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Modeling the influence of coupled mass transfer processes on mass flux downgradient of heterogeneous DNAPL source zones

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ABSTRACT

Sequestered mass in low permeability zones has been increasingly recognized as an important source of organic chemical contamination that acts to sustain downgradient plume concentrations above regulated levels. However, few modeling studies have investigated the influence of this sequestered mass and associated (coupled) mass transfer processes on plume persistence in complex dense nonaqueous phase liquid (DNAPL) source zones. This paper employs a multiphase flow and transport simulator (a modified version of the modular transport simulator MT3DMS) to explore the two- and three-dimensional evolution of source zone mass distribution and near-source plume persistence for two ensembles of highly heterogeneous DNAPL source zone realizations. Simulations reveal the strong influence of subsurface heterogeneity on the complexity of DNAPL and sequestered (immobile/sorbed) mass distribution. Small zones of entrapped DNAPL are shown to serve as a persistent source of low concentration plumes, difficult to distinguish from other (sorbed and immobile dissolved) sequestered mass sources. Results suggest that the presence of DNAPL tends to control plume longevity in the near-source area; for the examined scenarios, a substantial fraction (43.3–99.2%) of plume life was sustained by DNAPL dissolution processes. The presence of sorptive media and the extent of sorption non-ideality are shown to greatly affect predictions of near-source plume persistence following DNAPL depletion, with plume persistence varying one to two orders of magnitude with the selected sorption model. Results demonstrate the importance of sorption-controlled back diffusion from low permeability zones and reveal the importance of selecting the appropriate sorption model for accurate prediction of plume longevity. Large discrepancies for both DNAPL depletion time and plume longevity were observed between 2-D and 3-D model simulations. Differences between 2- and 3-D predictions increased in the presence of sorption, especially for the case of non-ideal sorption, demonstrating the limitations of employing 2-D predictions for field-scale modeling.

1. Introduction

Despite decades of efforts to restore sites contaminated by chlorinated solvents (e.g. tetrachloroethene (PCE), trichloroethene(TCE)), persistent groundwater contaminant plumes above regulated concentration levels are commonly observed after site closure (NRC, 2013; 2004; 1994; Stroo et al., 2003; US EPA, 2003). Chlorinated solvents are typically released into the subsurface as dense nonaqueous phase liquids (DNAPLs), which can serve as a long term source of groundwater contamination due to dissolved contaminants emanating from high saturation DNAPL pools or residual saturation ganglia (e.g., Lemke and Abriola, 2006). Partial removal of the DNAPL source mass is not uncommon in complex field sites (e.g., ITRC, 2011). At aged sites, as concentrations in the more transmissive zones decline, the contaminants sequestered in low permeability zones will be released back into the mobile plume. This process is often referred to as "back diffusion" (BD) (Mackay and Cherry, 1989). Along with DNAPL dissolution, BD has been increasingly recognized as an important process that sustains chlorinated solvent plumes (Abriola et al., 2012; NRC, 2013; Sale et al., 2013; Sale et al., 2008(a); Stroo et al., 2012).

Matrix diffusion has been studied extensively in the contaminant transport literature (e.g., Brown and Thomas, 1998; Foster, 1975; Gillham and Cherry, 1982; Guswa and Freyberg, 2000; Pankow et al., 1989; Parker et al., 1994; Starr et al., 1985; Sudicky et al., 1985). The

Abbreviations: NRC, National Research Council; BD, back diffusion; DNAPL, dense nonaqueous phase liquid; 1-D, one dimensional; 2-D, two-dimensional; 3-D, three-dimensional; MT3DMS, the modular three dimensional transport simulator; MVALOR, Michigan Vertical and Lateral Organic Redistribution; UTCHEM, the University of Texas Chemical Flooding Simulator; TP/MC, transition-probability-based Markov Chain; Tetrachloroethene, PCE; Dsp, dispersivity; GTP, ganglia to pool ratio; PF, pool mass fraction

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importance of BD has been increasingly appreciated and demonstrated by, analyses of groundwater monitoring well and soil core data at aged field sites (e.g, Ball et al., 1997; Brusseau and Guo, 2014; Chapman and Parker, 2005; Liu and Ball, 2002; Parker et al., 2008; Parker et al., 2004). At the laboratory scale, a number of benchmark experiments in aquifer cells have demonstrated that mass flux from low permeability zones can cause persistent plume tailing after DNAPL depletion (e.g., Chapman et al., 2012; Rodriguez, 2006; Sale et al., 2008(b); Wilking et al., 2013; Yang et al., 2015). Most of these laboratory experiments have been confined to idealized geometrical representations of physical heterogeneity and simple aqueous phase mass loading conditions. Real source zones, however, exhibit much greater physical and chemical complexity, characterized by more irregular physical heterogeneity and the presence of multiple phases (DNAPL, aqueous, sorbed) and co-existing mass transfer processes. Herein the term "source zone" refers to the subsurface region originally in contact with DNAPL, containing DNAPL, aqueous, and sorbed phase mass (NRC, 2004), To date, only a few laboratory studies have created source zones by injecting DNAPL into aquifer cells (Rodriguez, 2006; Wilking et al., 2013) but these have used highly simplified physical scenarios. Thus, while providing qualitative insights pertaining to the process of BD, the implications of these laboratory studies for field remediation practices are not easily identified.

Mathematical models have been used in a number of studies to identify influential factors in plume persistence and to interpret laboratory and field data. Based upon their simplicity and ease of application, analytical models have been employed by some researchers to predict the development of down-gradient plumes during BD in one- (1-D) and two- dimensional (2-D) domains (e.g., Adamson et al., 2015; Ball et al., 1997; Bear et al., 1994; Brown et al., 2012; Liu and Ball, 2002; Sale et al., 2008(b); Seyedabbasi et al., 2012; Wilson, 1997; Yang et al., 2015; Yang et al., 2017), as well as in three-dimensions (3-D) (Parker and Kim, 2015). These applications, however, have necessarily been restricted to idealized geometric configurations and have employed simplifying assumptions such as infinite or semi-infinite clay layers, no flow in low permeability zones, and non-diminishing DNAPL volumes.

In contrast, numerical models, with the potential to be tailored to more detailed and realistic conditions, have become important tools for long-term site management and decision-making. A number of studies have employed numerical models to capture diffusive mass transport into low permeability zones and to predict persistence of plume tailing due to BD (Chapman and Parker, 2005; Chapman et al., 2012; Maghrebi et al., 2015; Maghrebi et al., 2014; Matthieu et al., 2014; Parker et al., 2008; Rodriguez, 2006). In general, these previous numerical simulation studies have been implemented on idealized domains, i.e., those with horizontal layering (perfect stratification) (Chapman and Parker, 2005; Matthieu et al., 2014) or those consisting of homogeneous background units with one or several uniform inclusions of low permeable materials (Chapman et al., 2012; Maghrebi et al., 2014; Parker et al., 2008; Rodriguez, 2006). At real field sites, however, variability of permeability at the small scale can range over several orders of magnitude. Maghrebi et al. (2015) is the only previous numerical modeling investigation of BD that incorporated a heterogeneous permeability field generated by a geostatistical model. In addition to the previous research cited above, a few numerical studies have investigated the influence of diffusion on contaminant transport in complex heterogeneous formations (e.g., Janković et al., 2009; LaBolle and Fogg, 2001; Rolle et al., 2013). These studies, however, did not focus on plume persistence caused by BD.

Although sorption is an important process within many low permeability units and can influence mass transfer, the influence of sorption on the mass rebound process in chlorinated solvent source zones has not generally been as well-recognized as that of diffusion. While a few previous modeling studies (Maghrebi et al., 2015; Maghrebi et al., 2014; Rodriguez, 2006) have incorporated sorption and explored the effect of sorption properties on plume tailing, most have emphasized the effect of diffusion. In addition, these studies have typically assumed local equilibrium and isotherm linearity. Many experimental studies, however, have demonstrated that the linear equilibrium assumption fails to capture observed behavior. Thus, sorption processes in the subsurface should typically be characterized as nonlinear and/or rate-limited, particularly over the wide range of concentrations encountered within DNAPL source zones (e.g., Allen-King et al., 2002; Rivett et al., 2006; Wang et al., 2013). Although Matthieu et al. (2014) briefly discussed the potential influence of sorption kinetics and equilibrium on the rates of mass removal in their work, they did not use modeling results to support this discussion. Furthermore, the use of simplified configurations of permeability heterogeneity in previous simulation studies also resulted in limited spatial variation of sorption parameters. It is widely recognized, however, that heterogeneity of sorption properties can substantially influence solute transport and result in asymptotic concentration tailing (e.g., Aksoy and Culver, 2004; Rabideau and Miller, 1994).

Most of the previous simulation studies cited above modeled mass emanating from DNAPL source zones by incorporating source functions that were either constant (Chapman and Parker, 2005; Maghrebi et al., 2015, Maghrebi et al., 2014; Parker et al., 2008;) or adjusted based on known data (Chapman and Parker, 2005; Rodriguez, 2006). These models did not incorporate DNAPL dissolution and thus, could not include heterogeneous DNAPL saturation distributions as model inputs. However, it is now widely recognized that the distribution of DNAPL within a source zone (also known as DNAPL architecture), developed under the influence of a number of site-specific conditions (e.g. Dekker and Abriola, 2000; Lemke et al., 2004(a)), can be quite complex (e.g. Kueper et al., 1993; Mercer and Cohen, 1990), and that this DNAPL architecture will largely control the behavior and longevity of dissolved mass plumes (e.g. Christ et al., 2010, Christ et al., 2006; Lemke et al., 2004(b); Parker and Park, 2004; Phelan et al., 2004). Thus, it will be important to consider the spatial distribution of DNAPL in any investigation of BD and plume persistence in heterogeneous source zones.

Finally, most of the previous simulations investigating BD have been performed in 2-D domains (Chapman and Parker, 2005; Chapman et al., 2012; Parker et al., 2008; Rodriguez, 2006), with only a few conducted in 3-D (Maghrebi et al., 2015; Maghrebi et al., 2014). Reduced dimensionality simulations, however, may not be able to completely capture flow bypassing effects or accurately predict the magnitude and penetration depth of mass in lower permeability zones. Thus, plume persistence may vary with model dimensionality, and it will be important to compare concentration rebound predictions in two and three dimensions.

As highlighted above, although consideration of simplified scenarios can provide a preliminary assessment of the influence of BD on plume longevity, models based upon such idealized scenarios cannot capture the full complexity of field conditions. The objective of this study is to more comprehensively explore the influence of dissolution, sorption, and diffusion process coupling on source longevity and near-source plume persistence in complex geologic environments through numerical modeling. In this work, a series of transport simulations was undertaken for a suite of DNAPL source zone realizations in 2-D heterogeneous domains under a number of alternative sorption property scenarios. Selected comparisons with 3-D simulations provide additional insight into the influence of model dimensionality on plume longevity predictions.

2. Methodology

Transport simulations were performed using a modified version of the modular three dimensional transport simulator MT3DMS (Zheng and Wang, 1999), adapted to incorporate rate limited dissolution from an entrapped DNAPL source zone and transient groundwater flow associated with changes in DNAPL saturation (Christ et al., 2010; Christ et al., 2006; Parker and Park, 2004). Initial DNAPL source zone