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Title: Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport

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Objective: The objective of this project was to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

Project Description: This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE) model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

1. RESULTS

Background: Our work at the Colorado School of Mines was focused on the following questions: 1) What are the effects of multi-scale geologic variability on transport of conservative and reactive solutes? 2) Can those transport effects be accounted for by classical methods, and if not, can the nonlocal fractional-order equations provide better predictions? 3) Can the fractional-order equations be parameterized through a link to some simple observable geologic features? 4) Are the classical equations of transport and reaction sufficient? 5) What is the effect of anomalous transport on chemical reaction in groundwater systems?

The work is predicated on the observation that upscaled transport is defined by loss of information, or spatio-temporal averaging. This averaging tends to make the transport laws such as Fick's 2nd-order diffusion equation similar to central limit theory (e.g., Einstein [9]). The fractional-order advection-dispersion equations rely on limit theory for heavy-tailed random motion that has some diverging moments. The equations predict larger tails of a plume in space and/or time than those predicted by the classical 2nd-order advection-dispersion equation. The heavy tails are often seen in plumes at field sites.

1) Multi-scale variability: A long-standing result from classical stochastic transport theory [19] held that an aquifer with continuous (fractal) variability as a function of scale would engender "super-stratified" growth of a conservative plume. Super-stratified in this context means growth of the centered second moment (commonly called the variance) of a plume according to $\langle (X-\mu)^2 \rangle \sim t^{\varepsilon}$ with $\varepsilon > 2$. Adopting Fick's law to describe dispersion of a plume has $\varepsilon = 1$. To investigate this, we first had to define and develop [3, 18] the numerical generation of multi-scaling fractal fields to match measured aquifer material as closely as possible. To match observed data sets, the Hurst scaling coefficient must be different in each coordinate, and the means to produce these fields had yet to be proven or codified. We investigated the transport of solutes through these multi-scaling fractal fields and found that plume variance growth is always between perfectly Fickian (t^1) and purely stratified [17] (t^2) rates, with highly non-Gaussian shape, refuting the analytic results postulated over a decade ago. We also found a simple explanation for the apparent super-stratified anomalous growth of dispersivity without a need for universal structure of aquifers [18].

Our next challenge was to generalize the multi-scaling fractal field generators to allow conditioning by K measurements. This was used to analyze the data collected by Klise [15]. The details of the conditioning have only recently appeared [4], but allowed us to rigorously test the sufficiency of the classical, Fickian advection dispersion equation [16]. In that paper, we challenged the notion that, based solely on a better fit to solute breakthrough data, a temporally non-local model is necessary for transport in an advection-dominated system. One may counter that the classical advection-dispersion equation (ADE) is a valid model at some small scale and that the detailed hydraulic conductivity (K) data must be well represented: Then the nonlocality is only a result of upscaling and loss of information. But is the non-local model demonstrably necessary at all scales? We examined the experiment conducted by [15] in which a 30.5×30.5 cm slab of relatively homogeneous, cross-bedded sandstone was exhaustively sampled for K. The slab was sealed, saturated with potassium iodide, and x-rayed ten times while being flushed with fresh water. The 8,649 air-permeameter measurements were down- and up-scaled to make finer and coarser grids on which the velocity field was solved and the ADE applied. The optimized parameters

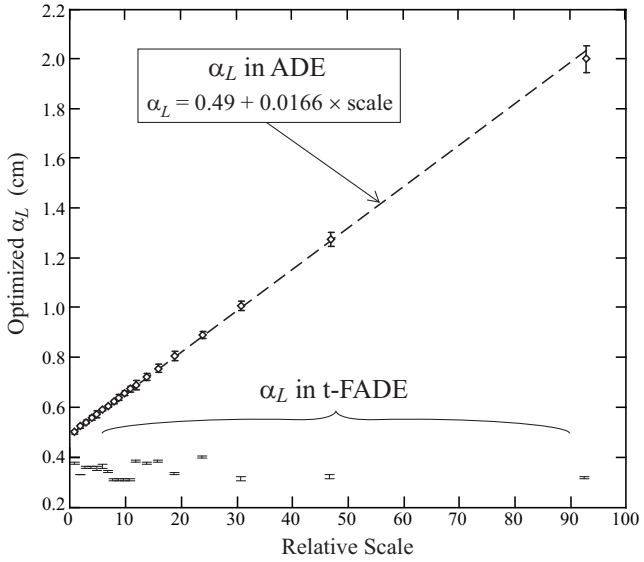

FIGURE 1. Linear plot of optimized values of longitudinal dispersivity α_L (versus scale)in both the classical ADE and the t-FADE applied to the Massillon sandstone slab. Error bars represent ± UCODE-reported parameter standard deviation. In addition to providing better fits, the t-FADE removed the scale dependence of parameters.

in the ADE were found to suffer from the scaling commonly noted in field plumes—most notably the longitudinal dispersivity (α_L), which grew linearly with up-scaling (Fig. 1). But at all levels of up- and down-scaling, the ADE did not adequately represent the late-time tails of the breakthrough curve. The temporally non-local, time-fractional, ADE (t-FADE) was applied and the optimized parameters (α_L and the immobile capacity β) did not depend on scale. The better fit provided by the t-FADE in the late BTC tails did not bring about a sacrificed fit elsewhere in the BTC. Furthermore, the optimized ADE and t-FADE solutions do not converge at the smallest scale, directly implying that the temporal non-locality is a necessary model component.

2) Multi-Rate Mobile/Immobile (Mass Transfer) Physics: We developed the one-to-one relationship between single particle dynamics and the upscaled continuum multi-rate mass transfer equations. This was done in such a way that the numerical implantation is extremely efficient and accurate [2]. The method can be incorporated in any existing particle tracking model (and was placed into the popular codes RWHet and Livermore National Lab's SLIM-FAST). Our findings also show that the effects of an immobile phase can be added to a mobile-only solution by subordinating to the inverse of the immobile waiting time distribution (related directly to the multiple rates). The subordination integral is similar to a convolution. The agreement between analytical and particle tracking solutions for several immobilization types is quite good and user-specified through the particle number.

3) Large-scale transport and fractional ADEs: Our investigations into field-scale transport followed two tacks. The first looked at the influence of sparse fracture networks on large-scale, ensemble transport. The second returned to the MADE site in Columbus,

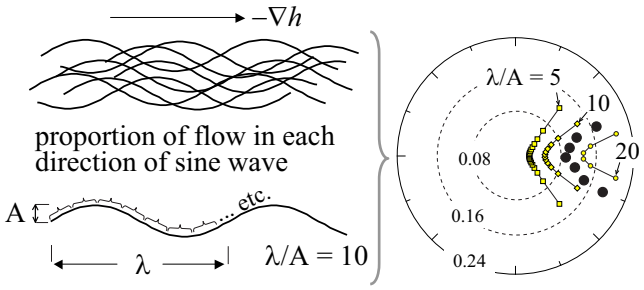

FIGURE 2. Theoretical $M(d\theta)$ for sinuous braided stream networks. Heavy circles in polar plot show average of fitted MADE site $M(d\theta)$.

Mississippi to look at highly heterogeneous granular material. Regarding this second line of research, we computed the growth of the first five integer moments predicted by several theories (continuous time random walks [CTRW], fractional mobile/immobile, and space-time fractional equations). We found that the space-fractional component is key to predicting fast-moving solute, and that a fractional mobile/immobile (fractal time) component is required to predict the decay of mobile mass [29]. Therefore, a governing equation that makes accurate predictions at the MADE site is:

$$\frac{\partial C}{\partial t} + \beta \frac{\partial^\gamma C}{\partial t^\gamma} = -\nabla \cdot vC - D\nabla_M^A C, \tag{1}$$

where $C(x,t)$ is total resident concentration, $\beta(x)$ is the immobile capacity coefficient, $0 < \gamma < 1$ is the fractal mobile/immobile coefficient, t is time, $v(x,t)$ is mean velocity vector, A is the direction-dependent fractional derivative matrix, and $M(\theta, v)$ is the mixing measure, which is essentially a three-dimensional dispersion coefficient. We followed classical techniques used to determine dispersivity for granular material based on simple geometric analogs and found that a model of superimposed braided stream networks could develop an accurate estimate of the mixing measure (Fig. 2). We could then apply [28] a very simple model (based on only three zones of heterogeneity) that closely resembles the real tritium plume at the MADE site (Fig. 3).

Regarding transport through fractured rock, we investigated whether the parameters for the fractional equation could be discerned from fracture data. It appears that fractures with power-law length distribution $P(L > l) \sim l^{-a}$ with $a < 2$ engender fractional-order transport [23, 24] that follows (1). Discerning the important parameters of fractional derivative order and mixing measure (the dispersivity in all directions) was closely related to fracture set statistics (see, for example, Fig. 4). The link allowed us to make generalizations about the suitability of geologic repositories based on fracture statistics [22].

4) Parameters from Geologic Information: The predictions at the MADE site required the estimation of a number of parameters. Some were gained from an observation of the plume itself (particularly those in the time operator on the left-hand side of eq. (1)), which amounts to fitting instead of prediction. The parameters for the space operator (order of derivative and mixing measure) were gleaned from the K distribution, with an assumption the the high-K deposits originated from a braided stream environment. To investigate the ability to estimate the time parameters from geologic information, we simulated a large

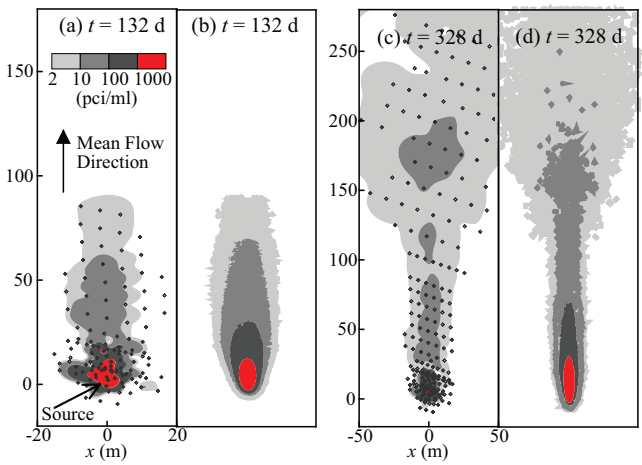

FIGURE 3. The concentration profiles at day 132 and 328, with the measurements ((a) and (c)) versus the simulations ((b) and (d)). The dots in (a) and (c) denote the locations of observation wells used for the measured concentration interpolation and model calibration (121 and 215 wells for day 132 and 328, respectively). The simulations use measured average velocities and the mixing measure shown in Fig. 2. It is important to note that the simulations of Eq. (1) use only three zones (i.e., nodes) yet reproduce very complex behavior.

number of aquifers using Markov-Chain facies simulators and compared these to an analytic expression for the late-time tailing of an ensemble plume. Our results show that the fractal parameters β and γ, which dictate sequestration in low-K (diffusion-limited) facies, can be very accurately estimated from boring logs by simply looking at the distribution of low-K unit thicknesses [27]. If the solute sequestered in these units is released primarily by diffusion, then the predictions of late-time tailing and remediation are very accurate.

5) Validation in Surface Water Systems: It is expensive and time-consuming to conduct studies in aquifers. The same type of heavy-tailed dynamics could be expected in rivers and streams, because solutes may partition into the sub-stream hyporheic zone in much the same way that solute may diffuse from a high-K aquifer unit into a low-K unit. This analogy allows us to gather lots of data quickly and cheaply to test the veracity of the fractional-order equations [21, 10]. Furthermore, there have been tests of sediment transport that show the hallmarks of space-fractional dispersion due to large particle jumps [7].

5) Mixing-Limited Reactions: It is a logical extension to think that highly heterogeneous material will lead to unmixed plumes. Therefore, reactive solutes will be sequestered in undermixed domains, and classical Eulerian codes that assume perfect mixing in any "block" will vastly overestimate reaction rates. We started from basic physics and formulated a reaction code for particle-tracking routines that explicitly determines the probability of mixing along with the thermodynamic probability of reaction upon meeting [1]. Our code calculates reactions without ever using concentrations, yet perfectly reproduces the transition from thermodynamic to diffusion-limited reaction rates first predicted in the theoretical physics literature (Fig. 5). Here we simulate a precipitation reaction $A + B \rightarrow C$, which would classically follow an equation:

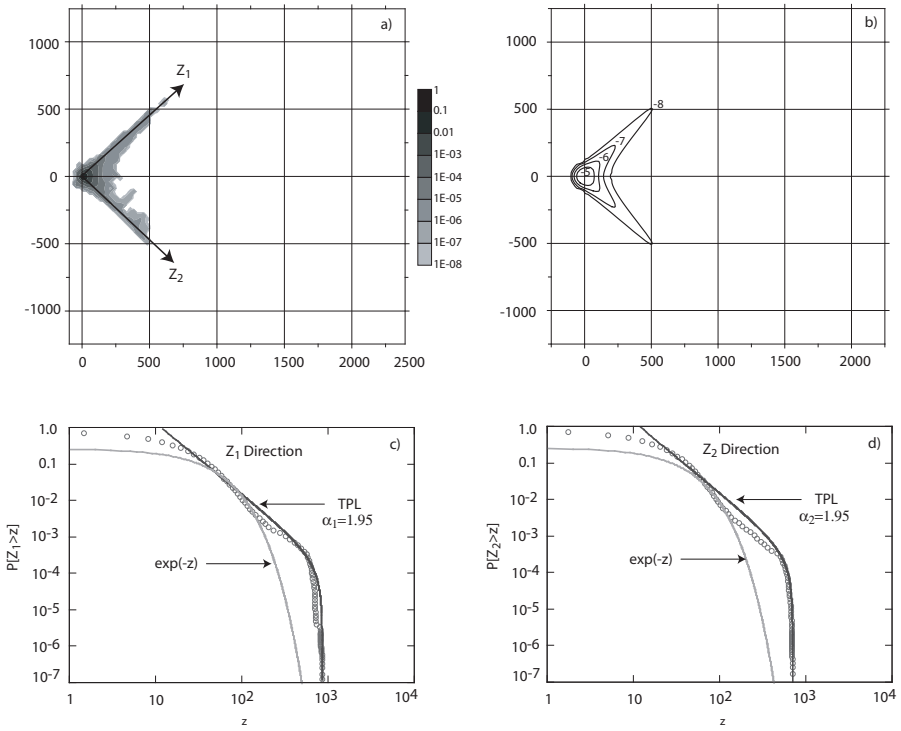

FIGURE 4. (a) Ensemble particle displacement plume for an example fracture network at a transport time of 21 years along with (b) best-fit operator-stable density and Mandlebrot plots of largest ranked particle displacements (circles) along (c) Z_1 and (d) Z_2 with best-fit truncated power-law (TPL) and exponential ($\exp(-z)$) models. Networks containing a combination of infinite variance and finite variance distributions of fracture length ($a_1 = 1.9$, a_2=2.2) produce solute plumes with super-Fickian growth rates and leading plume edges that appear to show a transition between power-law and exponential decay of the largest particle jumps.

$$\frac{\partial[A]}{\partial t} = \frac{\partial[B]}{\partial t} = -K_f[A][B], \tag{2}$$

where $[\cdot]$ denotes concentration and K_f is a thermodynamic reaction rate coefficient. A fascinating aspect to this is the self-organization of reactants into "islands" of separate reactants (Figure 1a inset). These self-organized poorly-mixed reactions follow a different functional form that does not correspond to (2). In other words, for less-than-perfect mixing, (2) is not the correct equation. We proved as much through a continuum-based approach [6], and work is ongoing to show the exact parameterization of the particle model [8, 20].

2. SUMMARY OF SUPPORT FROM THIS PROJECT

In addition to PI Benson, this project funded a post-doctoral researcher (Yong Zhang, now an Assistant Professor at the Desert Research Institute), and five successful Hydrologic Science and Engineering (HSE) Master's students (Nathan Monnig, Elizabeth Conover, Joanne Huie, Elizabeth Major, and Jordan Revielle). The grant led to publication of 18 articles

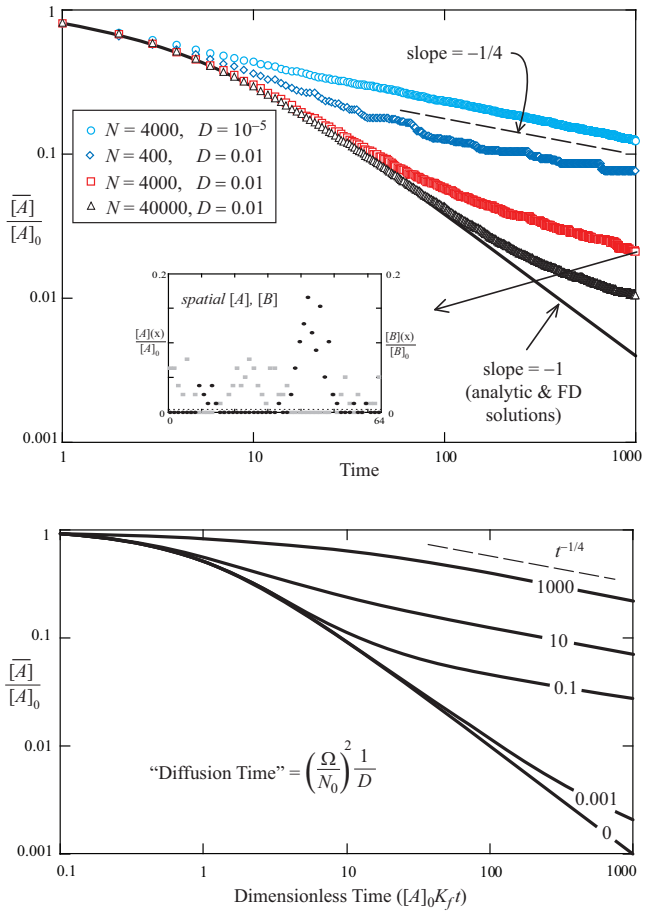

FIGURE 5. Top: Concentration change simulated by particle models (symbols) and analytic solution to continuum, rate-limited, equations (solid curve). Changes of a single numerical parameter are denoted on the plot. Deviations from the rate-limited solution are due to diffusion-limited reaction. Inset: Spatial concentration segregation of $[A]$ and $[B]$ in 4000 particle, $D = 0.01$ simulation at $t = 1000$. The $-1/4$ slope implies that and reactant segregation are asymptotically predicted by [26, 14]. Bottom: Dimensionless concentration versus dimensionless time curves, labeled by various values of a characteristic "diffusion time" $\frac{\Omega^2}{N_0^2}\frac{1}{D}$.

(plus 2 in review) by PI Benson in Hydrology and Physics journals, as well as dozens of conference presentations. In this study, PI Benson and co-workers:

- Showed that particle transport through fracture networks appears to have many of the characteristics of multi-dimensional space-nonlocal transport [22, 23, 24].
- Derived the exact particle dynamical formulation for the time-nonlocal form [2], which is equivalent to the Eulerian multi-rate mass transfer formulation of Haggerty et al. [11, 12]. The time-nonlocal aspect of mass transfer is a key feature because it accounts for the apparent loss of mobile mass that is often noted in field tests [25, 13]. Also applied the nonlocal models to more easily verifiable solute and sediment transport in streams [7, 21, 10].

- Described novel multi-scaling random field models and used the models to simulate flow and transport through realistic aquifer material [3, 18]. Developed a number of algorithms to allow for any degree of conditioning of these fields [4, 16].
- Used our particle-tracking codes from a previous BES grant to simulate plumes in synthetic and real aquifers [27, 28].
- Developed the particle-tracking algorithm for chemical reactions that reproduce diffusion-limited and/or thermodynamics rate-limited reactions under Brownian motion [1] or super-diffusive [5] regimes. Proved correspondence to upscaled PDEs [20] and applied to column studies [8].
- Performed a quantitative analysis of the veracity and information requirements of several nonlocal versus local transport theories [27, 28, 29, 30, 16].

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