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Effective ADE models for first-order mobile–immobile solute transport: Limits on validity and modeling implications

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ABSTRACT

Quasi-1D mobile–immobile transport processes which have exponentially distributed random waiting times in both mobile and immobile states are common in hydrologic models (for example, of transport subject to kinetic sorption). The central limit theorem implies that eventually such transport will be expressible with an effective ADE (i.e. a generalization of the common retardation factor approach with an added Fickian dispersion coefficient accounting for the effect of trapping). Previous works have determined formulae for the value of this coefficient based on the transport properties. However, the time until convergence to Gaussian behavior has not previously been quantified. To this end, exact Green's functions characterizing the transport at all times are derived for the case of pure advection. The Green's functions are expressed in terms of three dimensionless parameters, representing location, time, and capacity coefficient. In the pre-Gaussian regime, a parametric study characterizing concentration profile asymmetry as a function of the capacity coefficient is performed. Next, heuristics are presented in terms of the dimensionless parameters for the time until the effective ADE adequately reflects reality. For strongly retarded solute, the time until effective ADE validity is found inversely proportional to release (e.g., desorption) rate. The nature of the effective dispersion coefficient is examined, and the possibility of large trapping-driven dispersion even in cases where batch experiments would detect negligible trapping is demonstrated. Collectively, these results call into question reliance on retardation factors derived from batch experiments for many practical transport modeling efforts; knowledge of both the trapping and release kinetics appears essential.

1. Introduction

1.1. Mathematical treatment of mobile–immobile processes

In many subsurface solute transport scenarios, there may be two spatially coextensive domains that are out of equilibrium with each other, each having its own local concentration. Commonly this is seen in models where solute advects only when it is in one, "mobile", state (i.e. domain), with concentration $c(x, t)$, but can also sometimes be trapped in an "immobile" state, which has its own concentration, $c_{\text{im}}(x, t)$, and from which it is eventually released. These models may be expressed with the following set of equations:

$$\begin{aligned}\frac{\partial c}{\partial t}(x,t) + \frac{\partial c_{\text{im}}}{\partial t}(x,t) &= F\{c\}(x,t)\\ \frac{\partial c_{\text{im}}}{\partial t}(x,t) &= G\{c, c_{\text{im}}\}(x,t),\end{aligned} \tag{1}$$

where F is a linear differential operator representing some combination of advection, dispersion, and decay, and G is an arbitrary operator. There are a number of different causes of this sort of mobile–immobile non-equilibrium transport: including so-called *chemical* and *physical* non-equilibrium, as well as diffusion into porous media [1]. Both the standard chemical and physical non-equilibrium equations, though arising through different conceptual pictures, may be put into an equivalent mathematical form [2], where in our notation we define

$$G\{c, c_{\text{im}}\} \equiv \lambda c - \mu c_{\text{im}}. \tag{2}$$

Here λ represents the probability per unit time that a mobile particle will become immobile, and μ represents the probability per unit time that an immobile particle will become mobile. A variety of dual-porosity transport problems can also be modeled in this way [3]. In addition, local equilibrium sorption with a distribution of retardation factors has been shown, when upscaled, to be expressible in the same form [4].

In our analysis, we shall employ an alternative expression for G (which we call G^*), previously used by

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Margolin et al. [5]:

$$G^*\{c\} \equiv \lambda c - \lambda \int_0^t \psi_{\mathrm{im}}(\tau) c(x, t-\tau) d\tau, \tag{3}$$

which eliminates c_{im} as a dependent variable but introduces time non-locality. As in (2), λ is a spatially homogeneous probability per unit time that a mobile particle will become immobile. Here, $\psi_{\mathrm{im}}(t)$ is an arbitrary probability distribution for the length of a single sojourn in the immobile phase. Substituting this into (1) leads to the integrodifferential equation

$$\frac{\partial c}{\partial t}(x,t) = F\{c\}(x,t) - \lambda c(x,t) + \lambda \int_0^t \psi_{\mathrm{im}}(\tau) c(x, t-\tau) d\tau. \tag{4}$$

Similar forms have been used by Schumer et al. [6] to define what the authors call the fractal mobile–immobile (fMIM) paradigm, by Haggerty et al. [7] in the analysis of late-time BTC tails in the presence of trapping processes, and by Benson and Meerschaert [8] in their development of subordination technique for incorporating anomalous transport into ADE-based numerical models.

In the Laplace domain, it is not difficult to show that Eqs. (1) and (2) are equivalent to (4) so long as

$$\psi_{\mathrm{im}}(t) = \mu e^{-\mu t}. \tag{5}$$

While more general forms of ψ_{im} than (5) correspond to some physical systems, we restrict our attention to first-order mobile–immobile behavior, and so will use (4) and (5) as the basis for all analysis. Note that this model implicitly defines a comparable probability distribution,

$$\psi_{\mathrm{m}}(t) = \lambda e^{-\lambda t}, \tag{6}$$

for the time taken by a single sojourn in the mobile phase (i.e. time interval between release and subsequent capture). This particular model, with exponentially-distributed times in both the sorbed and free states, has found wide application in the literature: applications are found in the sediment transport literature [9,10], as well as in analysis of solute trapping [8,11].

1.2. Trapping-driven dispersion, breakthrough curve asymmetry, and effective ADE models

Commonly, transport for each solute particle, including the random trapping, is independent of all other particles. Where this trapping is a result of diffusion into an immobile zone, this is assured. For kinetic sorption, where there exists a great excess of sorption sites, it is justified as well, although in cases of competitive sorption (i.e. limited sites), this may not be the case. Any random transport process that acts independently on different particles must have a dispersive effect, and indeed: the dispersive effect of kinetic sorption has long been recognized in the chromatography literature, dating back at least to [12]. In the subsurface transport literature, some theoretical studies quantifying the dispersive effects of mobile–immobile systems have been published. Late-time first, second, and third temporal moments of breakthrough curves for advective-dispersive subsurface solute transport subject to first-order chemical and physical non-equilibrium were considered by Valocchi [2]. A similar moment analysis, except deriving *spatial* moments was later performed by Michalak and Kitanidis [13]. The authors further computed effective late-time velocities and dispersion coefficients. These studies were in 1D, and focused on late time limits in the case when (2) holds, and are in the school of classic mobile–immobile zone models with exponential ψ_{im}. Recently, Uffink et al. [11] employed random walk theory to derive an equivalent PDE to (4), and manipulated the equation to derive the same late-time dispersion coefficient shown in [13]. To our knowledge, they were the first to remark that λ and μ may affect the rate of late-time Gaussian convergence, but did not pursue this systematically, save for providing an approximate time until the effective dispersion coefficient stabilizes.

Related to the discussion of trapping-driven dispersion is a body of literature on the so-called local equilibrium assumption (LEA). The LEA essentially refers to conditions under which the trapped and free concentrations are related by the same ratio at all times [14]. In our terminology, we express this as $c(x,t) + c_{\mathrm{im}}(x,t) \approx Rc(x,t)$, for some constant, R, referred to as a *retardation factor*. By substitution of R into (1), one arrives at the retarded transport equation:

$$R\frac{\partial c}{\partial t}(x,t) = F\{c\}(x,t). \tag{7}$$

It is apparent that this form simply rescales time (R can be eliminated by a substitution $\tau \equiv t/R$), and so the dispersive effect of trapping is not considered. Nonetheless, some authors conflate applicability of the local equilibrium assumption with usage of a retarded transport equation (e.g. [15]). There are some circumstances under which this is reasonable, namely those in which F is an advection–dispersion operator representing a stronger source of dispersion, compared to which trapping-driven dispersion is negligible.

The LEA has been widely studied, with aforementioned paper [2] aiming to validate it by comparing moments, at late time, of exact solutions for chemical and physical non-equilibrium with a retarded advection–dispersion equation. A different approach, seeking directly to find conditions under which local equilibrium is nearly satisfied at a point and relating that to parameters in a system like (1) has also been presented [16]. Later, Wallach examined the domain of validity of the LEA through perturbation theory, treating (7) as an end member in a perturbation expansion for the exact solution which contains trapping-driven dispersion [17]. All of these authors, and many others (see the literature review in [16]) identified conditions under which the dispersive effect of sorption was comparatively negligible.

However, since Michalak and Kitanidis [13] computed the effective, late time dispersion coefficient for classic mobile–immobile systems, there is now a more flexible framework available than the dispersion-ignoring LEA approximation. Mobile–immobile solute transport may be treated at late time by a retardation coefficient *and* this effective dispersion coefficient, even in cases where trapping-driven dispersion cannot be ignored. We term such an approach an *effective ADE* model.

An effective ADE model still cannot apply in circumstances in which there is a significantly asymmetric transport Green's function, however, since the Green's function for the ADE is Gaussian. Further, it is well known that in many trapping-and-release processes, plume asymmetry occurs. Uffink et al. [11] showed how this develops in a system described by (1) and (2).

Since consideration of mobile–immobile problems is so common in contaminant hydrogeology, there are naturally many alternatives to the effective ADE approach, including exact solutions for specific geometries. A comprehensive survey is beyond the scope of this work, but classes of techniques include analytic solutions such as those included in the aforementioned van Genuchten paper [3], analytic solutions that treat discrete fractures [18,19], and by multi-rate mass transfer schemes [20]. Numerical approaches that treat multiple interacting continua [21,22] are also useful for specific problems.

Lastly, it bears noting that in addition to being indicative of early-time mobile–immobile behavior for exponential ψ_{im}, asymmetry may be caused by power-law distributed immobile times [23], as well as non-sorbing transport in heterogeneous media [24]. The difficulty of distinguishing between mobile–immobile models and transport in heterogeneous media has been remarked upon by Carrera et al. [25], among others. This implies that CTRW approaches [24] represent another viable approach for modeling mobile–immobile systems. Experimentally, at the column scale, asymmetric breakthrough curves have been examined using CTRW approaches by Deng [26] and Li and Ren [27]. This sort of behavior may arise due to anomalous transport