velocity fields. Likewise, two- and four-point closures (e.g. [29]) require distributional assumptions, such as the stationarity and Gaussianity of advective velocity. No such limitation applies to the numerical Monte Carlo equivalent of stnADE. As discussed in Section 4, CTRW requires flow to be stationary and unstructured (hence uncorrelated). Published attempts [13] to overcome the stationarity limitation by applying CTRW piecewise to “stationary” segments of a heterogeneous formation is ad hoc and inconsistent with the fact that, in any such finite segment, the velocity becomes nonstationary due to continuity conditions that have to be imposed at segment boundaries [86,87].

Additionally, CTRW relies on the transition rate function $\psi(\mathbf{z}, s)$, which is largely phenomenological and has one or a few parameters estimated by fitting the CTRW solution to a measured concentration breakthrough curve (BTC). However, since $\psi(\mathbf{z}, s)$ is univariate, the same parameters will generally not apply to BTCs at other points in space–time or under different flow regimes. In [8], this is evidenced by the need to vary the parameter β from one sampler to another (their Fig. 7), from one flow rate to another (their Fig. 9), and from one space–time location of a plume to another (their Fig. 11). What values of β and/or other parameters should one use to predict concentrations at as yet unsampled space–time locations, or under flow regimes other than those used to calibrate a CTRW model? No unique set of parameters could, in general, provide such predictions with any degree of reliability or confidence. Though some of this nonuniqueness has apparently been resolved by taking $\psi(\mathbf{z}, s)$ to be a power-law [9] or by adding another parameter to the transition rate function [14], it is far from clear that this alone is enough to resolve the nonuniqueness issue in all cases.

Like CTRW, fADE is limited to unstructured velocity fields and, in the case of constant coefficients, to velocity fields that are additionally stationary. Though the inclusion of variable fractional velocity and dispersion coefficient are said to allow conditioning fADE on spatially varying data [93,92], there does not appear to be any formal link between such fractional parameters and measurable medium properties (e.g. hydraulic conductivity and advective porosity) or flow parameters (e.g. hydraulic gradients, fluxes and advective porosities). A stated advantage of fADE over CTRW is the ability of the former to account for source and boundary terms [53]. It is not clear to us how fADE with constant coefficients could do so without violating the requirement that flow be stationary.

A seeming operational advantage of CTRW and fADE over stnADE is that they require much lesser computational effort and may, in some cases, yield analytical results. We are not convinced that the computational advantage justifies the conceptual or operational limitations and note that localized versions of stnADE and stnL have yielded a wealth of analytical results, some of which appear in [3,20–22,30,62,66,94].

7. Conclusions

We compared four conceptualizations and representations of non-Fickian advective–dispersive transport of nonreactive tracers

through heterogeneous porous and/or fractured continua: a space–time–nonlocal representation based on the assumption of advective–dispersive behavior at a reference support scale ω (stnADE); a space–time–nonlocal representation based on a Lagrangian representation of particle motions in a stationary random velocity field (stnL); a time–nonlocal representation of mean particle transport on a discrete lattice having arbitrarily small cell sizes based on a continuous time random walk concept (CTRW); and space–fractional representations of advection and dispersion that are nonlocal in space but local (except in the case of multirate mass transfer) in time (fADE). Our comparative exposé of these theories leads us to the following conclusions:

- (1) Since subsurface fluid flow and solute transport take place in a multiscale heterogeneous environment, neither these phenomena nor their host environment can be observed or described with certainty at all scales and locations of relevance. The resulting ambiguity is large enough to allow alternative conceptualizations of flow and transport and multiple ways of addressing their scale and space–time dependencies.
- (2) The generalized master equation underlying CTRW has been derived on the assumption that particle transition rates form a statistically incoherent homogeneous random field. Incoherence means that particle transition rates corresponding to different sites or displacements lack statistical interdependence. That CTRW does indeed reflect incoherent particle hopping rates between the sites is evidenced by the univariate nature of the underlying transition probability function $\psi(\mathbf{z}, s)$; to describe a coherent structure of such rates would require characterizing them by a multivariate probability function.
- (3) We have demonstrated a one-to-one correspondence between CTRW and space–time–nonlocal stnADE and stnL forms in which the velocity field is taken to be statistically homogeneous. Like CTRW, fADE is limited to unstructured (hence uncorrelated) velocity fields and, in the case of constant coefficients, to velocity fields that are additionally stationary. Though the inclusion of variable fractional velocity and dispersion coefficient is said to allow conditioning fADE on spatially varying data, there appears to be no formal link between such fractional parameters and measurable medium properties (e.g. hydraulic conductivity and advective porosity) or flow parameters (e.g. hydraulic gradients, fluxes and advective porosities). A stated advantage of fADE over CTRW is the ability of the former to account for source and boundary terms. It is not clear to us how fADE with constant coefficients could do so without violating the requirement that flow be stationary.
- (4) Other than particle trapping associated with multirate mass transfer models in mobile/immobile, dual or multiple continua models of porous or fractured media, there is no known physical mechanism that would contribute time-fractional derivatives to fADE. As our paper does not deal with multirate mass transfer, the only fADE models relevant to our analysis are those containing fractional derivatives in space but not in time. Such models are nonlocal in space but local in time.
- (5) fADE with constant coefficients is a special time-localized version of stnADE corresponding to a statistically homogeneous velocity field and, equivalently, of stnL. To render such fADE fully equivalent to these latter nonlocal forms, it would be necessary to replace its space-fractional derivatives with cross-fractional space and time derivatives. No such cross-fractional forms have so far been postulated in the absence of trapping.

- (6) It has been asserted that some recently proposed forms of fADE with variable coefficients are special cases of stnADE corresponding to a statistically nonhomogeneous velocity field. This, however, is true only in the limiting case of zero initial concentration, time- and (depending on the form) space-independent velocity, stationary velocity fluctuations about the mean, constant dispersion coefficient, and provided further that space-fractional derivatives in fADE are replaced with cross-fractional space and time derivatives even in the absence of trapping.
- (7) All existing models of nonlocal mean transport require a closure approximation, which formally limits their applicability. Current perturbative solutions of stnADE and stnL equations are limited to mildly variable or (in the case of stnADE) well-conditioned velocity fields. Likewise, two- and four-point closures require distributional assumptions, such as the stationarity and Gaussianity of advective velocity. No such limitations apply to the numerical Monte Carlo equivalent of stnADE, although its computational cost may become prohibitive. The same holds true for CTRW, which relies on assumed forms of the transition probability function $\psi(\mathbf{z}, s)$ whose parameters are estimated by fitting the CTRW solution to a measured concentration breakthrough curve (BTC). Since $\psi(\mathbf{z}, s)$ is univariate, the same parameters will not apply to BTCs at other points in space-time or under different flow regimes except in special cases.
- (8) A seeming operational advantage of CTRW and fADE over stnADE is that they require much lesser computational effort and may, in some cases, yield analytical results. We are not convinced that the computational advantage justifies the limitations and note that localized versions of stnADE and stnL have yielded a wealth of analytical results.
- (9) All experimental manifestations of non-Fickian nonreactive tracer transport in porous media have to date been based on deterministic interpretations of the available data. Deterministic models used for the interpretation of tracer experiments in heterogeneous media provide at best smoothed mean representations of actual tracer behaviors on scales much smaller than those of the experiments. Regardless of whether one takes transport on such small scales to be governed by a stochastic advection–dispersion equation (ADE) or to consist of random solute “particle” motions, the resultant mean behavior generally comes out to be nonlocal and hence non-Fickian. It follows that published observations of non-Fickian transport on experimental scales (whether in the laboratory or in the field) provide no information about the true nature of stochastic transport processes on much smaller scales.
- (10) Several experimental and numerical investigations concluded that the underlying stochastic transport process must likewise be non-Fickian regardless of how small one takes ω to be. Such findings, which imply that non-Fickian behavior might occur in homogeneous porous media, can be explained by the presence of dead-end pores and/or recirculation zones that lead to so-called holdup dispersion. Column length has been identified as another possible source of error in determination of dispersive behavior in column experiments.
- (11) In the absence of dead-end pores (a situation we consider in our paper), local-scale dispersion tends to be Fickian. This is because Fick’s law is known to be valid on the fluid continuum scale within pore interiors, and the Taylor–Aris Fickian analogy is known to hold on average across a set of pores connected in series. Hence, one may expect the macroscopic ADE to be valid on sufficiently small support scales ω of the kind commonly associated with random realizations of flow and transport, even if it does not apply to the much larger REV-size support scales required for deterministic analyses.
- (12) By the same token, one may expect a suitably modified ADE to account validly for additional ω -scale phenomena such as sorption–desorption, radioactive decay and bio-chemical reactions in each random realization even though these phenomena would generally be nonlocal in the mean. Representing fluid and/or tracer mass transfer between dual (such as fractures intersecting a porous matrix or mobile and immobile zones of pore fluid) or multiple continua as time-nonlocal phenomena on the scale of ω in any realization would result in space- as well as enhanced time-nonlocal mean behaviors.
- (13) Actual applications of stnADE to date have taken advective velocity to obey Darcy’s law on the scale of ω . To allow conditioning stnADE on measurements of medium hydraulic and transport properties as well as on observed hydraulic heads and sampled concentrations, ω has been selected so as to render all quantities (parameters, state variables, forcing terms) entering into the corresponding stochastic flow and transport equations measurable, or inferable from measurements, on this scale at any point in space-time (without requiring that ω constitute a representative elementary volume, or REV, in the traditional sense of this term). Doing so renders the approach operational at the cost of some underlying generality.
- (14) The fact that CTRW and fADE entail no support scale is sometimes cited as a theoretical advantage, said to render them applicable on all scales. We view it instead as an operational liability, which prevents one from estimating model parameters on the basis of data other than observed values of concentration and/or solute flux. Though fADE equations containing variable fractional velocities and dispersion coefficients are said to be amenable to conditioning, we are not aware of any specific theoretical framework that would lead formally to these equations, and are therefore unclear about the physical meaning of the corresponding fractional parameters. Hence we see no way of estimating these parameters on the basis of data other than observed values of concentration and/or solute flux. In the absence of such observations (e.g. prior to the time contamination develops and is sampled at a site) such models cannot be used to predict plume evolution (e.g. potential contamination) with any known degree of reliability.
- (15) Since stnL, CTRW and fADE with constant coefficients are limited to stationary fields of particle motion, they are not amenable to conditioning on measured values of quantities that control these motions. The fact that geologic media tend to be structured on a multiplicity of scales additionally imparts a corresponding degree of coherence to such motions which CTRW and fADE (with constant or variable coefficients) presently fail to capture. It thus appears that stnL, CTRW and fADE would have to be modified in major ways (the last two more so than the first) to render them operationally competitive with stnADE.
- (16) stnADE is unique among the four approaches to non-Fickian transport we discuss in providing not only predictions of solute concentrations and mass fluxes but also measures of associated prediction errors.

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