Dissolved plume attenuation with DNAPL source remediation, aqueous decay and volatilization — Analytical solution, model calibration and prediction uncertainty

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ABSTRACT

A vertically-integrated analytical model for dissolved phase transport is described that considers a time-dependent DNAPL source based on the upscaled dissolution kinetics model of Parker and Park with extensions to consider time-dependent source zone biodecay, partial source mass reduction, and remediation-enhanced source dissolution kinetics. The model also considers spatial variability in aqueous plume decay, which is treated as the sum of aqueous biodecay and volatilization due to diffusive transport and barometric pumping through the unsaturated zone. The model is implemented in Excel/VBA coupled with (1) an inverse solution that utilizes prior information on model parameters and their uncertainty to condition the solution, and (2) an error analysis module that computes parameter covariances and total prediction uncertainty due to regression error and parameter uncertainty. A hypothetical case study is presented to evaluate the feasibility of calibrating the model from limited noisy field data. The results indicate that prediction uncertainty increases significantly over time following calibration, primarily due to propagation of parameter uncertainty. However, differences between the predicted performance of source zone partial mass reduction and the known true performance were reasonably small. Furthermore, a clear difference is observed between the predicted performance for the remedial action scenario versus that for a no-action scenario, which is consistent with the true system behavior. The results suggest that the model formulation can be effectively utilized to assess monitored natural attenuation and source remediation options if careful attention is given to model calibration and prediction uncertainty issues.

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1. Introduction

Dense non-aqueous phase liquids (DNAPLs) pose a difficult groundwater remediation challenge due to the impracticability of complete DNAPL source removal and to the long-term persistence of contaminant fluxes when even small DNAPL amounts remain (Soga et al., 2004). The effectiveness of natural attenuation and the feasibility of engineered remediation strategies are contingent on a number of physical and biological processes that control net source zone mass flux and attenuation within the dissolved phase plume.

A number of recent studies have focused on relationships between contaminant mass flux from DNAPL sources and the amount and distribution of DNAPL remaining in the source. Sale and McWhorter (2001) presented a semi-analytical model for dissolution rates in sources with spatially distributed DNAPL within uniform velocity fields. Their results indicated that while near-equilibrium mass transfer may occur at the local-scale, field-scale mass transfer is primarily controlled by advective–dispersive transport and the geometry of the DNAPL zones. The authors concluded that field-scale dissolution rates will diminish little over time as a function of source mass depletion. Rao and Jawitz (2003) noted that this

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conclusion is conditioned on assumptions of uniform flow and spatially distributed DNAPL subzones that are uniform in terms of their size, geometry and mass. When these assumptions are not met, greater reductions in contaminant fluxes over time may occur as DNAPL is more quickly depleted in regions with higher velocities and/or smaller initial masses.

Parker and Park (2004) and Park and Parker (2005) presented a field-scale mass transfer function (Parker–Park model) for DNAPL dissolution kinetics and demonstrated its ability to quantify effects of DNAPL mass depletion over time, groundwater velocity within the source zone, and variations in source zone "architecture" based on high resolution numerical simulation results. The foregoing or similar mass flux versus mass depletion relationships have been utilized by a number of authors (Rao et al., 2001; Zhu and Sykes, 2004; Jawitz et al., 2005; Falta et al., 2005a,b; Christ et al., 2006; Fure et al., 2006; Basu et al., 2007; Saenton and Illangasekare, 2007).

While many studies have addressed the biotransformation of chlorinated solvents within dissolved phase plumes, relatively few studies have considered effects of biodecay within DNAPL source areas. Semprini et al. (1992), Mravik et al. (2003) and Ramsburg et al. (2004) have discussed various methods to enhance source zone biodecay. Mass losses due to volatilization of organic chemicals from groundwater under natural or engineered conditions have also been studied (Jury et al., 1990; Conant et al., 1996; Auer et al., 1996; Parker, 2003). To our knowledge, no models have been presented that incorporate effects of both source zone biodecay and plume-wide volatilization losses on dissolved plume attenuation.

The objective of this paper is to present a semi-analytical model for evaluating natural and engineered attenuation at DNAPL sites considering effects of DNAPL source depletion, source zone and dissolved plume biodecay, mass loss due to volatilization from groundwater, and various engineered measures, including partial source mass reduction and enhanced source zone biodecay. The Parker–Park field-scale DNAPL source model will be extended to consider source zone biodecay and will be incorporated into a semi-analytical solution for dissolved phase transport with spatially-variable aqueous decay coefficients subject to step-changes in source and dissolved plume properties following remedial action. An application of the model will be presented to address practical calibration and prediction uncertainty issues.

2. Model description

2.1. DNAPL dissolution and source zone biodecay

We consider a DNAPL source zone region of height L_z and width L_y with length L_x in the direction of groundwater flow in an aquifer of saturated thickness L_a (Fig. 1). DNAPL, which is non-uniformly distributed within this region, undergoes mass transfer-limited dissolution to groundwater, and some of the dissolved mass biodegrades within the source zone before reaching the downgradient source zone boundary. Assuming linear field-scale mass transfer kinetics, first-order dissolved phase biodecay, and pseudo-steady-state advective transport, the areally-averaged source zone concentration distribution along the flow path may be approximated by

$$q_s \frac{dC}{dx} = \kappa_{\text{eff}} (C_{\text{eq}} - C) - \gamma_s \phi_s C \tag{1}$$

where q_s is the source zone Darcy velocity [L T^{-1}], C is aqueous phase concentration [M L^{-3}], x is distance in the direction of flow [L], C_{eq} is the equilibrium dissolved phase concentration [M L^{-3}], γ_s is a source zone biodecay coefficient [T^{-1}], ϕ_s is source zone porosity [−], and κ_{eff} is an effective field-scale dissolution rate coefficient [T^{-1}] that may be described (Parker and Park, 2004; Park and Parker, 2005) by

$$\kappa_{\text{eff}} = \kappa'_o q_s \left(\frac{M}{M_o} \right)^{\beta} \tag{2}$$

where κ'_o is a flow-normalized initial dissolution rate coefficient [L^{-1}], M_o is initial DNAPL mass [M], M is the current DNAPL mass [M], and β is a mass depletion exponent [−]. Values of β greater than one indicate dissolution rates diminish more rapidly than relative mass reduction, while values less than one indicate disproportionately slower rate reductions. Studies by Park and Parker (2005) indicate β values greater than 1 for finger-dominated residual DNAPL and less than 1 for DNAPL pools and lenses, while Falta et al. (2005a,b) suggest that sites with DNAPL located predominantly in low permeability zones exhibit $\beta > 1$ while sites with DNAPL in higher permeability zones have $\beta < 1$. Integrating Eq. (1) along the source zone flow path gives

$$C(x') = \frac{C_{\text{eq}} \kappa_{\text{eff}}}{\kappa_{\text{eff}} + \gamma_s \phi_s} \left(1 - exp \left(\frac{-(\kappa_{\text{eff}} + \gamma_s \phi_s) x'}{q_s} \right) \right) \tag{3}$$

where $C(x')$ is the mean concentration within the source perpendicular to the flow direction at a distance x' from the
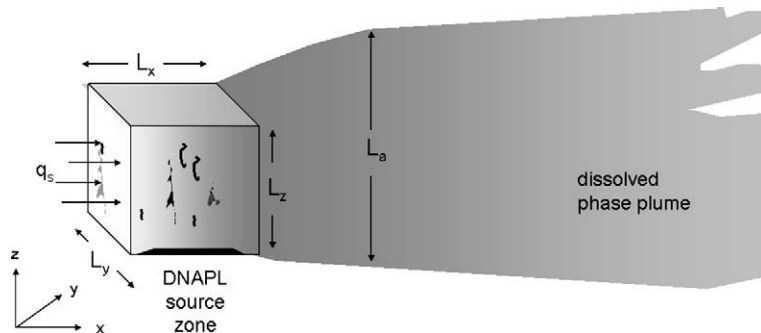

Fig. 1. Source zone geometry.