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Evaluation of simplified mass transfer models to simulate the impacts of source zone architecture on nonaqueous phase liquid dissolution in heterogeneous porous media

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ABSTRACT

Nonaqueous phase liquid (NAPL) dissolution was studied in three-dimensional (3D) heterogeneous experimental aquifers (25.5 cm×9 cm×8.5 cm) with two different longitudinal correlation lengths (2.1 cm and 1.1 cm) and initial spill volumes (22.5 ml and 10.5 ml). Spatial and temporal distributions of NAPL during dissolution were measured using magnetic resonance imaging (MRI). At high NAPL spill volume, average effluent concentrations initially increased during dissolution, as NAPL pools transitioned to NAPL ganglia, and then decreased as the total NAPL–water interfacial area decreased over time. Experimental results were used to test six dissolution models: (i and ii) a one-dimensional (1D) model using either specific NAPL–water interfacial area values estimated from MR images at each time step (i.e., 1D quasi-steady state model), or an empirical mass transfer (Sh') correlation (i.e., 1D transient model), (iii and iv) a multiple analytical source superposition technique (MASST) using either the NAPL distribution determined from MR images at each time step (i.e., MASST steady state model), or the NAPL distribution determined from mass balance calculations (i.e., MASST transient model), (v) an equilibrium streamtube model, and (vi) a 3D grid-scale pool dissolution model (PDM) with a dispersive mass flux term. The 1D quasi-steady state model and 3D PDM captured effluent concentration values most closely, including some concentration fluctuations due to changes in the extent of flow reduction. The 1D transient, MASST steady state and transient, and streamtube models all showed a monotonic decrease in effluent concentration values over time, and the streamtube model was the most computationally efficient. Changes during dissolution of the effective NAPL–water interfacial area estimated from imaging data are similar to changes in effluent concentration values. The 1D steady state model incorporates estimates of the effective NAPL–water interfacial area directly at each time point; the 3D PDM does so indirectly through mass balance and a relative permeability function, which causes reduced water flow through high saturation NAPL regions. Hence, when model accuracy is required, the results indicate that a surrogate of this effective interfacial area is required. Approaches to include this surrogate in the MASST and streamtube models are recommended.

1. Introduction

Nonaqueous phase liquids (NAPLs) released into the subsurface are a major source of long-term groundwater contamination due to their low solubility and high toxicity. Mass transfer limited dissolution from such NAPLs can hinder subsurface remediation and natural attenuation processes at contaminated sites (Hunt et al., 1988; Powers et al., 1991). Subsurface porous media are characterized by various degrees of heterogeneity (e.g., wide range of grain sizes and lithologies); which significantly impact NAPL distribution and dissolution (Schwille, 1988; Kueper et al., 1989).

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In early NAPL dissolution studies, empirical correlations of overall mass transfer rates (expressed in the form of a modified Sherwood number $Sh' = K_L l_c^2 / D_m$, where K_L is the lumped mass transfer coefficient, l_c is the characteristic length scale of mass transfer and D_m is the molecular diffusivity in water) were developed from dissolution experiments conducted in one-dimensional (1D) homogeneous porous media containing NAPL at residual saturation (e.g., Miller et al., 1990; Powers et al., 1992; Imhoff et al., 1994). Results from these studies showed the dependence of mass transfer rate on aqueous phase flow (q_w), NAPL saturation (S_n) and porous media grain diameter (d_{50}). While these mass transfer correlations revealed key parameters that affect NAPL dissolution, application to multi-dimensional heterogeneous systems was problematic because effects such as preferential flow (i.e., reduction of water flow through NAPL-contaminated regions), and nonuniform NAPL distribution were not considered.

More recent efforts have been devoted to modeling the impacts of source zone architecture on NAPL dissolution, and a variety of numerical modeling approaches have been used. Powers et al. (1998) simulated NAPL dissolution in two-dimensional (2D) flow through systems containing a sand lens contaminated with NAPL and surrounded by a clean sand matrix. MODFLOW was used to simulate the 2D flow field, and MT3D (using the local equilibrium assumption, LEA) was used to simulate advection, and longitudinal and transverse dispersion. Saba and Illangasekare (2000) also used MODFLOW and MT3D to simulate residual NAPL dissolution from a 2D system containing an emplaced NAPL subzone. Instead of assuming local equilibrium, a mass transfer rate correlation was determined from experiments and incorporated into the model. Last, Mayer and Miller (1996) developed a 2D multiphase flow and transport model to simulate NAPL dissolution in both homogeneous and heterogeneous porous media using either LEA or empirical mass transfer correlations (Miller et al., 1990; Parker et al., 1990; Powers et al., 1994). In the first two studies (Powers et al., 1998; Saba and Illangasekare, 2000), experiments were adequately modeled and NAPL dissolution was sensitive to relative permeability. In the third study (Mayer and Miller, 1996), NAPL dissolution was also sensitive to the NAPL distribution. In a more recent work, Christ et al. (2006) developed an upscaled mass transfer model by incorporating source zone parameters, i.e., the initial concentration and source zone ganglia-to-pool (GTP) mass ratio. This model has been shown to be applicable to source zones with GTP greater than 40%.

A number of simplified modeling approaches have also been developed for multi-dimensional systems based on analytical or semi-analytical solutions. Nambi and Powers (2003) and Parker and Park (2004) both developed mass transfer correlations using a 1D transport model to simulate dissolution in heterogeneous systems. The former considered dissolution from a single NAPL-contaminated zone surrounded by clean sand (2D), the latter from a heterogeneous NAPL source zone (3D). Sale and McWhorter (2001) simulated NAPL dissolution from discrete source zones located within a 2D homogeneous porous medium using a multiple analytical source superposition technique (MASST). NAPL was distributed in discrete rectangular zones, and these zones were arranged in different configurations. Falta (2003) formulated a sub-grid pool dissolution model that simulates dissolution of multiple heterogeneously distributed NAPL pools in a 2D dual permeability flow field. The contaminated zone is divided into two fractions: one contains NAPL pools and one is free of NAPL. Advective and dispersive mass flux from each NAPL zone is calculated using an integral finite difference method, and the dissolution rate was shown to match experimental data by Schwille (1988). Last, Jawitz et al. (2005) proposed a streamtube model to simulate NAPL dissolution based on the distribution of travel times and the trajectory-integrated NAPL content within heterogeneous NAPL source zones; Fure et al. (2006) showed that the streamtube model was adequate in capturing NAPL dissolution profiles from experiments performed in 2D heterogeneous systems.

While each of the aforementioned models have provided valuable insights to NAPL dissolution mechanisms, it remains unclear which ones are suitable for application to real sites, what modifications are necessary for application, or what field data is required for accurate dissolution modeling. One reason for this uncertainty is the lack of detailed data for testing, where the NAPL saturation distribution in a heterogeneous 3D permeability field is known as a function of NAPL mass remaining during dissolution. Recently, the NAPL saturation distribution was characterized during dissolution in two 3D spatially correlated random permeability fields using magnetic resonance imaging (MRI) (Zhang, 2006; Zhang et al., 2007). This new data creates an opportunity for model testing due to its complexity and care taken to represent field conditions.

The objective of this study is to test simplified NAPL dissolution models using the new 3D NAPL source zone architecture data (Zhang, 2006; Zhang et al., 2007). Specifically, we use data obtained from ^{19}F MR imaging of NAPL in 3D permeability fields to test six NAPL dissolution models: (i and ii) 1D transport model using the specific NAPL–water interfacial area estimated from MR images or a Sh' correlation, (iii and iv) a steady state or transient multiple analytical source superposition technique (MASST), (v) the equilibrium streamtube dissolution model of Jawitz et al. (2005), and (vi) a grid-scale NAPL pool dissolution model (PDM). While this suite of models is not exhaustive, it represents a range of conceptual models with various capabilities. More complex and fully 3D numerical models will not be tested in this work.

2. Methods

2.1. NAPL dissolution experiments

The details of the NAPL entrapment and dissolution experiment, and MR imaging methodology, have been presented elsewhere (Zhang et al., 2007). Following is an overview of the experimental procedures.

NAPL dissolution experiments were performed in a 3D flow cell with inner dimensions of 25.5 cm × 9 cm × 8.5 cm (length × width × height), packed with one of two correlated heterogeneous permeability fields (14 cm × 8 cm × 8 cm). Each permeability field had identical transverse (~1 cm) and vertical correlation lengths (~1.1 cm), but different longitudinal correlation lengths: 2.1 cm and 1.1 cm, respectively. The correlated permeability fields were generated using a