Groundwater

Local Equilibrium and Retardation Revisited

by Scott K. Hansen[1] and Velimir V. Vesselinov[2]

Abstract

In modeling solute transport with mobile-immobile mass transfer (MIMT), it is common to use an advection-dispersion equation (ADE) with a retardation factor, or *retarded ADE*. This is commonly referred to as making the *local equilibrium assumption* (LEA). Assuming local equilibrium, Eulerian textbook treatments derive the retarded ADE, ostensibly exactly. However, other authors have presented rigorous mathematical derivations of the dispersive effect of MIMT, applicable even in the case of arbitrarily fast mass transfer. We resolve the apparent contradiction between these seemingly exact derivations by adopting a Lagrangian point of view. We show that local equilibrium constrains the expected time immobile, whereas the retarded ADE actually embeds a stronger, nonphysical, constraint: that all particles spend the same amount of every time increment immobile. Eulerian derivations of the retarded ADE thus silently commit the gambler's fallacy, leading them to ignore dispersion due to mass transfer that is correctly modeled by other approaches. We then present a particle tracking simulation illustrating how poor an approximation the retarded ADE may be, even when mobile and immobile plumes are continually near local equilibrium. We note that classic "LEA" (actually, retarded ADE validity) criteria test for insignificance of MIMT-driven dispersion relative to hydrodynamic dispersion, rather than for local equilibrium.

Introduction

This work offers some observations on a classic topic: the relationship between mobile-immobile solute equilibrium, kinetics, and the retarded advection-dispersion equation (ADE).

Our primary motivation for revisiting this subject lies in the fact that two contradictory approaches to modeling mobile-immobile mass transfer (MIMT) have coexisted in the literature for decades, both underpinned by seemingly exact mathematical arguments. The first approach—usage of a retardation factor in the ADE—has been ostensibly derived under fast mass transfer, or "local equilibrium" conditions. In parallel, a second group of authors have shown that mass transfer is always dispersive and, for first-order kinetic mass transfer, analytically quantified its effect. We concur with this second group of authors that mass transfer is always dispersive. However, the approximation underpinning the ostensibly exact retarded ADE derivation does not appear to have been pinpointed in the literature. Furthermore, we document below numerous places in the literature where the retarded ADE is treated as exact, in which this error is not harmless.

Our secondary motivation is to correct a potential misconception regarding the relationship between degree of local equilibrium and degree of validity of the retarded ADE. While usage of the latter is sometimes referred to as the "local equilibrium assumption" (LEA), we present an example transport simulation that respects local equilibrium, but in which the retarded ADE is a very poor proxy for true behavior. It is actually the case that the solute remobilization rate is the control on the validity of the retarded ADE.

The remediation of contaminated groundwater sites is a topic of persistent interest in industrialized societies. Remediation is generally quite expensive—the U.S. National Research Council recently estimated that the cost to clean up existing sites in the United States at over $100 billion over the next 30 years (National Research Council (NRC) 2013). This high cost necessitates the development of accurate yet tractable groundwater models. Unfortunately, the trade-off between accuracy and tractability is made difficult by the presence of pore-scale mass transfer processes that are too complex to model at their natural support scale, but which also have macroscopically observable effects. One of the most important such processes is adsorption, the reversible chemical interaction between dissolved contaminants and solid-phase components of the pore structure.

In hydrogeologic and engineering models, it is common to model mobile-immobile (e.g., sorbing) solute

[1]Corresponding author: Computational Earth Science Group, Los Alamos National Laboratory, Mailstop T-003 (EES-16), Los Alamos, NM 87545; (505) 664-0712; skh3@lanl.gov

[2]Computational Earth Science Group, Los Alamos National Laboratory, Los Alamos, NM, 87545.

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transport with the retarded ADE. This is the equation:

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

where R (dimensionless) is a constant retardation factor, c (M/L^3) is aqueous resident solute concentration, t (T) is time, x (L) is the spatial coordinate, v (L/T) is the advection velocity, and D (L^2/T) is a Fickian dispersion coefficient. (In all unit expressions, [M] represents mass, [L] represents length, and [T] represents time.) This equation applies as well to MIMT processes other than sorption.

The R on the left hand side (LHS) accumulation term of Equation (1) can be viewed in two different ways: as a rescaling factor for time, or as a rescaling factor for solute accumulation. Based on this, there are two possible understandings of the retardation factor in homogeneous media. It may be conceived as the ratio of groundwater velocity to mean solute velocity (e.g., Rajaram 1997), or as the ratio of total (mobile and immobile) solute concentration to mobile solute concentration at equilibrium. This second conception motivates the idea that "local equilibrium" mass transfer provides support for usage of the retarded ADE.

However, there can be no exact equilibrium under transient conditions (only fast kinetics). While this may seem innocuous, its impact may be significant. To understand the degree of approximation that is occurring relative to fast kinetic behavior, we will consider the explicit transport equations for advection and dispersion in the presence of first-order single-rate mass transfer. The relevant equations may be written (Fetter 1999, 133):

$$\frac{\partial c}{\partial t}(x,t) + \frac{\partial s}{\partial t}(x,t) = -v\frac{\partial c}{\partial x}(x,t) + D\frac{\partial^2 c}{\partial x^2}(x,t)$$
$$\frac{\partial s}{\partial t}(x,t) = \lambda c(x,t) - \mu s(x,t), \qquad (2)$$

where s (M/L^3) is the immobile concentration, λ (T^{-1}) is the probability per unit time of immobilization of mobile solute, and μ (T^{-1}) is the probability per unit time for mobilization of immobile solute. Equations of this form have long been used as an empirical model for nonequilibrium mass transfer, both physical (diffusion into secondary porosity) and chemical (kinetic sorption)—see the discussion in Valocchi (1985) for details—and similar equations have been found appropriate for bacterial transport (Becker et al. 2004). The assumption $\mu = \lambda$ in Equations (2) is common in experimental studies of pseudo-first-order kinetics (e.g., Ho and McKay 1999).

We show in Appendix 1 how Equation (1) is a special case of Equations (2), in the $\mu \longrightarrow \infty$ limit. So while the first-order kinetic model is itself an idealization, it is no more so than the retarded ADE and additionally captures the true behavior of solute being continuously mobile or immobile for finite intervals. Equations of form (2) are widely used in the literature to capture general MIMT processes (see conceptual discussion in Valocchi 1985; Bahr and Rubin 1987; Fernandez-Garcia and Sanchez-Vila 2015). They are applicable over a range of advection velocities (Zhang et al. 2008; Zhang and Lv 2009) and spatial support scales (Raoof et al. 2010). Thus, the analysis of the system they describe is relevant to a large variety of hydrogeologic problems. This single-rate paradigm, while not encompassing all forms of MIMT—for example, nonlinear sorption and mobile-immobile phenomena with heavy-tailed immobile-state waiting times (Margolin et al. 2003; Schumer et al. 2003) are not covered—remains of sufficient generality to reveal the nature of the retardation factor approximation. For a comprehensive discussion of more general transport models than an ADE with first-order kinetic mass transfer, see Berkowitz et al. (2006).

That first-order kinetic MIMT has a dispersive effect (i.e., that capture and release of particles independent of one another drives spatial spreading of the distribution of c) has long been recognized. In Giddings and Eyring (1955), equations for the spreading of breakthrough curves at the output of a chromatograph, using essentially the assumptions of chemical nonequilibrium, were derived. Valocchi (1985) and Goltz and Roberts (1987) performed thorough parametric studies of moments for a variety of MIMT processes and their contributions to the spreading of plumes in the subsurface. Many other authors have considered aspects of this topic, as well. Regardless of the rapidity of the MIMT, the retarded ADE does not capture dispersion due to mass transfer: the time-scaling retardation factor does not change the qualitative shape of the solution by adjusting the relative weights of advection and dispersion. In fact, that Equation (1) fails to capture dispersion encoded by Equations (2) was made explicitly in a numerical study by Elfeki (2007). Furthermore, it is known that MIMT generates anomalous (asymmetric) plumes that are not well described by an ADE at early time. Hansen (2015) presented the guideline, for small μ, in the $D \longrightarrow 0$ limit, that an ADE model with an additional Fickian dispersion to account for MIMT becomes adequate after time $t\mu > 70$. Slow mobile-immobile kinetics, and thus and small values of μ, are in reality widespread (Pignatello and Xing 1996), so these limitations are practically important.

At the same time, however, the substitution of retardation factors from equilibrium batch experiments—i.e., the use of Equation (1)—to modify transport equations in the presence of kinetic sorption is frequently presented in expository works as though it is exact. A derivation of the retarded ADE by such means is presented as mathematically exact in the canonical *Hydraulics of Groundwater* text (Bear 1979, 242), given "equilibrium" sorption, and in the authors' experience is believed by many hydrogeologists to be exact. Bouwer (1991) also developed a relationship between a soil distribution coefficient and retardation factor by assuming that all solute released at the same instant has been, at any moment, immobile for the exact same amount of time. In a recent textbook (Hiscock 2014, 208), the Bouwer result is also reported without any explicit indication that transport with mass

transfer is a dispersive process in which different particles may be immobile for different fractions of any given time interval (although a caveat is given that the Bouwer result assumes instantaneous sorption and equilibrium—i.e., instantaneous desorption—which implies no effect of sorption at all). Other textbook treatments similarly provide ostensibly exact paths to Equation (1) without indication that dispersion is being suppressed. Zheng and Bennett (1995, 66) provide an extensive derivation leading to an apparently exact Equation (1), but silently introduce an instantaneous remobilization approximation analogous to Equation (A4), in Appendix 1. Fetter (1999, 117) similarly discusses linear isotherms in a transport-free context, and then introduces a retardation constant into the ADE, apparently exactly.

In practice, Equation (1) has also been used for the interpretation of push-pull tracer tests aimed at quantifying D and R (Schroth et al. 2000); ignoring the dispersive effect of sorption. The retarded ADE has also commonly been incorporated in numerical codes that handle more complicated geometries. As the user guide for the popular MT3DMS transport modeling software states, "[i]t is generally assumed that equilibrium conditions exist between the aqueous-phase and solid-phase concentrations and that the sorption reaction is fast enough relative to groundwater velocity so that it can be treated as instantaneous....Equilibrium-controlled sorption isotherms are generally incorporated into the transport model through the use of the retardation factor" (Zheng and Wang 1999, 12). So while it is well established that kinetic mass transfer is a cause of dispersion, the use of retardation factors that ignore it under "local equilibrium" conditions is common in practical subsurface hydrology, as well as in the literature. In particular, we note that this is the practice in remediation studies performed on U.S. Environmental Protection Agency Superfund sites (Zheng et al. 1991; Chen et al. 1999), as well as U.S. Department of Energy sites (Rogers 1992). In light of the above, new conceptual arguments pinpointing the approximation being made in the apparently exact derivation of Equation (1) appear timely.

Regarding the relationship between degree of local equilibrium and usage of the retarded ADE, there is more to be said. Wallach (1998) and Valocchi (1985) acknowledge dispersion due to mass transfer and identify validity of the LEA with applicability of the retarded ADE in light of large hydrodynamic dispersion relative to MIMT-driven dispersion (see Appendix 2). However, they do not directly investigate the degree of local disequilibrium. By contrast, Bahr and Rubin (1987) qualify the extent to which fast kinetic mass transfer leads to pointwise local equilibrium (i.e., reduces the difference between s and $(R-1)c$), without directly addressing dispersion due to mass transfer. However, a direct discussion of the degree of support that a given maximum amount of local disequilibrium provides for a given maximum amount of dispersion due to mass transfer (including the potentially surprising answer, *zero*) does not seem to exist in the literature.

In the section "A Hidden Approximation in the Retarded ADE", we examine mathematically the implications of the two conceptions of the retardation factor and show how the derivation of the ADE makes a hidden assumption—akin to the gambler's fallacy—that hides its inexactitude. In the section "Local Equilibrium and Retarded ADE Validity", we present a numerical study of plume evolution on a heterogeneous two-dimensional (2D) conductivity field, as modeled with rapid first-order MIMT and with a retarded ADE. We show a substantial difference in plume evolution despite the fact that local equilibrium is maintained by the mobile and immobile plumes, highlighting the incorrectness of using the term *local equilibrium assumption* to refer to assumed ADE validity. In the section "Summary and Concluding Discussion", we sum up what we have demonstrated and draw lessons from it. In Appendix 1, we show how the retarded ADE may be derived as a special case of first-order MIMT in an Eulerian context, and that the remobilization rate is the parameter that controls the divergence between the formulations. In Appendix 2, we explicitly discuss past results concerning when it is proper to employ the retarded ADE, highlighting the centrality of the remobilization rate.

A Hidden Approximation in the Retarded ADE

In this section, we establish that interpreting the retarded ADE as exact is to essentially ask for ergodicity to equalize the *absolute amount* of time that each particle is immobile in some long time interval, rather than the *fraction* of time immobile. This conflation of absolute and relative frequencies is tantamount to the gambler's fallacy. This fallacy (e.g., Ayton and Fischer 2004; Sundali and Croson 2006) represents the erroneous belief that the law of large numbers requires negative auto-correlation in sequences of independent events in order to obtain "balance" (informally, that if one has just flipped an unbiased coin for a long string of tails, then heads is now more probable than tails in future flips). In our context, instead of the two states of a coin, we imagine solute particles periodically making a Markovian selection between mobile and immobile states.

It is immediately apparent from viewing R as a scaling factor for time in Equation (1), that values of R different from unity do not cause any extra dispersion: they simply map the concentration profile at t for any given initial distribution to that at t/R in the case when $R = 1$, for the same initial distribution. This is to say: it generates the distribution that would occur if *every* particle spent t/R of the time immobile. If different particles spend different amounts of time immobile during the interval $[0, t]$, then this will represent an additional source of dispersion (which becomes clear when the case $D = 0$, $v > 0$ in Equation (1) is considered).

Relations Between Mobile and Immobile Concentrations

The hypothesis of local equilibrium is *local* in both space and time: it constrains the fraction of the solute particles at a given location (i.e., small representative

pore volume), at any given time that are mobile (or equivalently, the instantaneous probability that a given individual particle is mobile). The retarded ADE it ostensibly justifies depends on a constraint on the *exact amount of time* in a given time interval that *each* of the particles is mobile. In other words, the retardation factor approach attempts to equate an aggregate spatial relationship with a deterministic temporal quantity. A priori, there is no problem with translating between an Eulerian and a Lagrangian perspective. However, by adopting the Lagrangian perspective ourselves, it is easy to see how the (Eulerian) retarded ADE embeds a hidden, nonphysical approximation. (In Appendix 1, an alternative, Eulerian argument is presented, which lacks the physical intuition underlying the one presented here.)

We consider the simplest possible mobile-immobile "transport" system—a batch experiment with first-order MIMT—freeing us from the need to consider extraneous processes. Specifically, we consider a steady-state batch system consisting of N_{m} mobile particles and N_{i} immobile particles, where these numbers are both large. For our analysis, we employ the conceptual model implied by the system defined in Equations (2) which, as we have already mentioned, is a generalization of the retarded ADE, and allows for explicit treatment of individual mobile and immobile intervals. Our analysis proceeds in a similar spirit to that of Benson and Meerschaert (2009), considering the aggregate behavior that results from independent particles, each of which has the same defined probability distributions for lengths of its mobile and immobile intervals. In this system, the mobile particles have probability λ of immobilization per unit time, and the immobile particles have a probability μ of remobilization per unit time. It follows the expected duration of a single immobilization event is μ^{-1}. We assume all particles are mutually independent and define K as the rate of immobilization, in particles per second: $K = \lambda N_{\mathrm{m}}$. Based on the equilibrium conception of retardation and the principle of conservation of mass, the retardation factor satisfies

$$R = \frac{E\left[N_{\mathrm{i}} + N_{\mathrm{m}}\right]}{E\left[N_{\mathrm{m}}\right]}, \tag{3}$$

where $E[\cdot]$ represents mathematical expectation. Little's law is the intuitive statement that the expected number of particles in a state is equal to their rate of arrival multiplied by their expected wait in that state (Bhat 2008, 37). If the state of interest is the immobile state, this implies $E[N_{\mathrm{i}}] = E[K]/\mu$. Then we can conclude that

$$R = \frac{E\left[N_{\mathrm{m}}\right](\lambda/\mu + 1)}{E\left[N_{\mathrm{m}}\right]} = 1 + \lambda/\mu. \tag{4}$$

It is possible to take this aggregate (multiparticle) spatial behavior and draw conclusions about the temporal behavior of any single particle by assuming interchangeably between particles. Under such conditions, we are justified in positing *ergodicity*, that is, that the long-run temporal statistics (for immobility) of a single particle are distributed as that of the ensemble of all particles at any point in time. However, we shall see that ergodicity only serves to constrain the *expected* behavior of any particular particle. This is to say that if we define F_t to be the a random variable representing the amount of time a particular particle is mobile in the interval $[0, t]$, the assumptions underlying the retardation approach will correctly establish that $E[F_t] = t/R$. They will not, however, establish that $F_t = t/R$, which is what would be required for the retarded ADE to be exact. The former condition is naturally weaker—constraining only the average of a whole population of solute particles—whereas the latter states that *each* solute particle in a population is immobile for the same amount of time. It is useful to consider these claims precisely.

The Expected Time a Single Particle is Immobile is Fixed by *R*

By symmetry of particle behavior (i.e., all have the same tendencies to immobilize and remobilize), the retardation approach implies that each particle is expected (in the mathematical sense) to spend $1/R$ of the *time* mobile. To see this, imagine a steady-state, batch system in which N particles are immobilizing and remobilizing independently of each other. Define, for particle n, the indicator function

$$I_n(t) \equiv \begin{cases} 0 & \text{if immobile at } t \\ 1 & \text{if mobile at } t \end{cases}, \tag{5}$$

which is only nonzero in such cases as the particle is mobile at time t. Define

$$\Omega_t(N) \equiv \int_0^t \frac{1}{N} \sum_{n=1}^{N} I_n(\tau)\, \mathrm{d}\tau. \tag{6}$$

Then

$$\lim_{N\to\infty} \Omega_t(N) = \int_0^t \frac{1}{R} \mathrm{d}\tau = \frac{t}{R}, \tag{7}$$

which follow because, in the limit $N \to \infty$, a sample mean converges to the expectation (by the law of large numbers), and the expected value of an indicator function is the probability of being mobile, and $1/R$ of the N particles are mobile at every instant. Because of linearity, it is possible to rearrange the order of summation and integration, so that

$$\begin{aligned} \lim_{N\to\infty} \Omega_t(N) &= \lim_{N\to\infty} \frac{1}{N} \sum_{n=1}^{N} \int_0^t I_n(\tau)\, d\tau \\ &= E\left[\int_0^t I_n(\tau)\, \mathrm{d}\tau\right] = E\left[F_t\right]. \end{aligned} \tag{8}$$

Since $I_n(t)$ is just the indicator function that is unity when the particle is mobile, the integral represents the amount of time in the interval $[0, t]$ in which particle n is mobile. Combining Equations (7) and (8), we see $\mathrm{E}[F_t] = t/R$.

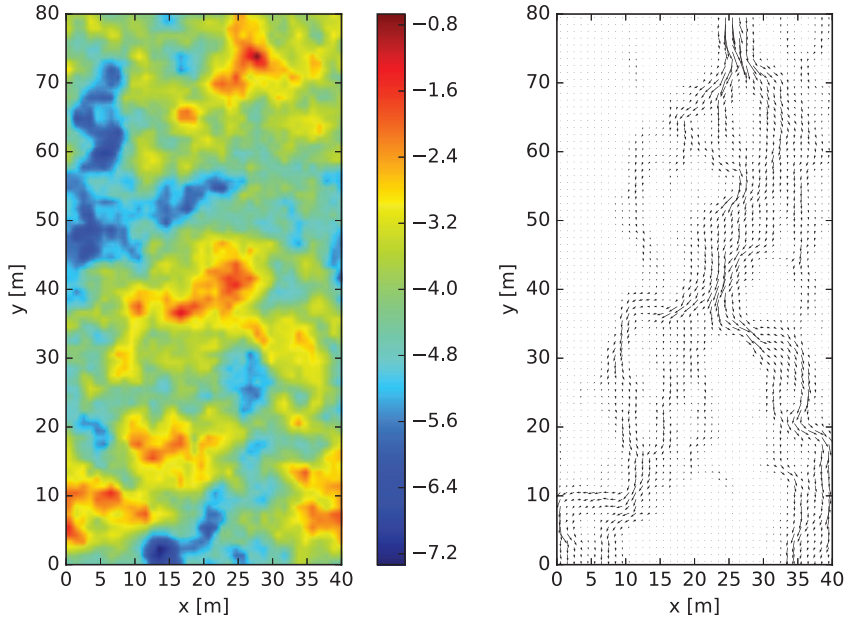

Figure 1. Left: Heat map of $\log_{10} K$, where K is the local hydraulic conductivity of the field in which the particle tracking simulations were performed. Right: Quiver plot of heterogeneous velocity field computed by PFLOTRAN using the same K-field. Each cell-center velocity is indicated by an arrow whose length represents its relative speed and orientation indicates its direction.

The Absolute Time a Single Particle is Immobile is Not Fixed by R

The conclusion that $\mathrm{E}[F_t] = t/R$ is the strongest that can be made. The stronger statement, that $F_t = t/R$, for any given particle, is false. To see this, consider a system over some interval in which all the particles with even index are always immobile and all the particles with odd index are never immobile during the interval t (not because they are qualitatively different, just that the particles are independent and this is one possible, though not likely, configuration). Then this system satisfies Equations (6) and (8) for $R = 2$, though it is not true for any particle that $\frac{t}{2} = \int_0^t I_n(t)\,\mathrm{d}t$.

It is true that, applying the law of large numbers for large t, it follows that after a long time (i.e., a large number of immobilization and remobilization events), the actual fraction of time every particle spends mobile, F_t/t, approaches $1/R$. Naturally, if each particle were to spend *exactly* $1/R$ of the time immobile, for all t, then we could compute $F_t \equiv t/R$ (valid for every particle) and the retardation factor approach would be exact. However, there is no reason to expect F_t to converge to t/R as $t \to \infty$. While possibly unintuitive, such situations are common: consider that as $t \to \infty$, $(t+1)/t \to 1$ but $(t+1) \nrightarrow t$. The law of large numbers concerns itself exclusively with *relative* frequencies, not absolute frequencies. This is a subtle distinction, but an important one: this distinction is what the gambler's fallacy (discussed earlier) turns on.

Local Equilibrium and Retarded ADE Validity

In this section, we directly consider the degree of support which "local equilibrium" (this is to say, fast kinetics) provides to the usage of the retarded ADE. We perform two particle tracking simulations: one employing first-order MIMT, governed by Equations (2), and one employing the retarded ADE (Equation (1)) with the corresponding R (Equation (4)). In so doing, we are able to monitor the degree of local equilibrium between mobile and immobile plumes in the first-order MIMT model, and its coherence with the retarded ADE model that purports to capture it.

Our study begins by generating a 40 by 80 m random log-hydraulic conductivity field with a multi-Gaussian correlation structure described by an exponential semivariogram with correlation length 5 m, geometric mean conductivity $1\mathrm{e}-4$ m/s, and $\sigma^2_{\ln K} = 2$ (moderate heterogeneity), discretized into blocks 1 m on a side. The resulting conductivity field is shown in Figure 1. This log-conductivity field is used with the finite-volume numerical flow and transport solver PFLOTRAN (Lichtner et al. 2015) to determine the steady-state cell-center velocities. For this computation no-flow boundary conditions are imposed at $x = 0$ and $x = 40$, a constant pressure of 111.135 kPa is imposed at $y = 80$, and constant pressure of 101.325 kPa is imposed at $y = 0$. The resulting velocity field is also illustrated in Figure 1.

The single velocity field calculated by PFLOTRAN is then used for both particle tracking simulations. These are performed using a Lagrangian equivalent to the advection-dispersion equation, and commence by introduction of 500 particles at random locations within a circle of radius 2 m, centered at $x = 25$ m, $y = 75$ m. When particles are mobile, their positions are tracked by making successive steps of constant duration 0.1 h, during which they passively follow the flow lines. At the end of each

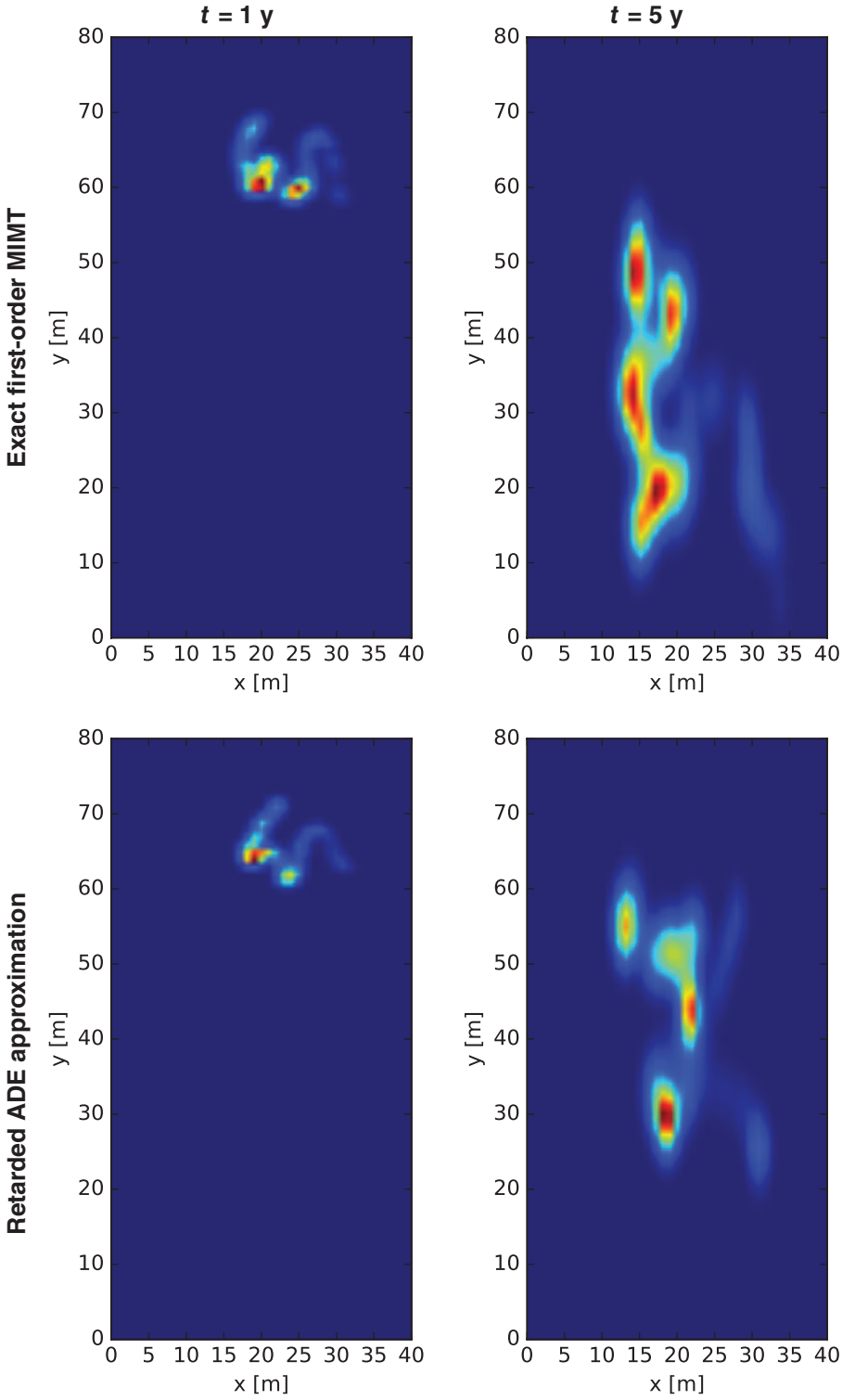

Figure 2. Heat maps of plume concentration at two times under exact first-order MIMT and the retarded ADE approximation. All plumes used the same velocity field and release location. Hue closer to the red end of the spectrum indicates higher concentration, but scales differ between heat maps.

step, a small random translation is added to model local-scale dispersion, described by longitudinal dispersivity 0.01 m, and transverse dispersivity 0.001 m. We note that numerical dispersion does not occur with particle tracking approaches, so we are assured that all dispersion during the simulation results from the modeled physics.

For the MIMT simulation, the times of successive immobilization and remobilization events for each particle are generated by draws from exponential random number generators with rate parameters $\lambda = 10$ and $\mu = \frac{1}{3}$, respectively. For the retarded ADE simulation, particle immobilization was disabled altogether and instead the

PFLOTRAN-derived velocity field was scaled everywhere by $1/R$, where $R = 1 + \frac{\lambda}{\mu} = 31$. This is to say: the velocity field used in the retarded ADE simulation features directions that are everywhere identical to those used in the MIMT simulation, but whose magnitudes are all diminished by the same factor.

Plume concentrations from both particle tracking simulations are determined at $t = 1$ year and $t = 5$ years by performing kernel density estimation using the locations of all particles at the relevant time. These plumes are shown in Figure 2. From examination of the figure, the strong divergence of the two models is apparent.

Approximate local equilibrium for the MIMT model is established by comparing mobile and immobile plumes at fixed times, and by tabulating each plume's spatial moments over time and verifying their coherence. Graphs of the first two spatial moments are presented in Figure 3 to illustrate how closely the mobile and immobile plumes cohere. To improve smoothness of the mobile-phase curves, this figure is obtained from a second run of the MIMT simulation using 50,000 particles instead of 500. This is necessary because the ratio of immobile to mobile particles is always approximately 30, so a large number of particles are needed to obtain sufficient representation of the mobile phase.

We thus demonstrate an example of a realistic system in which *local equilibrium is satisfied, but performance of the retarded ADE is very poor*. Consequently, the use of the term *LEA* to refer to the assumption of retarded ADE validity is misleading. Indeed, as we note in Appendix 2, classic "local equilibrium" metrics actually quantify the relative strengths of MIMT-driven dispersion and hydrodynamic dispersion. They are legitimate metrics for the validity of the retarded ADE, but do not concern local equilibrium, per se.

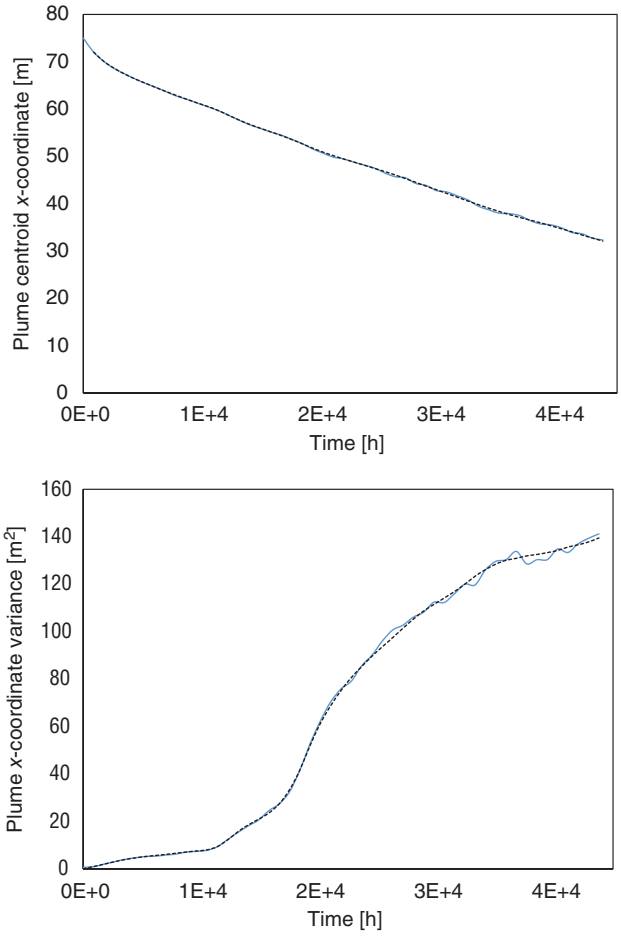

Figure 3. Spatial moments of mobile (solid blue lines) and immobile (dashed black lines) plumes. Top: Centroid *x*-coordinate. Bottom: Plume *x*-coordinate variance.

Summary and Concluding Discussion

Despite common assumptions to the contrary, the dispersive effect of MIMT, even under "local equilibrium" conditions, cannot be discarded a priori. Since this extra dispersion may cause un-modeled early- or late-time breakthrough, how to treat it presents a practical question to working hydrogeologists and environmental engineers. The critical role of the remobilization rate, μ, in driving dispersion at late time is clear (see Appendices 1 and 2), with only truly *instantaneous* remobilization (i.e., no mass transfer) recovering Equation (1), and the dispersive effect of sorption increasing as μ shrinks.

Against this background, the two major contributions of this work are the following:

1 We note that the retarded ADE for *arbitrary* R is derived in canonical sources in a seemingly exact fashion, and is often treated as exact in the literature. We also note that the retarded ADE approach is a special case of first-order kinetic MIMT equations in the limit of instantaneously fast remobilization (i.e., when $R = 1$), and otherwise neglects the dispersion that has long been known to be a feature of kinetic mass transfer. We resolve the contradiction by showing how the ostensibly exact derivation of the retarded ADE introduces a hidden approximation (equivalent to the gambler's fallacy), which is not justified by ergodicity or the law of large numbers. This is to say: that all particles spend exactly the same fraction of *every* interval immobile. In reality, only the average fraction of time immobile in the ensemble of all particles is constrained, but no exact statements can be made about individual particles, whose trajectories diverge on account of MIMT.

2 Through a numerical study of transport in a heterogeneous aquifer, we demonstrate how misleading the use of the term *LEA* to describe the assumption of ADE validity can be. In our example, we demonstrate an MIMT-generated plume that is largely disjoint from the plume predicted by use of the corresponding retarded ADE, despite the fact that local equilibrium between mobile and immobile plumes holds. We note in Appendix 2 that previously published criteria for the validity of the local equilibrium assumption are actually criteria for conditions in which the dispersive effect of MIMT is overwhelmed by that of local-scale

hydrodynamic fluctuations. We concur that this is the correct condition for usage of the retarded ADE.

We hope that by revisiting this classic topic, we are able to clear up some misconceptions that—as we established in the introduction—continue to persist in the literature, and which have the potential to adversely impact remedial actions.

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Appendix A: Eulerian Derivation of Retarded ADE from First-Order MIMT Equations

In this paper, we analyze the retarded ADE in Equation (1) using the rate constants in Equations (2). To justify this, we show here how Equation (1) represents a special case of Equations (2). The analysis also incidentally shows rapid remobilization as the limiting factor for dispersion due to mass transfer.

We first solve the second of Equations (2) using the standard approach for first-order ordinary differential equations to yield

$$s(x,t) = \lambda \int_0^t \mathrm{e}^{-\mu(t-\tau)} c(x,\tau)\,\mathrm{d}\tau. \tag{A1}$$

Differentiating both sides with respect to time yields

$$\frac{\partial s}{\partial t}(x,t) = \lambda c(x,t) - \lambda \int_0^t \mu \mathrm{e}^{-\mu(t-\tau)} c(x,\tau)\,\mathrm{d}\tau, \tag{A2}$$

and it is apparent from integration by parts that

$$\frac{\partial s}{\partial t}(x,t) = \lambda \int_0^t \mathrm{e}^{-\mu(t-\tau)} \frac{\partial c}{\partial t}(x,\tau)\,\mathrm{d}\tau. \tag{A3}$$

Note that for large μ (fast remobilization), $\mu \mathrm{e}^{-\mu(t-\tau)} \approx \delta(t-\tau)$, the Dirac delta function. This implies that, only in the circumstance of rapid remobilization,

$$\frac{\partial s}{\partial t}(x,t) \approx \frac{\lambda}{\mu}\frac{\partial c}{\partial t}(x,t). \tag{A4}$$

Substituting this into the first of Equations (2) yields:

$$\left(1+\frac{\lambda}{\mu}\right)\frac{\partial c}{\partial t}(x,t) \approx -v\frac{\partial c}{\partial x}(x,t) + D\frac{\partial c}{\partial x}(x,t). \tag{A5}$$

Thus, employing the large μ assumption, we can define $R \equiv 1 + \frac{\lambda}{\mu}$, as in Equation (4), and approximately recover the retarded ADE in Equation (1). Note that a memory function convolution such as the one seen in Equation (A3) generates time "smearing" and its neglect when moving to the retarded ADE underestimates the resulting dispersion. The relationship used to approximately derive the ADE in Equation (A4) is only exact in the limit as $\mu \to \infty$, meaning that remobilization occurs instantaneously after immobilization. This, naturally, generates concentration profiles identical to those in the absence of MIMT.

Appendix B: Conditions for Proper Use of the Retarded ADE

The relative effects of local-scale hydrodynamic dispersion, D, and dispersion due to MIMT have been explicitly quantified by Goltz and Roberts (1987) and Uffink et al. (2012), who determined an equivalent effective dispersion coefficient, D^{e}, that describes the behavior of Equations (2) at late-time. In our notation:

$$D^{\mathrm{e}}(\lambda,\mu) = \frac{\mu}{\lambda+\mu}D + \frac{\lambda\mu}{(\lambda+\mu)^3}v^2. \tag{B1}$$

Using this expression, Equation (1) can be recast, using Equation (4), as:

$$R\frac{\partial c}{\partial t}(x,t) = -v\frac{\partial c}{\partial x}(x,t) + \left(D + \frac{v^2}{\mu}\frac{R-1}{R^2}\right)\frac{\partial^2 c}{\partial x^2}(x,t). \tag{B2}$$

Clearly, the dispersive effect of MIMT can only be neglected if it is everywhere small relative to the local-scale hydrodynamic dispersion, as encapsulated by D. This aligns totally with the diagnostic criteria for the "local equilibrium assumption" derived, using different means, by Wallach (1998) and by (Valocchi 1985): $v^2/\mu \ll D$. Note that a comparison of dispersive strengths does not quantify local equilibrium!

A point to note—implicit in previous literature, but often neglected in practice—is that one must know the remobilization rate of the MIMT in order to know whether one is making an acceptable approximation in using the retarded ADE. First-order sorption kinetics can be measured in the laboratory under the assumption $\lambda = \mu$ (e.g., Ho and McKay 1999; Wu et al. 2001; Reddad et al. 2002), and distinct λ and μ can also be measured experimentally for both abiotic sorption (e.g., Strawn and Sparks 2000) and bio-sorption (e.g., Meinders et al. 1992).

In the case of physical nonequilibrium (i.e., diffusion into secondary porosity), μ can be approximated from the zero-order terms of the multi-rate mass transfer expressions presented in Table 1 of Haggerty et al. (2000).

References

Ayton, P., and I. Fischer. 2004. The hot hand fallacy and the gambler's fallacy: Two faces of subjective randomness? *Memory & Cognition* 32, no. 8: 1369–1378.

Bahr, J.M., and J. Rubin. 1987. Direct comparison of kinetic and local equilibrium formulations for solute transport affected

by surface reactions. *Water Resources Research* 23, no. 3: 438–452.
Bear, J. 1979. *Hydraulics of Groundwater*. Mineola, New York: Dover Publications.
Becker, M.W., S.A. Collins, D.W. Metge, R.W. Harvey, and A.M. Shapiro. 2004. Effect of cell physicochemical characteristics and motility on bacterial transport in groundwater. *Journal of Contaminant Hydrology* 69, no. 3–4: 195–213.
Benson, D.A., and M.M. Meerschaert. 2009. A simple and efficient random walk solution of multi-rate mobile/immobile mass transport equations. *Advances in Water Resources* 32, no. 4: 532–539.
Berkowitz, B., A. Cortis, M. Dentz, and H. Scher. 2006. Modeling non-Fickian transport in geological formations as a continuous time random walk. *Reviews of Geophysics* 44, no. 2: RG2003.
Bhat, U.N. 2008. Simple Markovian queueing systems. In *An Introduction to Queuing Theory, Statistics for Industry and Technology*, 29–73. Cambridge, Massachusetts: Birkhäuser Boston.
Bouwer, H. 1991. Simple derivation of the retardation equation and application to preferential flow and macrodispersion. *Groundwater* 29, no. 1: 41–46.
Chen, D.W., R.F. Carsel, L. Moeti, and B. Vona. 1999. Assessment and prediction of contaminant transport and migration at a Florida superfund site. *Environmental Monitoring and Assessment* 57: 291–299.
Elfeki, A. 2007. Modeling kinetic adsorption in porous media by a two-state random walk particle method. *Journal of King Abdulaziz University: Meteorology, Environment and Arid Land Agriculture Sciences* 18, no. 1: 61–74.
Fernandez-Garcia, F., and X. Sanchez-Vila. 2015. Mathematical equivalence between time-dependent single-rate and multi-rate mass transfer models. *Water Resources Research* 51: 3166–3180.
Fetter, C.W. 1999. *Contaminant Hydrogeology*. Upper Saddle River, New Jersey: Prentice Hall.
Giddings, J.C., and H. Eyring. 1955. A molecular dynamic theory of chromatography. *Journal of Physical Chemistry* 59, no. 5: 416–421.
Goltz, M.N., and P.V. Roberts. 1987. Using the method of moments to analyze three-dimensional diffusion-limited solute transport from temporal and spatial perspectives. *Water Resources Research* 23, no. 8: 1575–1585.
Haggerty, R., S.A. McKenna, and L.C. Meigs. 2000. On the late-time behavior of tracer test breakthrough curves. *Water Resources Research* 36, no. 12: 3467–3479.
Hansen, S.K. 2015. Effective ADE models for first-order mobile-immobile solute transport: Limits on validity and modeling implications. *Advances in Water Resources* 86: 184–192.
Hiscock, K. 2014. *Hydrogeology: Principles and Practice*, 2nd ed. Oxford, UK: Wiley-Blackwell.
Ho, Y.S., and G. McKay. 1999. The sorption of lead(II) ions on peat. *Water Research* 33, no. 2: 578–584.
Lichtner, P.C., G.E. Hammond, C. Lu, S. Karra, G. Bisht, B. Andre, R.T. Mills, and J. Kumar. 2015. PFLOTRAN user manual: A massively parallel reactive flow and transport model for describing surface and subsurface processes. Technical Report LA-UR-15-20403. Los Alamos, New Mexico: Los Alamos National Laboratory.
Margolin, G., M. Dentz, and B. Berkowitz. 2003. Continuous time random walk and multirate mass transfer modeling of sorption. *Chemical Physics* 295: 71–80.
Meinders, J.M., J. Noordmans, and H.J. Busscher. 1992. Simultaneous monitoring of the adsorption and desorption of colloidal particles during deposition in a parallel plate flow chamber. *Journal of Colloid and Interface Science* 152, no. 1: 265–280.
National Research Council (NRC). 2013. *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites*. Washington, DC: National Academy Press.
Pignatello, J.J., and B. Xing. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology* 30, no. 1: 1–11.
Rajaram, H. 1997. Time and scale dependent effective retardation factors in heterogeneous aquifers. *Advances in Water Resources* 20, no. 4: 217–230.
Raoof, A., S.M. Hassanizadeh, and A. Leijnse. 2010. Upscaling transport of adsorbing solutes in porous media: Pore-network modeling. *Vadose Zone Journal* 9, no. 3: 624.
Reddad, Z., C. Gerente, Y. Andres, and P. Le Cloirec. 2002. Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies. *Environmental Science & Technology* 36, no. 9: 2067–2073.
Rogers, L. 1992. History matching to determine the retardation of PCE in ground water. *Groundwater* 30, no. 1: 50–60.
Schroth, M.H., J.D. Istok, and R. Haggerty. 2000. In situ evaluation of solute retardation using single-well push–pull tests. *Advances in Water Resources* 24, no. 1: 105–117.
Schumer, R., D.A. Benson, M.M. Meerschaert, and B. Baeumer. 2003. Fractal mobile/immobile solute transport. *Water Resources Research* 39, no. 10. 1296. Doi:10.1029/2003 WR002141.
Strawn, D.G., and D.L. Sparks. 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. *Soil Science Society of America Journal* 64: 144–156.
Sundali, J., and R. Croson. 2006. Biases in casino betting: The hot hand and the gambler's fallacy. *Judgment and Decision making* 1, no. 1: 1–12.
Uffink, G., A. Elfeki, M. Dekking, J. Bruining, and C. Kraaikamp. 2012. Understanding the non-Gaussian nature of linear reactive solute transport in 1D and 2D. *Transport in Porous Media* 91, no. 2: 547–571.
Valocchi, A.J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resources Research* 21, no. 6: 808–820.
Wallach, R. 1998. A small perturbations solution for nonequilibrium chemical transport through soils with relatively high desorption rate. *Water Resources Research* 34, no. 1: 149–154.
Wu, F.-C., R.-L. Tseng, and R.-S. Juang. 2001. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. *Water Research* 35, no. 3: 613–618.
Zhang, X., and M. Lv. 2009. The nonlinear adsorptive kinetics of solute transport in soil does not change with pore-water velocity: Demonstration with pore-scale simulations. *Journal of Hydrology* 371, no. 1–4: 42–52.
Zhang, X., J. Crawford, and I. Young. 2008. Does pore water velocity affect the reaction rates of adsorptive solute transport in soils? Demonstration with pore-scale modelling. *Advances in Water Resources* 31, no. 3: 425–437.
Zheng, C., and P.P. Wang. 1999. MT3DMS: A modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; Documentation and user's guide.
Zheng, C., and G.D. Bennett. 1995. *Applied Contaminant Transport Modeling*. New York: Van Nostrand Reinhold.
Zheng, C., G.D. Bennett, and C.B. Andrews. 1991. Analysis of ground-water remedial alternatives at a superfund site. *Groundwater* 29, no. 6: 838–848.

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