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Anomalous mixing and reaction induced by superdiffusive nonlocal transport

Diogo Bolster[*]
Environmental Fluid Dynamics Laboratories, Department of Civil Engineering and Geological Sciences,
University of Notre Dame, Indiana 46556, USA

David A. Benson
Hydrologic Science and Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

Tanguy Le Borgne
Géosciences Rennes, UMR 6118, CNRS, Université de Rennes 1, Rennes, France

Marco Dentz
Institute of Environmental Analysis and Water Studies (IDAEA), CSIC, Barcelona, Spain

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Spatially nonlocal transport describes the evolution of solute concentration due to mass transfer over long ranges. Such long-range mass transfer, present in many flow situations, changes the character of mixing and consequent chemical reactions. We study mixing in terms of the scalar dissipation and reaction rates for mixing-limited equilibrium reactions, using the space-fractional advection-dispersion equation (fADE) to model long range mass transfer. The scalar dissipation and global reaction rates decay as power-laws at late time. As opposed to the Fickian (local) transport model, local reaction rates are not zero where the concentration has zero gradient. As α, the fractional derivative exponent, decreases from two in the fADE, the reaction rate grows larger at the position of zero gradient, due to long-range transfer of reactants from distances larger than Fick's law allows. The reaction rates are also greater far from the reactant source for non-Fickian transport; however, the globally integrated reaction rate decreases with smaller α. This behavior may provide a method to investigate spatial nonlocality as a proper model of upscaling: the reaction products would be found in places precluded by Fickian dispersion, and overall reaction rates are suppressed.

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I. INTRODUCTION

Fick's law has been commonly used to model tracer dispersion in flows. In this transport framework, the evolution of the tracer concentration $c(x,t)$ is governed by the advection-dispersion equation (ADE)

$$\frac{\partial c(x,t)}{\partial t} + v\frac{\partial c(x,t)}{\partial x} = D\frac{\partial^2 c(x,t)}{\partial x^2}, \tag{1}$$

where v is the flow velocity, and D the dispersion coefficient.

The ADE describes mass accumulation or depletion due to the difference in advective and dispersive fluxes immediately upstream and downstream of any point. It also describes the probability density function of the location of particles undergoing Brownian motion with a deterministic drift (e.g., [1]) and a random increment that is Gaussian with zero mean and variance $2D\tau$, where τ is a constant mass transfer time scale. The typical spatial mass transfer scales are given by advection, $l_a = v\tau$ and dispersion $l_d = \sqrt{D\tau}$. While the former measures a constant displacement in the flow, the latter quantifies the mixing length, which is the typical length over which concentration contrasts are dissipated. For a unit-mass, pointlike, tracer injection in an infinite medium, both the centroid travel distance and the centered second moment (i.e., variance) of $c(x,t)$ grow linearly with time. This is known as Fickian behavior.

A wide array of physical systems display non-Fickian behavior for transport (e.g., [2–5]). The non-Fickian behavior is characterized by superlinear or sublinear growth of the centroid and variance of the tracer distribution, heavy tails of the spatial distribution, and early or late arrival times. Various models exist that capture such behavior. These are typically characterized by spatially and temporally nonlocal transport equations that can account for long-range mass transfer from distant locations, and variability of mass transfer times. Among these models are projector formalisms [6], continuous time random walks [7] and spatially fractional advection-dispersion equations (fADE) [8–11].

We focus on the fADE, which models long-range mass transfer. While this is one of a large variety of spatially nonlocal equations, we use it for several reasons: it is the governing equation of the density of Lévy motion, which is commonly observed in many physical settings [12]; it has been used to explain anomalous behavior of well-studied field-scale aquifer tracer tests [13]; and the model yields tractable solutions that give insight into the general effect of spatially nonlocal transport on mixing and chemical reaction. For simplicity we consider one-dimensional and symmetric dispersion characterized by (e.g., Refs. [8,9]):

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[*] bolster@nd.edu

$$\frac{\partial c(x,t)}{\partial t} + v\frac{\partial c(x,t)}{\partial x} = D_\alpha \frac{\partial^\alpha c(x,t)}{\partial |x|^\alpha}, \tag{2}$$

where $1 \leq \alpha \leq 2$. The generalized dispersion coefficient D_α has units $[L^\alpha T^{-1}]$. The Riesz fractional derivative may be defined through its Fourier transform by

$$\frac{\partial^\alpha c(x,t)}{\partial |x|^\alpha} \equiv -\int_{-\infty}^{\infty} \exp(ikx)|k|^\alpha \tilde{c}(k,t)\frac{dk}{2\pi}, \tag{3}$$

although slightly different definitions do exist (see, e.g., [14]). We specify natural boundary conditions (concentration and its derivatives are zero) at $x = \pm\infty$. The structure of the equation changes slightly within the context of the fADE, if one has a finite domain with boundary effects (see for example [15] for details). Note that Eq. (2) describes the evolution of the distribution density of a Lévy motion with a constant mean drift and random increments ξ characterized by a density function that decays with the asymptotic power law $|\xi|^{-1-\alpha}$. Therefore, unlike Brownian motion governed by the ADE, the fADE lacks a typical dissipation scale.

While the accurate prediction of conservative solute motion is very important in its own right, an emerging need is to be able to properly calculate mixing, because it is a primary driver in many chemical reactions (e.g., [16–18]), and also leads to solute dilution, as opposed to mere spreading. For transport described by the ADE, mixing has been quantified by the scalar dissipation rate (e.g., [19–21]). This quantity is global, that is, a spatially integrated measure for mixing. Its local counterpart is quantified in terms of concentration gradients. This reflects that short range mass transfer is the dominant mixing process. For Fickian transport this happens on the mixing scale $l_d = \sqrt{D\tau}$. For transport described by the fADE there is no typical mass transfer scale. Thus, the local measures defined for the ADE do not apply here, and mixing has to be described in terms of global measures, which integrate mass fluxes over all spatial scales.

Lacking a characteristic scale of mass transfer or dissipation, the fADE is expected to describe different solute mixing than the Fickian formulation. Indeed it can be expected that anomalous transport will affect mixing processes and reactions in a nontrivial way. The influence of subdiffusive and superdiffusive transport on reaction/diffusion front propagation has received much attention (e.g., [22–27]). The effect of large motion deviations on the propagation speed and shape of reaction/diffusion fronts is often counter intuitive. Lévy motion, while engendering fast growth of the front when there is no reaction, causes a slowing of the front when simple Fisher-type reactions are present, due to the "standing" of small amounts of reactants far from the bulk of the plume (e.g., Refs. [22,23]). These small, distant "packets" are rapidly removed via reaction [23], an effect that is missing from the Fickian model. This suggests that the global degree of mixing induced by Lévy motion will also have the largest control on global reaction rates. Because of the nonlocality of the mixing, the behavior of the reaction front should propagate throughout a moving cloud of reactants. Here, we consider a different type of reaction to those previously considered, namely an equilibrium bimolecular reaction. Unlike previous studies (e.g., [22–25]) we do not focus on front propagation, but rather investigate the global mixing and subsequent impact on mixing-driven reactions in a Lévy motion regime.

The choice of this type of reaction is motivated by the work of [18], who show that, within the context of the ADE for mixing-limited equilibrium reactions, the local reaction rate r can be calculated as the product of a speciation term (that depends on the reaction) and the mixing factor $D\nabla c \cdot \nabla c$. This concept was extended to a temporally nonlocal model in the multirate mass transfer formulation by [28,29]. Here, we examine the reaction rates and mixing that would occur within the fADE formulation, particularly as they relate to mass transfer over relatively large distances (e.g., [30]).

II. SPATIAL FRACTIONAL ADVECTION DISPERSION REACTION SYSTEM

We consider a mixing-limited chemical reaction of two solutes of concentrations c_1 and c_2 that react and precipitate to form c_3 with local chemical equilibrium conditions [18]. c_1 and c_2 are transported by space-fractional dispersion,

$$\frac{\partial c_i(x,t)}{\partial t} + v\frac{\partial c_i(x,t)}{\partial x} - D_\alpha \frac{\partial^\alpha c_i(x,t)}{\partial |x|^\alpha} = r(x,t) \quad i = 1,2, \tag{4}$$

while c_3 is immobile

$$\frac{\partial c_3(x,t)}{\partial t} = -r(x,t). \tag{5}$$

The two species c_1 and c_2 are in local equilibrium such that

$$c_1(x,t)c_2(x,t) = K \tag{6}$$

with K the equilibrium constant. We can now define a conservative component $u(x,t) = c_1(x,t) - c_2(x,t)$ that satisfies Eq. (2). Using the equilibrium condition in Eq. (6) and the definition of u the species concentration can be written as $c_{1,2}(x,t) \equiv c_{1,2}[u(x,t)]$. Doing so results in

$$c_{1,2}(x,t) = \pm\frac{u(x,t)}{2} + \sqrt{\frac{u(x,t)^2}{4} + K}. \tag{7}$$

III. CALCULATION OF LOCAL REACTION RATE

Following [18], the reaction rate can be calculated by inserting $c_i[u(x,t)]$ from (7) into (4), resulting in

$$r(x,t) = \frac{dc}{du}\frac{\partial u}{\partial t} + \frac{dc}{du}q\frac{\partial u}{\partial x} - D_\alpha \frac{\partial^{\alpha-1}}{\partial|x|^{\alpha-1}}\left[\frac{dc}{du}\frac{\partial u}{\partial x}\right]. \tag{8}$$

Using the generalized Leibnitz product rule for fractional calculus (e.g., [31])

$$\frac{\partial^{\alpha-1}}{\partial|x|^{\alpha-1}}\left[\frac{dc}{du}\frac{\partial u}{\partial x}\right] = \frac{dc}{du}\frac{\partial^\alpha u}{\partial|x|^\alpha} + \sum_{k=1}^{\infty}\binom{\alpha-1}{k}\frac{\partial^{\alpha-k}u}{\partial|x|^{\alpha-k}}\frac{\partial^k}{\partial x^k}\left[\frac{dc}{du}\right]. \tag{9}$$

Combining Eqs. (2), (8), and (9) allows us to calculate the reaction rate as

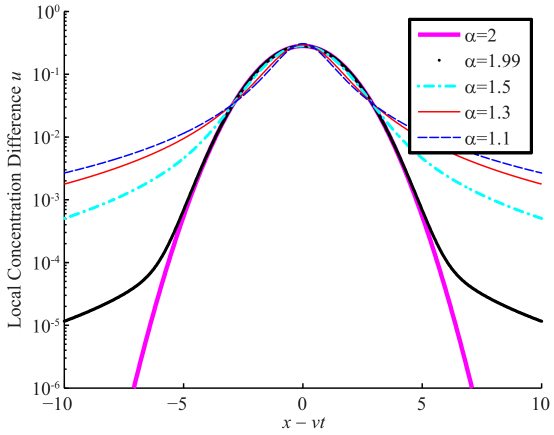

FIG. 1. (Color online) The conservative component $u(x,t)$ with a delta initial condition for various values of α for $K=0.1$ and at $t=1/D_\alpha$.

$$r(x,t) = D_\alpha \sum_{k=1}^{\infty} \binom{\alpha-1}{k} \frac{\partial^{\alpha-k}u}{\partial|x|^{\alpha-k}} \frac{\partial^k}{\partial x^k} \frac{dc}{du}. \tag{10}$$

For $\alpha=2$, all terms for $k>1$ in the binomial series $\binom{\alpha-1}{k}$ are zero, and this expression reduces to the one derived by [18]. This infinite sum and dependence of r on multiple fractional derivatives of u reflects, and retains, the nonlocal nature of the fADE. In short, particles do not have to begin directly next to one another to interact during some short time period. This expression suggests that estimating reactions in the fADE formulation is not as simple as the case of the classical ADE, where it is just the product of a local mixing and speciation term. Here, the relationship is more complex and depends on multiple derivatives of u as well as more complicated speciation terms.

We illustrate the spatial behavior of the conservative component $u(x,t)$ and the reaction rate $r(x,t)$ in an example characterized by the equilibrium constant $K=0.1$. The initial condition we consider is $u(x,t=0)=\delta(x)$. Decreasing the index α shifts more of the mass of u into the tails (Fig. 1). The local reaction rate $r(x,t)$ given in Eq. (10) for $\alpha=2$ (Fig. 2) displays a double hump with zero reaction rate at $x-vt=0$, which is because the gradient of $u(x,t)$ is zero here. All non-Fickian $\alpha<2$ curves display a very interesting feature: the reaction rate at the centroid at $x-vt=0$ is not zero. This point actually has the greatest reaction rate for the lowest value ($\alpha=1.1$) investigated here. This is noteworthy, because while the value of α codes the tails of conservative solute transport, it dictates the extreme distances that one reactive solute can infringe upon another through long range mass transfer. Hence the regions of greatest reaction rates are very different from classical small-range Fickian dispersion. The nonlocal expression Eq. (10) for the reaction rate r illustrates why the reaction rate is not zero at the peak concentration point. When $\alpha<2$, r depends on all higher-order (nonlocal) derivatives of u and not just the gradient (as is the case for $\alpha=2$). The enlarged range over which reactions may occur suggests that the global reaction rates (and other measures of plume mixing) may also be larger for smaller values of α.

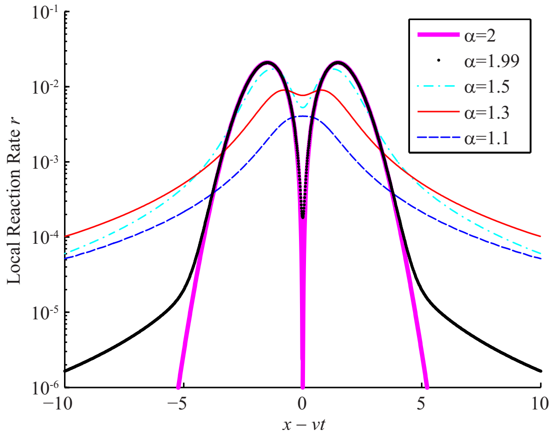

FIG. 2. (Color online) Local reaction rate r with a delta initial condition for u for various values of α at $t=1/D_\alpha$ and $K=0.1$.

IV. GLOBAL MEASURES OF MIXING AND REACTION

Let us consider the global reaction rate $R(t)=\int_{-\infty}^{\infty} r(x,t)dx$. Applying this integral to Eq. (10) and successively applying integration by parts we obtain

$$R = D_\alpha \int_\Omega \frac{\partial^{\alpha-1}u}{\partial|x|^{\alpha-1}} \frac{\partial u}{\partial x} \frac{d^2c}{du^2} dx. \tag{11}$$

It is interesting that this global measure can be simplified such as this [i.e., the infinite sum in Eq. (10) disappears], and leads us to speculate that other global measures may also display this type of simplification.

As a global mixing measure we consider the scalar dissipation rate which is defined by [19] $M(t)=-\frac{\partial}{\partial t}\int_\Omega u^2(x,t)dx$. Multiplying Eq. (2) by $u(x,t)$ and integrating over space gives

$$M = D_\alpha \int_{-\infty}^{\infty} \frac{\partial^{\alpha-1}u}{\partial|x|^{\alpha-1}} \frac{\partial u}{\partial x} dx. \tag{12}$$

Note that for Fickian transport ($\alpha=2$), the local scalar dissipation and reaction rates are defined in terms of the concentration gradient because it is (local) mass transfer from short distances that determines mixing. For transport as described by the fADE Eq. (2), mixing is a nonlocal phenomenon. This is expressed by Eq. (10) for the local reaction rate. Due to the long-range mass transfer mechanisms that are inherent in the fADE, it seems to be intuitive that mixing needs to be described by a global measure that integrates mass transfer over all scales.

Now we derive an explicit expression for $M(t)$ for the scenario described above, that is, a pointlike initial condition in a coordinate system moving with velocity v. The solution to the fADE with a Dirac-delta initial condition can be written as

$$u(x,t) = \int_{-\infty}^{\infty} e^{-D_\alpha t|k|^\alpha + ikx} \frac{dk}{2\pi}. \tag{13}$$

Integrating $u^2(x,t)$ over the spatial domain and taking a time derivative gives the scalar dissipation rate

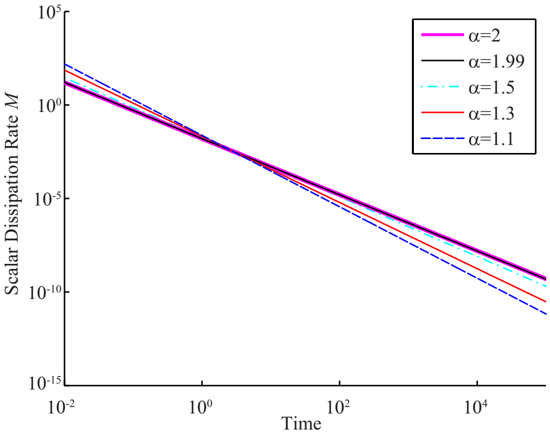

FIG. 3. (Color online) The scalar dissipation M against time for various values of α.

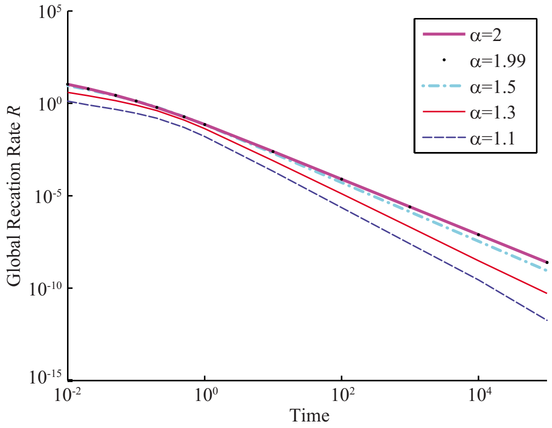

FIG. 4. (Color online) The global reaction rate R against time for various values of α and K=0.1.

$$M = \frac{\Gamma(1/\alpha)}{2\pi^2\alpha^2(2D_\alpha)^{1/\alpha}} t^{-(\alpha+1)/\alpha}. \qquad (14)$$

This is a power law in time that scales as $t^{-(\alpha+1)/\alpha}$. Note that Fickian mixing is characterized by a $t^{-3/2}$ scaling. In analogy to anomalous transport we term mixing that deviates from this behavior as "anomalous mixing," which occurs for all $\alpha \neq 2$. The behavior for various values of α is shown in Fig. 3. At early times mixing is larger for smaller values of α. This is because smaller values of α enable larger degrees of long range mass transfer thus making it more effective at smoothing out concentration contrasts and inducing more efficient mixing. At late times the systems with lower α have lower rates of mixing reflecting the fact that the enhanced early time mixing has led to a better mixed state. It is worth noting that all curves cross at the same point marking the time where anomalous mixing transitions from being greater to smaller than Fickian mixing.

This behavior suggests that the greater early-time mixing associated with small α may generate significant increases in the global reaction rates R. The integrand in Eq. (11) for R is equal to the one in Eq. (12) for M multiplied by the stoichiometric term d^2c/du^2. Some authors ([32]) show that under certain circumstances it is reasonable to assume that the speciation term is approximately constant, meaning that R is then directly proportional to the scalar dissipation rate M. However, a close look (Fig. 4) shows that this is not true during an initial transient region, where the reaction rates do not follow this power-law behavior at early times (with greater decreases for lower values of α). This is a reflection of the nonconstant stochiometric term d^2c/du^2. For very large values of u, d^2c/du^2 tends to become very small ([29]). The net effect is that the global reaction rate remains smaller at all times as the value of α decreases. These decreased rates, along with the simple observation that reactions are predicted to occur in regions precluded by Fickian formulations (Fig. 2), should allow independent tests of the veracity of the fADE as a proper model of upscaled transport. From a practical perspective, if traditional ADE models are used to predict reactions in systems where a nonlocal model is more appropriate, the location and amount of reaction occurring could be drastically incorrect. This would, for example, have severe implications for the design and implementation of remediation strategies that rely on delivery of reactive components (e.g., [33]).

V. CONCLUSION

In conclusion, we have studied mixing and subsequent chemical reactions that occur in a system with long range mass transfer. We chose the fADE to model this. We find that long range mass transfer leads to anomalous non-Fickian mixing, which is characterized by the scaling behavior $M \propto t^{-(\alpha+1)/\alpha}$. In particular, the smaller α, the greater the mixing rate at early times reflecting the fact that long-range mass transfer smooths out concentration contrasts more rapidly. As has been previously commented upon, the impact of Lévy motion on reactive system can be counterintuitive (e.g., [23]). In particular, within this study we note that the anomalous mixing induced by Lévy flights leads to the occurrence of reactions in regions where no such reaction could occur within a Fickian system. In some cases the regions of zero reaction within a Fickian system can even become the regions of maximum reaction within a Lévy motion system.

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