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Not All Mass Transfer Rate Coefficients Are Created Equal

by Rui Ma¹ and Chunmiao Zheng^{2,3}

Introduction

The dual-domain (dual-porosity) conceptual model was first introduced by [Barenblatt et al. \(1960\)](#) to analyze seepage in fractured rocks and shortly afterward by Warren and Root (1963) to characterize flow behaviors in fractured reservoirs (see Anderson (2008) for a historical note on the two references). A conceptually similar dual-domain model was proposed by Coats and Smith (1964) to account for mass transfer into and out of the dead-end pore volume as an additional transport process to advection and dispersion. Since then, the dual-main model has been extended to simulate mass transfer processes of both physical and chemical nature with single or multiple rate coefficients (Zheng and Bennett 2002; Ma et al. 2010). This commentary focuses on the application of the dual-domain model to physical transport in soils and aquifers with preferential flow paths and relative flow barriers (van Genuchten et al. 1974; Nkedi-Kizza et al. 1983; Brusseau et al. 1994; Feehley et al. 2000; Harvey and Gorelick 2000; Zheng et al. 2010). A key parameter for the dual-domain mass transfer model is the mass transfer rate coefficient between the mobile and immobile domains. However, different definitions of the mass transfer rate coefficient have existed in the literature with the same terminology but different physical meaning. In this commentary, we attempt to clarify the confusion resulting from the different definitions of the mass transfer rate coefficient and discuss their implications for model applications.

Formulation 1

Coats and Smith (1964) was the first to derive the classic dual-domain mass transfer model that we are still using today. With this model, the aquifer is conceptualized as consisting of two distinct but overlapping domains: a mobile domain filled with moving fluids in which solute transport is by advection and hydrodynamic dispersion, and an immobile domain filled with relatively stagnant fluids in which solute transport is controlled by molecular diffusion between the mobile and immobile fluid zones. As a simplified approximation to diffusional mass transfer, the effective exchange between the two domains is represented by a first-order kinetic mass transfer term. The governing equations for the dual-domain mass transfer model of a conservative tracer can be expressed, with some variations, as follows (Coats and Smith 1964; van Genuchten et al. 1974; Griffioen et al. 1998; Feehley et al. 2000; Zheng and Gorelick 2003; Flach et al. 2004; Liu et al. 2010):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta_m \mathbf{D}_{ij} \frac{\partial C_m}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (q_i C_m) + q_s C_s \quad (1)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \zeta (C_m - C_{im}) \quad (2)$$

where C_m and C_{im} are the concentrations in the mobile and immobile domains, respectively; θ_m and θ_{im} are the porosities of mobile and immobile domains, respectively; $\mathbf{D}_{ij}$ is the hydrodynamic dispersion tensor; q_i is the specific discharge or Darcy's flux; q_s and C_s are the flux and concentration of the fluid sink/source term, respectively; and ζ is the first-order mass transfer rate coefficient between the mobile and immobile domains. It is noteworthy that the symbol ζ is used here to avoid preconceived association with either α or β , two symbols that have been commonly used to denote the mass transfer

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rate coefficient in various forms. Equations 1 and 2 are implemented in the commonly used numerical transport code MT3DMS (Zheng and Wang 1999; Zheng 2010). A form of Equation 2 is also implemented in the popular analytical transport code CXTFIT (Toride et al. 1999).

In Equation 2, the porosity of the immobile domain appears on the left-hand side, which represents the change in the solute mass in the immobile domain. This becomes clear if we replace Equation 2 by a finite difference approximation and multiply both sides by the size of a finite difference block and a time increment, that is,

$$\Delta x \Delta y \Delta z \theta_{im} \Delta C_{im} = \Delta x \Delta y \Delta z \zeta (C_m - C_{im}) \Delta t \quad (3)$$

The mass transfer rate coefficient, ζ , on the right-hand of Equation 2 has a dimension of $[T^{-1}]$. We refer to ζ as the *classic* mass transfer rate coefficient to distinguish it from an alternate form discussed next.

Formulation 2

An alternate form of the dual-domain mass transfer model can also be commonly seen in the literature in which Equation 2 is replaced by Equation 4 as follows (Haggerty and Gorelick 1995; Harvey and Gorelick 2000; Schumer et al. 2003; Haggerty et al. 2004; Salamon et al. 2006):

$$\frac{\partial C_{im}}{\partial t} = \zeta^* (C_m - C_{im}) \quad (4)$$

where ζ^* is the mass transfer rate coefficient, also with a dimension of $[T^{-1}]$. It can be seen, however, that to turn Equation 4 into a statement of mass balance in the immobile domain in finite difference form, we need to multiply both sides by $\Delta x \Delta y \Delta z \theta_{im} \Delta t$, that is,

$$\Delta x \Delta y \Delta z \theta_{im} \Delta C_{im} = \Delta x \Delta y \Delta z \theta_{im} \zeta^* (C_m - C_{im}) \Delta t \quad (5)$$

Comparing Equations 5 and 3, we can see clearly that

$$\zeta = \theta_{im} \zeta^* \quad (6)$$

Thus, even though ζ^* in Equation 4 also has a dimension of $[T^{-1}]$, it differs from ζ in Equation 2 by a factor of θ_{im} , the immobile porosity, that is, $\zeta^* = \zeta / \theta_{im}$. We refer to ζ^* as the *alternate* mass transfer rate coefficient to distinguish it from ζ .

For an aquifer system with a uniform immobile porosity, it is conceptually simple to switch between the two alternative definitions of the mass transfer rate coefficient. However, when the immobile porosity is spatially variable, the conversion between the two is less straightforward. A spatially uniform mass transfer rate coefficient defined in one form will become spatially variable when converted to the other form.

Implications

Because both ζ and ζ^* have the same dimension but differ by a dimensionless factor of immobile porosity, it can be difficult to discern which form of the mass transfer rate coefficient is referred to by an author if the first-order kinetic mass transfer equation is not given explicitly. Thus, great care must be taken to ensure proper estimation and consistent comparison of mass transfer rate coefficients for a dual-domain mass transfer model. (It is of interest to note that this problem is not unique to the first-order mass transfer as [Stauffer et al. \(2009\)](#) cautioned that the porous medium diffusion coefficient $[D^*]$ should not be confused with the effective diffusion coefficient $[D_{eff}]$ used in large-scale simulations to account for interaction between fractures and the surrounding porous medium. The two are related by the dimensionless water content.)

As an example, [Feehley et al. \(2000\)](#) developed a dual-domain mass transfer model to simulate the tritium tracer test at the Macrodispersion Experiment (MADE) site in Columbus, Mississippi, using the MT3DMS code (Zheng and Wang 1999). For the transport simulation with a three-dimensional (3D) hydraulic conductivity field based on ordinary kriging, the mass transfer rate coefficient and immobile porosity obtained from model calibration to the 3D observed tritium plume were 0.001/d and 0.306, respectively. [Harvey and Gorelick \(2000\)](#) simulated the same tritium tracer test using a dual-domain mass transfer model based on a 2D vertically integrated and analytically generated velocity field. The mass transfer rate coefficient and immobile porosity obtained from curve fitting to the 1D tritium mass profile along the flow direction were 0.011/d and 0.3, respectively.

The mass transfer rate coefficients from these two studies are expected to be different because of the disparity in the modeling approach (2D vs. 3D) and the calibration target (3D plume vs. 1D mass profile). However, the difference was exacerbated by the use of alternate forms of the rate coefficient. The mass transfer rate coefficient obtained by [Feehley et al. \(2000\)](#) is in the classic form as defined in Equation 2, whereas that obtained by [Harvey and Gorelick \(2000\)](#) is in the alternate form as defined in Equation 4. To compare the former with the latter, the classic form of the mass transfer rate coefficient $\zeta = 0.001/\text{d}$ from [Feehley et al. \(2000\)](#) needs to be divided by the immobile porosity of 0.306, resulting in the alternate form of the mass transfer rate coefficient $\zeta^* = 0.0033/\text{d}$, as opposed to $\zeta^* = 0.011/\text{d}$ in Harvey and Gorelick (2000). Conversely, the value $\zeta^* = 0.011/\text{d}$ from Harvey and Gorelick (2000) needs to be multiplied by the immobile porosity of 0.3, resulting in the value $\zeta = 0.0033/\text{d}$, for comparison with $\zeta = 0.001/\text{d}$ from Feehley et al. (2000).

As a simplified first-order approximation to the primarily diffusive process, which is second-order, between the mobile and immobile domains, the first-order mass transfer rate coefficient ζ is directly related to the molecular diffusion coefficient of the solute being transported.

However, a number of other factors affect the first-order mass transfer rate coefficient, depending on the characteristics of the porous media and hydraulic properties (Griffioen et al. 1998). These factors include: (1) the particle size and shape of aggregated porous media (van Genuchten and Wierenga 1974); (2) the magnitude of mobile zone fluid velocities (Brusseau et al. 1994); (3) connectivity of high-conductivity zones embedded in a low-conductivity matrix (Gorelick et al., 2005); and (4) experimental duration and transport spatial scale (Guan et al. 2007). Although in most field applications the mass transfer rate coefficient is treated as an empirical fitting parameter and obtained through model calibration, research efforts are continuing to develop more theoretically based and generally applicable expressions for the mass transfer rate coefficient under field conditions.

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