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Eulerian derivation of the fractional advection–dispersion equation

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Abstract

A fractional advection–dispersion equation (ADE) is a generalization of the classical ADE in which the second-order derivative is replaced with a fractional-order derivative. In contrast to the classical ADE, the fractional ADE has solutions that resemble the highly skewed and heavy-tailed breakthrough curves observed in field and laboratory studies. These solutions, known as α-stable distributions, are the result of a generalized central limit theorem which describes the behavior of sums of finite or infinite-variance random variables. We use this limit theorem in a model which sums the length of particle jumps during their random walk through a heterogeneous porous medium. If the length of solute particle jumps is not constrained to a representative elementary volume (REV), dispersive flux is proportional to a fractional derivative. The nature of fractional derivatives is readily visualized and their parameters are based on physical properties that are measurable. When a fractional Fick's law replaces the classical Fick's law in an Eulerian evaluation of solute transport in a porous medium, the result is a fractional ADE. Fractional ADEs are ergodic equations since they occur when a generalized central limit theorem is employed.

Keywords: Solute transport; Heterogeneity; Dispersivity; Power law; Stochastic processes; Statistical distribution

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1. Introduction

An equation commonly used to describe solute transport in aquifers is the advection–dispersion equation (ADE):

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + \mathscr{D}\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is solute concentration, v is the average linear velocity, x is the spatial domain, t is time, and $\mathscr{D}$ is a constant dispersion coefficient. The transport coefficients in the ADE are constitutive properties equivalent to the average of unmeasurable smaller-scale mechanical properties. It is assumed that the motion of particles has a random component and that the paths of particles are represented by sums of random variables describing particle jump size. A large number of tracer particles, initially located at a point source, will disperse according to a limiting probability distribution, from which relative concentrations can be derived for any given time (Bear, 1972, p. 589). Thus, the ADE is a deterministic equation describing the probability function for the location of particles in a continuum. The fundamental solutions to the ADE over time will be Gaussian densities with means and variances based on the values of the macroscopic transport coefficients v and $\mathscr{D}$. However, the ADE typically underestimates concentrations in the leading and/or trailing edges of contaminant plumes. Application of the ADE to field data reveals an apparent scale-dependence of dispersivity complicating the prediction of plume evolution in time or space. Early stochastic approaches based on the ADE that use small perturbation techniques (e.g., Dagan, 1984; Neuman, 1993) rely upon a dispersion coefficient which grows with time. Serrano (1995) proposed an analytic solution that does not require the mathematical assumptions of perturbation theory and has parameters based on measurable physical properties, though the dispersion coefficient remains time dependent and does not reach a constant value.

Since the ADE is based on the fulfillment of a limit theorem, the analytic solution is only valid when the ergodic assumption is satisfied (e.g., Gelhar, 1993; Dagan, 1990, 1991; see Zhan, 1999 for a review). This occurs when a particle has made enough uncorrelated motions that its overall probability distribution is asymptotically close to a limit distribution (Bhattacharya and Gupta, 1990). When a solute plume reaches ergodic conditions, it is assumed that the random motion of one tracer particle in space represents an ensemble of many such particles. If the ergodic requirement is not fulfilled, plume evolution will deviate from theoretical predictions (Tompkins et al., 1994). Thus, semi-analytic or pre-asymptotic solutions have been derived to treat non-ergodic transport in heterogeneous aquifers. Non-local stochastic techniques have also been developed in both Eulerian (Neuman, 1993) and Lagrangian (e.g., Cushman, 1993 and references therein) frameworks. These theories require either numerical solution in transform space, high resolution Monte Carlo simulations, or closure approximations that reduce their applicability. Berkowitz and Scher (1995) provided an excellent summary of non-local stochastic theories. A more general review of recent developments in stochastic hydrology is presented by Rubin (1997). While many of these theories have increased our understanding of the mechanisms controlling transport in porous media, they also require mathematical restrictions or assumptions that reduce their resemblance to physical processes (Serrano, 1995). Furthermore, practitioners still use some sort of numerical implementation of the classical ADE or particle tracking methods in modeling contaminant transport (Zheng and Jiao, 1998; Pollock, 1994).

The central limit theorem is valid for sums of independent and identically distributed (iid) *finite-variance* random variables (Feller, 1968). This means that Gaussian breakthrough curves and strictly Fickian scaling behavior only occur when:

1. the particle jump size (velocity field) is uncorrelated in time and
2. the particle jump size (velocity field) has finite mean and variance.

Since non-Gaussian breakthrough curves for non-reactive solutes are often observed in the field, one or both of these conditions are failing. It is well documented that violation of the first assumption leads to enhanced diffusion, diffusion that is faster than Gaussian analytical solutions predict (e.g., Sahimi, 1993). Most non-Fickian ergodic transport theories are based on the effects of long-range temporal correlation due, for example, to solute sorption or preferential pathways. However, it is only recently that the assumption of a finite-variance velocity field has been addressed (e.g., Painter, 1996; Liu and Molz, 1996, 1997; Molz et al., 1997; Benson, 1998).

The purpose of this paper is to demonstrate that highly skewed, non-Gaussian contaminant plumes with heavy leading edges can be a result of the infinite-variance particle jump distributions that arise during transport in disordered (non-homogeneous or not well structured) porous media. Additional factors such as long-term velocity dependence serve to enhance non-Gaussian plume growth, but are not required for this type of evolution. We demonstrate that a fractional ADE (Benson, 1998) is a governing equation for conservative solute transport in porous media in cases where temporally correlated velocity fields do not dominate transport processes. Section 2 explains that Fickian dispersion can only occur in homogeneous aquifers. Section 3 provides a physical justification for the use of a fractional derivative in describing particle transport. In Section 4, we derive a fractional Fick's law and use Eulerian conservation of mass methods to obtain a fractional ADE. Section 5 links the concepts developed in previous sections with probability theory. Issues of scaling and ergodicity are addressed in Section 6. Finally, Section 7 links the topics presented in this paper to the terminology of stochastic theory and related studies.

2. Implications of Fickian dispersion

An underlying assumption of the ADE is that mechanical dispersion, like molecular diffusion, can be described by Fick's first law:

$$F = -\mathscr{D}_d \frac{\partial C}{\partial x} \tag{2}$$

where F is the mass flux of solute per unit area per unit time and $\mathscr{D}_\mathrm{d}$ is the effective diffusion coefficient in a porous medium. Fick's law states that particle flux is directly

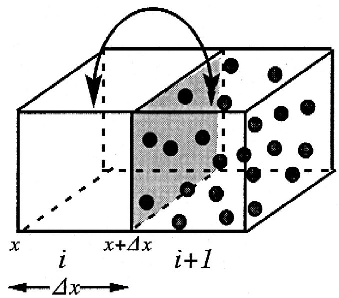

Fig. 1. Particles diffusing between two cells of length Δx.

proportional to the spatial concentration gradient. However, it is not the spatial concentration gradient that causes particle movement, i.e., particles do not "push" each other (Crank, 1976). Particles exhibit random motion on the molecular level. This random motion ensures that a tracer will diffuse, decreasing the concentration gradient (Crank, 1976). The particle motion implied by Fick's law can be examined using a finite-difference model for the diffusion of particles between two cells (Fig. 1). For simplicity, we consider particle transport in one dimension.

Let M_i be the number of particles in box i. Then, the concentration in each box is given by

$$C_i = \frac{M_i}{\Delta v} \tag{3}$$

where $\Delta v = A\Delta x$ is the volume of each box and A is the area of the box face normal to Δx.

Assuming that each particle jumps randomly backwards or forwards with rate R (with units jumps$/\Delta t$), then the number of particles that jump in a small time, Δt, is $M_i R\Delta t$. The flux, F_i, is the net number of particles per unit area that move from box i to box $i+1$ in the interval Δt:

$$F_i = \frac{\left(\frac{1}{2}M_i - \frac{1}{2}M_{i+1}\right)R}{A} = \frac{\frac{1}{2}(C_i - C_{i+1})\Delta v R}{A} = \frac{1}{2}(C_i - C_{i+1})R\Delta x. \tag{4}$$

Now, $C_{i+1} - C_i$ is equivalent to $C(x+\Delta x,t) - C(x,t)$. Since the Taylor series approximation for x at time t is

$$C(x+\Delta x,t) = \sum_{n=0}^{\infty} \frac{\partial^n C(x,t)}{\partial x^n}\frac{\Delta x^n}{n!} = C(x,t) + \frac{\partial C}{\partial x}(x,t)\Delta x + \mathcal{O}(\Delta x) \tag{5}$$

where

$$\mathcal{O}(\Delta x) = \frac{\partial^2 C}{\partial x^2}(x,t)\frac{\Delta x^2}{2!} + \frac{\partial^3 C}{\partial x^3}(x,t)\frac{\Delta x^3}{3!} + \dots,$$

Eq. (4) becomes

$$F = \frac{1}{2}\left[\frac{\partial C}{\partial x}\Delta x + o(\Delta x)\right] R \Delta x. \tag{6}$$

In order to recover Fick's law when the limit as $\Delta x \to 0$ is taken, we require:

1. $\frac{1}{2}\Delta x^2 R \to \mathscr{D}$
2. $\frac{1}{2} o(\Delta x^2) R \to 0$

Since $\mathscr{D}$ is a constant and $\Delta x \to 0$, it follows that $R \to \infty$. Thus, Δx^2 must decrease at the same rate that R increases, meaning Δx must grow like $(\Delta t)^{1/2}$ if $\mathscr{D}$ is to remain constant.

For accounting purposes, particle "jumps" that occur during a given Δt are constrained to a Δx. This means that there cannot be large deviations from the average particle velocity. Hence, the entire aquifer must have constant hydraulic properties on scales larger than some very small representative elementary volume (REV) in order for Fick's law to hold with a constant dispersion coefficient. Experiments by Bear (1961) and others have suggested that solute tracers in homogenous porous media exhibit Fickian dispersion.

Now consider mechanical dispersion in a heterogeneous aquifer. In this case, large velocity variations at the pore scale are caused by the motion of fluid through a disordered porous medium. Since the hydraulic conductivity at different locations in an aquifer can vary over many orders of magnitude, there may always be particle velocities that are large enough that particle jumps are not constrained to a small REV. Assuming that an REV must exist on some scale and increasing the size of the control volume to meet it is analogous to increasing the discretization size in a Riemann sum when approximating an integral; the approximation becomes too coarse to provide any valuable information about the function. It has also been suggested that some particles travelling in aquifers move at velocities many orders of magnitude slower than the mean velocity (i.e., Brusseau, 1992; Haggerty and Gorelick, 1995), significantly affecting plume evolution.

It would be useful if particle jumps occurring in a given Δt could be modeled without limiting them to the length of a single control volume. A more robust model might also permit the probability of forward jumps and backward jumps to be different. If we describe the flux of particles as proportional to a *fractional derivative*, then the size of particle jumps, and hence the magnitude of the particle velocities, are unconstrained. The fractional derivative will also permit unique jump direction probabilities. Before developing the notion of "fractional dispersion", an introduction to fractional calculus and utility of fractional derivatives is provided.

3. Fractional calculus

Fractional calculus is concerned with rational-order, rather than strictly integer-order, derivatives and integrals. The majority of fractional calculus theory was developed in the

19th century (see the history compiled by Oldham and Spanier, 1974). The mathematics of fractional calculus is a natural extension of integer-order calculus. Long thought to be a mathematical construct with little application, fractional calculus is now being used in many scientific and engineering fields, including fluid flow, electrical networks, electromagnetic theory, and probability and statistics (e.g., Miller and Ross, 1993; Oldham and Spanier, 1974; Zaslavsky, 1994; Gorenflo and Mainardi, 1998a). Fig. 2 demonstrates that fractional-order derivatives form a continuum between their integer-order counterparts.

Benson et al. (2000a) and Gorenflo and Mainardi (1998a) provide an introduction to fractional calculus as it applies to diffusion problems while Oldham and Spanier (1974),

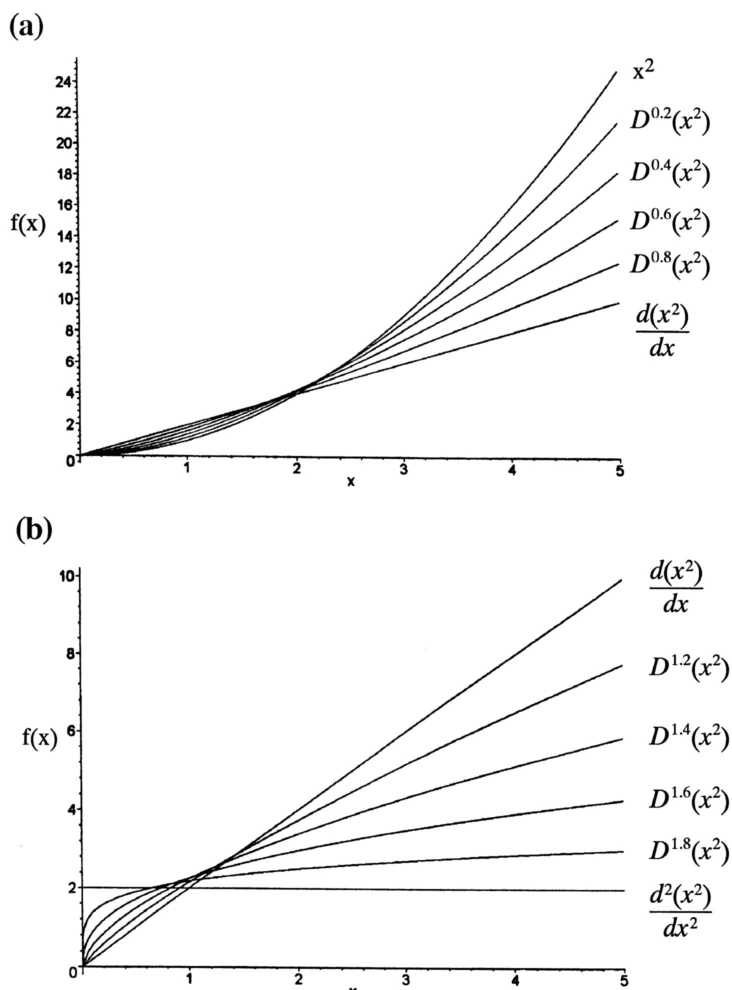

Fig. 2. (a) Plot of the function $f(x) = x^2$ and its 0.2, 0.4, 0.6, 0.8, and 1st derivatives. (b) Plot of the 1st, 1.2, 1.4, 1.6, 1.8, and 2nd derivatives of $f(x) = x^2$.

Miller and Ross (1993), or Samko et al. (1993) present complete treatises on the subject. For the purposes of this discussion, it is only critical to understand the differences in the behavior of integer-order and fractional-order derivatives.

Integer-order derivatives depend only on the local behavior of a function, meaning the slope of the function at an infinitesimally small interval. Fractional derivatives, however, are non-local functions. The fractional derivative of a function at a given point depends on the character of the entire function (Blank, 1996). This is most easily demonstrated by expressing the fractional derivative as a linear combination of a left and right sided derivative:

$$D_{\beta}^{q} = \left[\tfrac{1}{2}(1-\beta)\right] D_{+}^{q} + \left[\tfrac{1}{2}(1+\beta)\right] D_{-}^{q} \tag{7}$$

where $-1 \leq \beta \leq 1$ and $\frac{1}{2}(1-\beta)$ and $\frac{1}{2}(1+\beta)$ are the probabilities that a particle will jump backwards or forwards. D_{+}^{q}, known as the Riemann–Liouville operator, is the derivative of a function from $-\infty$ to x while D_{-}^{q}, known as the Weyl fractional derivative, is the derivative from x to ∞ (Gorenflo and Mainardi, 1998b).

If the series definition of the Riemann–Liouville operator (Miller and Ross, 1993),

$$D_{+}^{q} f(x) = \lim_{\Delta x \to 0} \frac{1}{\Gamma(-q)} \Delta x^{-q} \sum_{k=0}^{\infty} \frac{\Gamma(k-q)}{\Gamma(k+1)} f(x - k\Delta x) \tag{8}$$

is rewritten in the form

$$D_{+}^{q} f(x) = \lim_{\Delta x \to 0} \frac{\sum_{k=0}^{\infty} w_k f(x - k\Delta x)}{\Delta x^{q}}, \tag{9}$$

where

$$w_k = \frac{\Gamma(k-q)}{\Gamma(k+1)\Gamma(-q)},$$

it is readily apparent that a Riemann–Liouville fractional derivative is the limit of a weighted average of the values over the function from $-\infty$ to x. These weights, w_i, correspond (in the limit) to a power function defined by the order of the fractional derivative, q. Fig. 3 includes a log–log plot of the weights representing the dependence of a fractional derivative at a given point of a function on points up to 100 cells away. Weights corresponding to the 0.1, 0.5, and 0.9th derivatives are presented. The larger-order fractional derivatives place more weight on proximal cells and dependence on distal cells decrease very quickly with distance. Conversely, lower-order fractional derivatives place relatively less weight on proximal cells and the dependence on distal cells decreases slowly. As $x \to \infty$, the slope of the weight function is equal to $-q$.

While the Riemann–Liouville operator has memory over the function from $-\infty$ to x, the Weyl operator is the limit of a weighted average of the values over the function from x to ∞. Thus, the fractional derivative, Eq. (7), at a point on a function has a unique power law “memory” both forwards and backwards on the function.

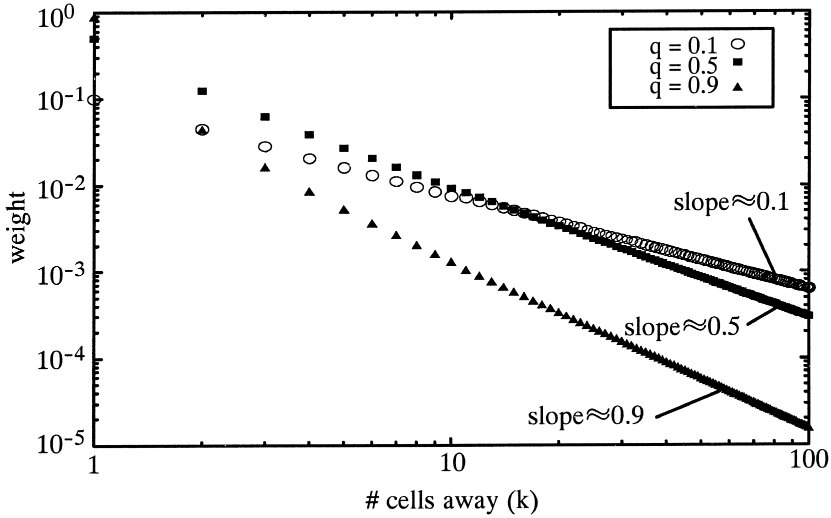

Fig. 3. Log–log plot demonstrating the power law decay in weights placed on the 100 closest cells in calculating the qth fractional derivative.

If the probability distribution for forward jumps follows one power law, $P(X > x) = C_1 x^{-q_1}$, where $x > 0$, and the probability distribution for backwards jumps follows a second power law, $P(-X > x) = C_2 x^{-q_2}$ $(x > 0)$, then the ratio of forward to backward jump probabilities, $(1+\beta)/(1-\beta)$, is equal to the ratio of the densities as x becomes large (Fig. 4). If $q_1 = q_2$, then the ratio is constant and $-1 \leq \beta \leq 1$ is the skewness. If $q_1 < q_2$, then the probability of large jumps in the forward direction will be much larger than the probability of large jumps in the backward direction. As $x \to \infty$, $(1+\beta)/(1-$

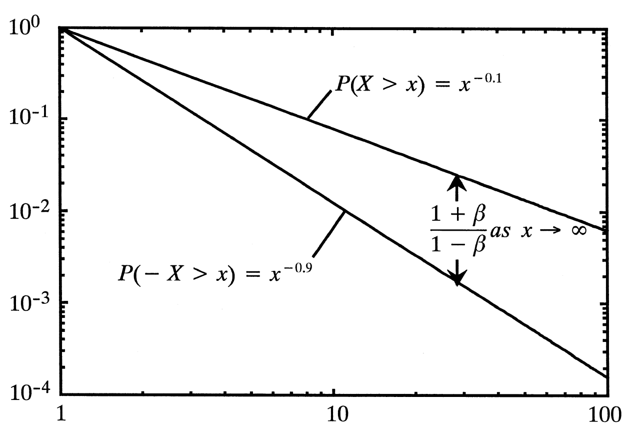

Fig. 4. The ratio of the probability of forward jumps to negative jumps is the distance between the power law probabilities on a log–log plot.

$\beta) \to \infty$ so we must have $\beta = 1$. Since the lower value of q_1 and q_2 tends to dominate, the fractional derivative in this case will take the form $D_\beta^q = D_1^{q_1}$. If $q_2 < q_1$, then as $x \to \infty$, $(1+\beta)/(1-\beta) \to 0$, so $\beta = -1$ and the appropriate fractional derivative will be $D_\beta^q = D_{-1}^{q_2}$. Since it is highly unlikely that the probabilities of forward and backward jumps decrease with the same power law in a heterogeneous porous medium, dispersive flux should be proportional to a fractional derivative of form $D_\beta^q = D_1^{q_1}$ or $D_\beta^q = D_{-1}^{q_2}$.

4. Fractional dispersion and the fractional ADE

The generalized Taylor series (Osler, 1971):

$$C(x+\Delta x,t) = \sum_{n=-\infty}^{\infty} D_\beta^{n+q}(C)\frac{\Delta x^{n+q}}{\Gamma(n+q+1)}$$

$$= D_\beta^q C(x,t)\frac{\Delta x^q}{\Gamma(q+1)} + o(\Delta x^q) \tag{10}$$

where q is a rational number and D_β^q, the qth derivative, is valid for both integer and fractional-order derivatives. Since the gamma function is equivalent to the factorial function for integers, Eq. (10) reduces to Eq. (5) for integer-order derivatives. Note that each term of a fractional-order Taylor series includes the weighted average of the values over the entire function.

Using the generalized Taylor series for $C(x+\Delta x,t)$ in the equation for particle flux, Eq. (4), we have

$$F = \frac{1}{2}\left[D_\beta^q(C)\frac{\Delta x^q}{\Gamma(q+1)} + o(\Delta x^q)\right]R\Delta x. \tag{11}$$

Taking the limit as $\Delta x \to 0$ yields a fractional Fick's law:

$$F = \mathscr{D} D_\beta^q(C) \tag{12}$$

which, because of the multi-directional nature of the fractional derivative can also be expressed as

$$F = \mathscr{D}\left[\left(\tfrac{1}{2}(1+\beta)\right)D_+^q(C) + \left(\tfrac{1}{2}(1-\beta)\right)D_-^q(C)\right]. \tag{13}$$

The fractional Fick's law is valid as $\Delta x \to 0$ when:

1. $\frac{1}{2}\dfrac{\Delta x^{q+1}}{\Gamma(q+1)}R \to \mathscr{D}$
2. $\frac{1}{2}o(\Delta x^{q+1})R \to 0$

In contrast to the non-fractional case, when a limit is taken as $\Delta x \to 0$, it must be true that $R \to \infty$ at the same rate as $\Delta x^{q+1} \to 0$ in order for $\mathscr{D}$ to be constant. Thus, Δx must grow at the same rate as $(\Delta t)^{1/\alpha}$, where $\alpha = q+1$.

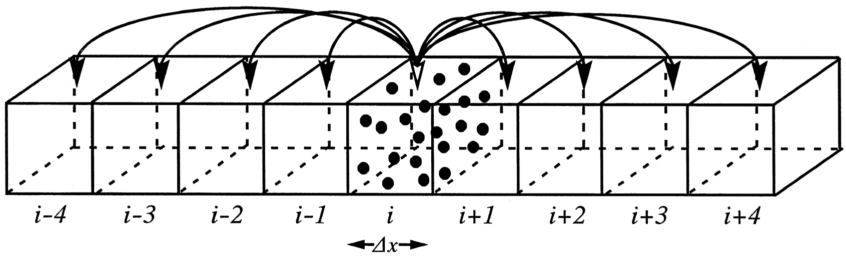

Fig. 5. A fractional Fick's law allows the particles in box i to move more than one box in a small Δt. Note that the probability a particle moves one box forward or backward is greater than the probability that a particle moves forward or backward two boxes, which is greater than the probability that a particle moves three boxes, etc.

The hydraulic conductivity of a perfectly homogeneous aquifer can be measured in a single control volume. As we seek to describe the variation in hydraulic conductivity of heterogeneous aquifers, a non-local function is required. The first-order derivative in Fick's law describes a uniform velocity field in a homogenous porous medium. As the order of the fractional derivative in the fractional Fick's law decreases, that is, as q is reduced, a more heterogeneous porous medium is represented because there is a higher probability that particles may travel farther in a given Δt (Fig. 3). Since the heterogeneity of the system is characterized by the fractional derivative, there is no need for the dispersion coefficient, $\mathscr{D}$, to be scale-dependent.

As depicted in Fig. 5, a particle whose motion is governed by a fractional Fick's law can move any distance from its original location in a given Δt, with the probability that a particle moves a given distance backwards decaying as one power law and the probability that it moves forwards decaying as a second power law. The precise power laws are governed by the order, α, and skewness coefficient, β, of the fractional derivative as previously described. Also note that the particle model in Fig. 5 represents solute dispersion. If box i is advected at the mean groundwater velocity, then the forward particle jumps represent particle velocity that is faster than the mean flow, while backward jumps represent particle velocity below the average velocity. The parameter β describes the relative probabilities of particle travel ahead or behind the mean velocity.

The Eulerian derivation of the one-dimensional ADE based on the conservation of mass of solute flux into and out of a small control volume of porous media (e.g., Freeze and Cherry, 1979) can be generalized to that of a solute transported by advection and fractional dispersion.

Let solute transport in the x direction be given by:

$$\text{Advective transport} = v_x n_e C dA \tag{14}$$

$$\text{Dispersive transport} = n_e \mathscr{D}_x D_\beta^q(C)\, dA \tag{15}$$

where $D_\beta^q(C)$ is the qth derivative of concentration, n_e is the effective porosity and dA is the cross-sectional area of the element perpendicular to the direction of flow. Then, the mass flux in the i direction, F_i, is the sum of the advective and dispersive components:

$$F_x = v_x n_e C - n_e \mathscr{D}_x D_\beta^q (C) \tag{16}$$

where $0 < q < 1$.

Substituting Eq. (16) into the equation for conservation of mass in one dimension,

$$-n_e \frac{\partial C}{\partial t} = \frac{\partial F_x}{\partial x}, \tag{17}$$

yields

$$\frac{\partial C}{\partial t} = \left[\frac{\partial}{\partial x} \left(-v_x C + \mathscr{D}_x D_\beta^q (C) \right) \right]. \tag{18}$$

If we let $\alpha = q + 1$ be the order of the fractional derivative in both the forward and backward directions and assume that porosity, velocity, and the dispersion coefficient are constant, a fractional ADE is obtained:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + \mathscr{D} D_\beta^\alpha (C). \tag{19}$$

The fractional ADE can describe solute plume evolution with a large probability of particles moving significantly ahead of and behind the mean solute velocity. The order of the fractional derivative, $1 < \alpha \leq 2$, will be close to 1 for highly heterogeneous aquifers, closer to 2 for more homogenous aquifers, and equal to 2 for homogenous aquifers. Furthermore, $\beta = 1$ when solute disperses preferentially at velocities ahead of the mean velocity and $\beta = -1$ when more of the solute remains behind the mean groundwater velocity. Statistical–mechanical derivations for Eq. (19) can be found in Meerschaert et al. (1999), Benson (1998), Benson et al. (2000a), and Chaves (1998). Cushman and Ginn (in review) demonstrate that the fractional ADE is a special case of the non-local transport equations found in Cushman and Ginn (1993). The three dimensional case is more complicated (as discussed in Meerschaert et al., 1999), as the order of the fractional derivative is not necessarily equal in all directions and the “skewness” can assume many directions.

5. Stochastic modeling and stochastic hydrogeology

Stochastic modeling uses the laws of probability theory to predict the outcome of processes that contain random elements. Central to these laws are limit theorems, which specify the distribution of the sum of a large number of n iid random variables. DeMoive’s well known central limit theorem,

$$\lim_{n \to \infty} \frac{X_1 + X_2 + \ldots + X_n - n\mu}{\sigma n^{\frac{1}{2}}} = Y \sim N(\mu = 0, \sigma^2 = 1), \tag{20}$$

states that an appropriately shifted and normalized sum of iid, *finite-variance* random variables, X_i, divided by the square root of n, will converge to a Gaussian distribution with zero mean and unit variance. This implies that the sum of the random variables $X_1 + X_2 + \dots + X_n$ grows at the same rate as $n^{1/2}$.

The central limit theorem is not the only limit theorem. It is a special case of Lévy's general limit theorem,

$$\lim_{n \to \infty} \frac{X_1 + X_2 + \dots + X_n - n\mu}{\sigma n^{\frac{1}{\alpha}}} = Y \sim S_\alpha(\sigma = 1, \beta, \mu = 0) \tag{21}$$

which states that normalized sums of iid random variables of *any* distribution will converge to a "α-stable" or "Lévy-stable" distribution with index of stability $0 < \alpha \leq 2$, skewness coefficient $-1 \leq \beta \leq 1$, shift parameter $\mu = 0$, and spread parameter $\sigma = 1$ (Feller, 1971; Gnedenko and Kolmogorov, 1968). Because all stable densities cannot be written in closed form, they are typically expressed in terms of their Fourier transforms:

$$\begin{aligned} Ee^{(i\theta x)} &= \int_{-\infty}^{\infty} e^{i\theta X} f(x)\,dx \\ &= \exp\left(-\sigma^\alpha |\theta|^\alpha \left(1 - i\beta(\operatorname{sign}\theta)\tan\frac{\pi\alpha}{2} \right) + i\mu\theta \right) \qquad \text{if } \alpha \neq 1 \end{aligned} \tag{22}$$

where $f(x)$ is a stable density and

$$\operatorname{sign}\theta = \begin{cases} 1 \text{ if } \theta > 0 \\ -1 \text{ if } \theta < 0. \end{cases}$$

The Gaussian distribution is a stable distribution with $\alpha = 2$ (the skewness coefficient is irrelevant when $\alpha = 2$.) The Cauchy distribution, omitted from Eq. (22) for clarity, is stable with $\alpha = 1$. The densities of several symmetric ($\beta = 0$) stable distributions are compared in Fig. 6. The effect of varying the skewness coefficient of a stable density is demonstrated in Fig. 7.

Random variables whose limiting sums are normally distributed are said to be in the Gaussian "domain of attraction". The densities in α-stable domains of attraction have at least one tail that decays as the power function $|x|^{-\alpha-1}$. The power-law tails result in such large probabilities of extreme values (values far from the mean) that these distributions do not have a defined second moment (or variance). These densities are thus referred to as *heavy-tailed* or *infinite-variance* distributions. Infinite variance occurs when the integral

$$\mathrm{VAR} = \int_{-\infty}^{\infty} (x - \mu)^2 f(x)\,dx, \tag{23}$$

diverges. When $\alpha < 2$, the stable distribution is still described with a scale parameter, σ, but the second moment diverges so the variance is undefined. Note that the standard deviation for a Gaussian distribution ($\alpha = 2$) is equal to the square root of two multiplied by the stable scale parameter, though both are denoted with a sigma.

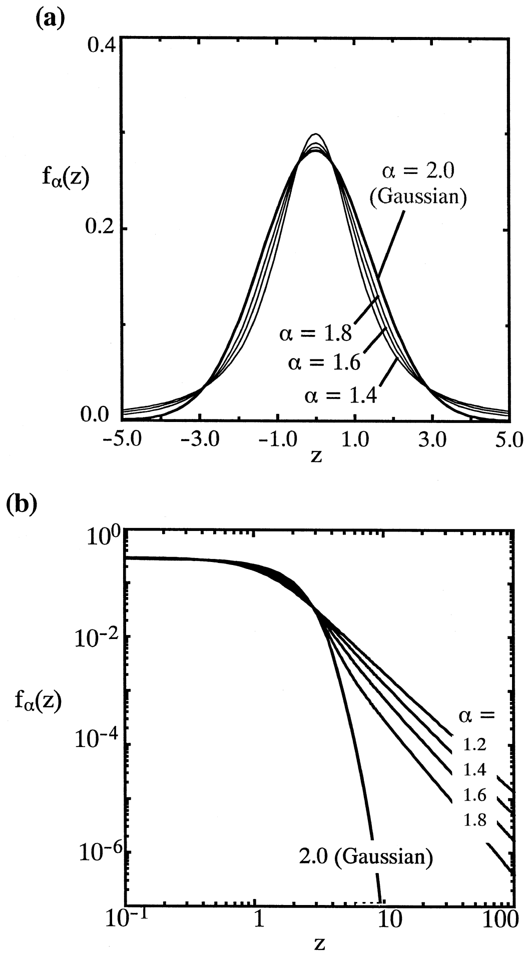

Fig. 6. Plots of symmetric standard α-stable densities showing power-law "heavy" tailed character. (a) linear axes, and (b) log–log axes. From Benson (1998).

It is important to remark that the finite-variance Gaussian distribution is defined from $-\infty$ to ∞. Using an infinite-variance α-stable distribution only changes the shape of the distribution, it does not change the domain over which the distribution is defined. Thus, an infinite-variance velocity model does not imply infinite magnitude particle velocities any more than the Gaussian does. Rather, the probabilities are different. In practice, infinite variance means that the sample variance (the calculated variance for a data set) for a set of random variables will not converge to a constant value as is generally expected by the law of large numbers. Fig. 8a demonstrates that if sample variance is calculated as standard normal random variables are generated, the sample variance does indeed converge to 1. However, in Fig. 8b, the sample variance for α-stable random variables is always finite but never converges to a constant value.

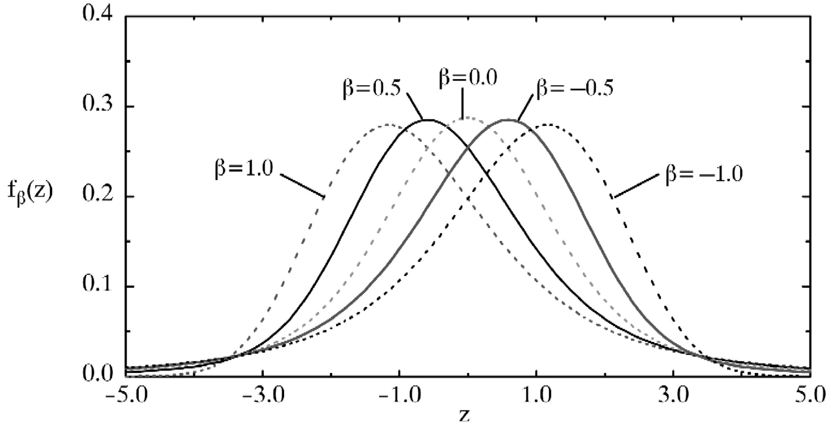

Fig. 7. Plot of $\alpha = 1.5$ stable densities with varying skewness.

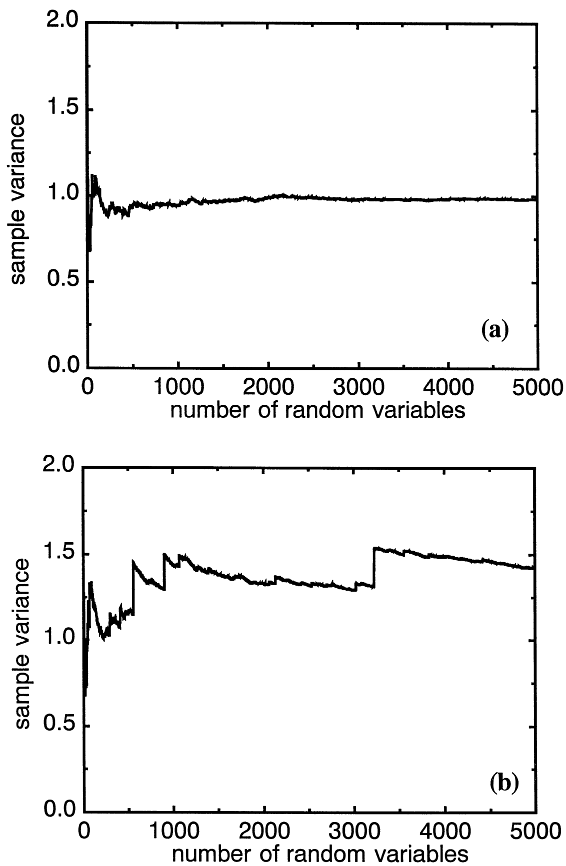

Fig. 8. Sample variance for of a set of (a) 5000 iid finite variance random variables and (b) 5000 iid infinite variance (1.9-stable) random variables.

Noting that the number of jumps, n, is equivalent to the total time divided by the time per jump, $t/\Delta t$, we can recast the classical central limit theorem to suit the problem of Fickian particle jumps:

$$\lim_{\frac{t}{\Delta t}\to\infty} \frac{\Delta x_1 + \Delta x_2 + \dots + \Delta x_{\frac{t}{\Delta t}} - \frac{t}{\Delta t}\mu}{\sigma\left(\frac{t}{\Delta t}\right)^{\frac{1}{2}}} = Y \sim N(0,1), \tag{24}$$

where the individual jump lengths, Δx_i, have mean μ and variance σ^2 and $\Delta x_1 + \Delta x_2 + \dots + \Delta x_{t/\Delta t}$ is the location of the particle at time t. Define the average particle velocity, $v = \mu/\Delta t$ and the dispersion coefficient, $\mathscr{D} = \sigma^2/\Delta t$. The central limit theorem then takes the form

$$\lim_{\frac{t}{\Delta t}\to\infty} \frac{\Delta x_1 + \Delta x_2 + \dots + \Delta x_{\frac{t}{\Delta t}} - vt}{\sqrt{\mathscr{D}t}} = Y \sim N(0,1). \tag{25}$$

As in the derivation of the equation for Fickian dispersion, for proper convergence of the central limit theorem, the length of particle jumps is proportional to $(\mathscr{D}t)^{1/2}$. The location of a particle at time t, the sum of particle jumps, $\Delta x_1 + \Delta x_2 + \dots + \Delta x_n$, must grow as $t^{1/2}$.

Note that the normalized sum of any finite-variance random variables, i.e., log-normal, uniform, etc., converges to the Gaussian. Stochastic theory mandates that Gaussian densities will be the solutions to a Fickian ADE. Similarly, the derivation for the fractional Fick's law implies the generalized central limit theorem in the form

$$\lim_{n\to\infty} \frac{\Delta x_1 + \Delta x_2 + \dots + \Delta x_n - n\mu}{\sigma\left(\frac{t}{\Delta t}\right)^{\frac{1}{\alpha}}} = Y \sim S_\alpha(\sigma = 1, \beta, \mu = 0) \tag{26}$$

or, substituting $v = \mu/\Delta t$ and $\mathscr{D} = \sigma^\alpha/\Delta t$,

$$\lim_{\frac{t}{\Delta t}\to\infty} \frac{\Delta x_1 + \Delta x_2 + \dots + \Delta x_{\frac{t}{\Delta t}} - vt}{(\mathscr{D}t)^{\frac{1}{\alpha}}} = Y \sim S_\alpha(\sigma = 1, \beta, \mu = 0) \tag{27}$$

where no assumption need be made about the specific distribution of particle velocity. Hence, the solutions to the fractional ADE are stable densities with $\alpha = 2$ (Gaussian) for homogeneous media and stable densities with $\alpha < 2$ for heterogeneous media. The stable densities with $\alpha < 2$ include information about the drift, spread, and skewness of the contaminant plumes. Note that the parameters α and β in the stable densities are the same as those in the fractional derivative. If particle dispersion in an aquifer is governed by a fractional Fick's law with fractional derivative D_β^α, then the corresponding conservative solute snapshot will look like the stable density $S_\alpha(\sigma,\beta,\mu)$ where $\sigma = (\mathscr{D}t)^{1/\alpha}$ and $\mu = v\Delta t$. Benson et al. (2000a,b) describe methods for estimating the parameters in the fractional ADE and applying the equation in both the laboratory and field settings.

6. Ergodicity

A *stochastic process* is a collection of random variables that describes the evolution of a physical process through time or space. As described in previous sections, the stochastic process under consideration in groundwater contaminant transport is the path of a solute particle through a porous medium. The random variables we sum are the individual "jump" lengths that occur in a small Δt. It is generally assumed that correlation decays rapidly beyond some Δt. A *stationary* stochastic process will follow the same probability law, regardless of its point of origin (Ross, 1997). Assuming that the hydraulic conductivity distribution of an aquifer dictates the distribution of solute particle velocities, a stationary conductivity field implies that a contaminant plume will evolve in the same way regardless of the source location.

A stochastic process is *ergodic* if the distribution of the sum of random variables reaches some limit that does not depend on its initial conditions (Feller, 1968). If particle travel is ergodic, then the probability that a particle will be located a distance x from its starting point will follow the appropriate stable distribution for a given time, t. As a result of the ergodic hypothesis, the concentration profile of an ensemble of such particles with a common starting location will follow the same distribution. Thus, in the case of solute transport, ergodicity is a statement of the conditions under which limit theorems can be applied: when a sufficient number of normalized, iid random variables have been added. Ergodic conditions are those under which equations based on limit theorems are good approximations of stochastic processes. Zhan (1999) indicates that the ergodic hypothesis for transport in aquifers is usually invalid when heterogeneity is strong. This study suggests that it is only Gaussian limiting conditions that will not be reached when heterogeneity is strong. Early-time, pre-asymptotic, or pre-ergodic equations may not be necessary for the description of non-Gaussian breakthrough curves because ergodic conditions can produce plume evolution following any one of the many limiting, α-stable, distributions. The spread and index of stability of the proper limiting distribution are directly related to the dispersion coefficient and the order of the fractional derivative in the corresponding fractional ADE. When ergodic conditions are reached, these non-local parameters do not vary with time. Thus, the scaling properties of the dispersion coefficient are eliminated.

7. Stochastic processes

This study addresses the concepts behind the fractional ADE in a context that does not require a familiarity with statistical mechanics. However, most studies of particle motion in the presence of disordered media have been published by physicists. In this section, the concepts of aquifer contaminant transport discussed in this paper are linked with their statistical mechanics or mathematical counterparts and mention significant references. Here, "stochastic processes" refer to the random processes leading to partial differential equations (PDEs), not the stochastic theories in which the parameters and dependent variables in deterministic PDEs are randomized (e.g., Gelhar and Axness, 1983).

The model of the random motion of a particle as composed of discrete jumps is commonly known as a random walk. The Fickian random walks taken by particles in homogeneous media are discrete approximations of Brownian motion processes or Wiener processes. Transport that exhibits non-Fickian or non-"Boltzmann" scaling is termed "anomalous diffusion". Kochubei (1990) provides a mathematical proof that the fractional-order diffusion equation describes anomalous transport.

The term "stable" in Lévy's distributions indicates that a distribution is in its own domain of attraction. The motion of particles that requires use of the generalized central limit theorem is known as Lévy motion. Brownian motion is a subset of Lévy motion. An argument for the ubiquity of Lévy distributions in nature is provided by Tsallis et al. (1995). The relationship between Lévy processes and anomalous diffusion is discussed by Compte (1996), Gorenflo and Mainardi (1998b), Zumofen et al. (1990) and many others.

A stochastic process is self-similar if it has stationary increments (jump lengths) and is invariant if the proper scaling index is used. The scaling index for Brownian motion is $1/2$ while the index for Lévy motion is $1/\alpha$. Random walks on self-similar fractal objects have been investigated by a number of authors (e.g., Metzler et al., 1994; Roman and Giona, 1992). While Brownian and Lévy motion have statistically independent increments, other self-similar processes display long-range temporal dependence. It has been demonstrated that long-range spatial correlation alone can result in enhanced dispersion rates (Makse et al., 1998), implying faster-than-Fickian plume evolution in finite-variance hydraulic conductivity fields with long-range spatial correlation. Fractional Brownian motion (fBm), the counterpart to Brownian motion that includes long-range temporal dependence, has been used to characterize aquifer heterogeneity with correlation (see Molz et al., 1997 and references therein). The scaling parameter for fBm is known as the Hurst coefficient. Other studies have suggested that aquifer heterogeneity can be modeled using fractional Lévy motion (fLm), which combines long range dependence with heavy tails, or even multifractals, a generalization of fLm which permits distributions describing different heterogeneity scales to follow different power laws (Molz et al., 1997; Liu and Molz, 1996, 1997). These formalisms have been used to generate conductivity fields for use in numerical simulations demonstrating that transport in disordered, correlated porous media is non-Fickian and heavy-tailed (Molz et al., 1999). The relationship between the structure of the hydraulic conductivity field and solute particle distribution remains an open question.

Continuous-time random walks (CTRWs), which generalize random walks by allowing a time delay between particle jumps were developed by Montroll and Weiss (1965). Scher and Lax (1973) present CTRWs as a general theory for transport in disordered systems, which include a coupled spatial–temporal memory. Berkowitz and Scher (1998) suggest that the anomalous spreading of solutes in both fractured and porous media can be modeled using the CTRW formalism.

8. Summary

A Fickian model for solute dispersion in aquifers implies that the probability distribution governing solute velocity must have a finite variance. However, the large variation in hydraulic conductivity values in heterogeneous aquifers may lead to an infinite-variance velocity field. In this case, dispersive flux is best described using a fractional Fick's law, in which flux is proportional to a fractional-order derivative. The non-local nature of the fractional derivative means that this model does not rely on an REV. When a fractional Fick's law replaces the classical Fick's law in an Eulerian evaluation of solute transport in a porous medium, the result is a fractional ADE. Fractional ADEs have α-stable solutions with tail and skewness parameters equal to those in the fractional derivative. These solutions can be asymmetric and can have heavy leading and/or trailing edges, resembling breakthrough curves observed in the laboratory and field.

The Gaussian is a subset of stable distributions, the classical central limit theorem is a special case of a generalized central limit theorem, integer-order derivatives are subsets of fractional-order derivatives, and homogeneity and heterogeneity are two types of ordered media. The connection between these generalizations tend to support a fractional ADE, which describes a scale-invariant stochastic process, as an appropriate model for conservative solute transport in porous media.

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