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A mobile-mobile transport model for simulating reactive transport in connected heterogeneous fields

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ABSTRACT

Mobile-immobile transport models can be effective in reproducing heavily tailed breakthrough curves of concentration. However, such models may not adequately describe transport along multiple flow paths with intermediate velocity contrasts in connected fields. We propose using the mobile-mobile model for simulating subsurface flow and associated mixing-controlled reactive transport in connected fields. This model includes two local concentrations, one in the fast- and the other in the slow-flow domain, which predict both the concentration mean and variance. The normalized total concentration variance within the flux is found to be a non-monotonic function of the discharge ratio with a maximum concentration variance at intermediate values of the discharge ratio. We test the mobile-mobile model for mixing-controlled reactive transport with an instantaneous, irreversible bimolecular reaction in structured and connected random heterogeneous domains, and compare the performance of the mobile-mobile to the mobile-immobile model. The results indicate that the mobile-mobile model generally predicts the concentration breakthrough curves (BTCs) of the reactive compound better. Particularly, for cases of an elliptical inclusion with intermediate hydraulic-conductivity contrasts, where the travel-time distribution shows bimodal behavior, the prediction of both the BTCs and maximum product concentration is significantly improved. Our results exemplify that the conceptual model of two mobile domains with diffusive mass transfer in between is in general good for predicting mixing-controlled reactive transport, and particularly so in cases where the transfer in the low-conductivity zones is by slow advection rather than diffusion.

1. Introduction

Concentration breakthrough curves (BTCs) measured in heterogeneous porous media often exhibit anomalous behavior, such as multiple peaks and enhanced tails (Berkowitz et al., 2000, Edery et al., 2014). This can be caused by preferential flow paths, which contribute marginally to the overall void-space but dominantly to the mass flux, and slow release of dissolved constituents from predominant stagnant zones in heterogeneous media (Zheng and Gorelick, 2003; Zinn et al., 2004). Advection-dispersion-mass transfer (ADMT) models or mobile-immobile models have been widely used to describe anomalous transport in heterogeneous porous media (Liu et al., 2007; Willmann et al., 2008; Tyukhova and Willmann, 2016). Classical mobile-immobile models with kinetic mass transfer include the first-order model (e.g., Coats and Smith, 1964; van Genuchten and Wierenga, 1976), slab, cylindrical and spherical diffusive models (e.g., Crank, 1975), multirate mass transfer models (Haggerty and Gorelick, 1995), and the double diffusion model (Cunningham et al., 1997), all focusing on the conceptualization of matrix block geometries. Other advanced models include continuous time random walk (Berkowitz et al., 2006) and fractal dispersion models (Benson, et al., 2000).

Mobile-immobile models with different conceptualizations of the immobile domain are particularly effective in reproducing heavily-tailed breakthrough curves by choosing appropriate memory functions (Haggerty et al., 2000; Schumer et al., 2003). However, mobile-immobile models adopting only a single permeable region may not adequately describe advection in multiple flow paths in connected fields, which is the primary solute transport

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process (Zinn et al., 2004; Leij et al., 2012). Both laboratory and field experiments have demonstrated that the mesoscale features may embody substantial water flow and delineate structured subsurface media into multiple flow paths with intermediate permeability and velocity contrasts, which may not be sufficiently characterized by models with a single permeable region (Luxmoore et al., 1990; Jardine et al., 1990; Jury and Fluhler, 1992; Zinn et al., 2004; Leij et al., 2012). More importantly, such models may yield erroneous prediction for reactive transport because they neglect the concentration differences among different flow paths (Kapoor et al., 1997; Cirpka and Kitanidis, 2000; Fiorotto and Caroni, 2002, 2003; Bellin and Tonina, 2007; Oates, 2007; Cirpka et al., 2008; Luo et al., 2008; Chiogna and Bellin, 2013). In weakly or highly heterogeneous media, mobile-immobile models demonstrated good prediction for mixing-controlled reactive transport with low concentration variances (Edery et al., 2009; Willmann et al., 2010). However, in media with intermediate hydraulic conductivity contrast, such models yield significant errors (Luo and Cirpka, 2011). The decisive point is that they conceptualize a single concentration within the solute flux in the mobile domain and slow advection effects are completely considered as a part of kinetic mass transfer in the immobile domain (Guswa and Freyberg, 2000; Zinn et al., 2003). Thus, they cannot account for reaction rate variations caused by concentration fluctuations within the flux (Kapoor et al., 1997; Gramling et al., 2002; Dentz et al., 2010). Many approaches have been developed to simulate such reactive transport with non-negligible effects of incomplete mixing or concentration variations (e.g., Kapoor et al., 1997; Cirpka and Kitanidis, 2000; Oates, 2007; Luo and Cirpka, 2008; Sanchez-Vila et al., 2010; Chiogna and Bellin, 2013; Bolster et al., 2016; Ginn, 2018).

In this study, we use a mobile-mobile transport model to upscale reactive transport in connected heterogeneous media. The model considers advective-dispersive transport in two continua with different velocity and an exchange term between the two continua. This concept is also known as dual-permeability model (in contrast to dual-porosity model as synonym for the mobile-immobile model) or as dual-continuum model and has been used to simulate flow and transport in unsaturated zones, structured soils and fractured/karstified aquifers (Dykhuizen, 1987; Gerke and van Genuchten, 1993). Mean concentrations can be achieved by flux- or volume-weighted averaging of the concentrations in the two domains, whereas mobile-immobile models can only provide volume averages. By construction, the model involves a variance of both the residence and flux concentration. Thus, the mobile-mobile model is possible to quantify concentration variances involved in flux-based concentration BTCs. In addition, the model is set in an Eulerian framework, which is convenient when incorporating complex reaction models. For conservative transport, analytical and approximate analytical solutions have been reported (Leij et al., 2012; Scioritno et al., 2015). We aim to demonstrate that including one more flow domain is an appropriate parametrization to simulate reactive transport in connected fields with intermediate hydraulic conductivity contrast and multiple flow paths. We will particularly show the improvement of the mobile-mobile model compared with mobile-immobile models with a single mobile domain to quantify both concentration mean and variance for reactive transport in such fields.

This paper is organized as follows: Section 2 recapitulates the governing equations of the mobile-mobile transport model and its dimensional analysis. Section 3 discusses the effects of various processes on the concentration variances within the flux and its effects on reactive transport. Section 4 presents the application of the mobile-mobile transport model for simulating an instantaneous bimolecular reactive transport in connected structured and heterogeneous fields and compare its performance with a mobile-immobile model. Finally, in Section 5 we draw conclusions.

2. Mobile-mobile transport model

2.1. Governing equations

The subsurface medium is conceptualized as two overlapping domains with different flow velocities and dispersion coefficients and a linear kinetic mass transfer term between. The transport governing equations for a conservative tracer are given by (Dykhuizen, 1987; Gerke and van Genuchten, 1993; Leij et al., 2012):

$$\begin{aligned}\theta_f\frac{\partial c_f}{\partial t} &= -q_f\frac{\partial c_f}{\partial x}+\theta_f D_f\frac{\partial^2 c_f}{\partial x^2}+\alpha(c_s-c_f)\\ \theta_s\frac{\partial c_s}{\partial t} &= -q_s\frac{\partial c_s}{\partial x}+\theta_s D_s\frac{\partial^2 c_s}{\partial x^2}+\alpha(c_f-c_s)\end{aligned} \tag{1}$$

where c_f and c_s are concentrations in the fast- and slow-flow domain, respectively; t is time; x is travel distance; θ_f and θ_s are porosities of the fast- and slow-flow domains, respectively; q_f and q_s are specific discharges; D_f and D_s are dispersion coefficients, and α is the first-order mass transfer rate coefficient. All parameters are assumed constant. More complex (e.g., nonlocal) laws for the exchange between the two domains could be defined if deemed necessary, but they would require additional parameters.

By neglecting molecular diffusion and assuming the same dispersivity, D_f and D_s are written as:

$$D_f=\alpha_l v_f,\quad D_s=\alpha_l v_s \tag{2}$$

in which α_l is the apparent longitudinal dispersivity, and v_f and v_s are fast and slow velocities. Here the same longitudinal dispersivity is assumed to have fewer unknown parameters. Leij et al. (2012) presented an analytical solution of concentrations to Eqs. (1) and (2) with a first-type step input boundary condition.

The mobile-mobile model is more general than classical advection-dispersion equations (ADE) and mobile-immobile models. Under the following conditions, the mobile-mobile model can be simplified to:

(1) If the slow velocity is much smaller than the fast velocity, the slow-flow domain may be considered as immobile so that the mobile-mobile model becomes a mobile-immobile model;
(2) If the porosity of the slow-flow domain is negligible, it becomes the standard ADE model;
(3) If the mass transfer is very fast, the concentrations in the slow- and fast-flow domains approach equilibrium and the mobile-mobile model becomes a simple ADE model;
(4) If the mass transfer is very slow and negligible, the mobile-mobile model becomes the superposition of two ADE models, which represents advective-dispersive transport in two non-interacting stream tubes.

It is straightforward to extend the mobile-mobile model to reactive transport by incorporating reaction kinetics in the fast and slow domains.

$$\begin{aligned}\theta_f\frac{\partial c_{f,i}}{\partial t} &= -q_f\frac{\partial c_{f,i}}{\partial x}+\theta_f D_f\frac{\partial^2 c_{f,i}}{\partial x^2}+\alpha(c_{s,i}-c_{f,i})+\theta_f r_{f,i}(c_{f,1},c_{f,2},\ldots)\\ \theta_s\frac{\partial c_{s,i}}{\partial t} &= -q_s\frac{\partial c_{s,i}}{\partial x}+\theta_s D_s\frac{\partial^2 c_{s,i}}{\partial x^2}+\alpha(c_{f,i}-c_{s,i})+\theta_s r_{s,i}(c_{s,1},c_{s,2},\ldots)\end{aligned} \tag{3}$$

in which $c_{f,i}$ and $c_{s,i}$ are the concentrations of i th reactive species in the fast and slow flow domains, and $r_{f,i}$ and $r_{s,i}$ are the