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A stochastic-advective transport model for NAPL dissolution and degradation in non-uniform flows in porous media

T.P. Chan [a], Rao S. Govindaraju [b,*]

[a] Land Resource Management Group, 525 East North Street, Suite F, Bradley, IL 60915, USA
[b] School of Civil Engineering, Purdue University, West Lafayette, IN 47907, USA

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Abstract

Remediation schemes for contaminated sites are often evaluated to assess their potential for source zone reduction of mass, or treatment of the contaminant between the source and a control plane (CP) to achieve regulatory limits. In this study, we utilize a stochastic stream tube model to explain the behavior of breakthrough curves (BTCs) across a CP. At the local scale, mass dissolution at the source is combined with an advection model with first-order decay for the dissolved plume. Field-scale averaging is then employed to account for spatial variation in mass within the source zone, and variation in the velocity field. Under the assumption of instantaneous mass transfer from the source to the moving liquid, semi-analytical expressions for the BTC and temporal moments are developed, followed by derivation of expressions for effective velocity, dispersion, and degradation coefficients using the method of moments. It is found that degradation strongly influences the behavior of moments and the effective parameters. While increased heterogeneity in the velocity field results in increased dispersion, degradation causes the center of mass of the plume to shift to earlier times, and reduces the dispersion of the BTC by lowering the concentrations in the tail. Modified definitions of effective parameters are presented for degrading solutes to account for the normalization constant (zeroth moment) that keeps changing with time or distance to the CP. It is shown that anomalous dispersion can result for high degradation rates combined with wide variation in velocity fluctuations. Implications of model results on estimating cleanup times and fulfillment of regulatory limits are discussed. Relating mass removal at the source to flux reductions past a control plane is confounded by many factors. Increased heterogeneity in velocity fields causes mass fluxes past a control plane to persist, however, aggressive remediation between the source and CP can reduce these fluxes.

Keywords: Remediation; Stochastic stream tube modeling; Temporal moments; Effective parameters; Anomalous dispersion; Mass fluxes; Plume remediation

* Corresponding author. Tel.: +1 765 496 3402; fax: +1 765 496 1988.
E-mail address: govind@ecn.purdue.edu (R.S. Govindaraju).

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1. Introduction

Contamination of an aquifer by accidental or intentional release of non-aqueous phase liquids (NAPLs) is an important environmental problem. Of particular concern are the so-called DNAPLs that have densities higher than water, and tend to migrate by gravity down to the saturated zone and become a source of groundwater contamination (Frind et al., 1999). Many of these organic chemicals are highly toxic and also highly persistent in the subsurface environment; thus cleanup or remediation of the source zone and the plume of the dissolved chemicals is needed for reducing the risks associated with the exposure of the chemicals to plants, animals, and humans. Developing a sound remedial strategy requires the modeling of dissolution of the DNAPL source and the transport of its dissolved plume. However, this problem is complicated by a lack of complete understanding of the physical, chemical, and biological processes governing the mass transfer of contaminants from the source to the moving fluid and their subsequent migration in heterogeneous formations. A topic that continues to be debated is the assessment of concentration levels and mass fluxes past a control plane (CP), and the role of source zone remediation (Sale and McWhorter, 2001; Rao and Jawitz, 2003; McWhorter and Sale, 2003; Jawitz et al., 2005; Falta et al., 2005a,b).

In modeling efforts, representation of dissolution and mass–transfer processes from discrete sources of NAPLs to the mobile water has been a challenge. The dissolution process occurs at the interface between water and NAPLs, and is frequently represented as a rate-limited process. Many studies (e.g. Miller et al., 1990; Powers et al., 1992, 1994a,b; Imhoff et al., 1994; Chrysikopoulos and Kim, 2000; Nambi and Powers, 2003) have tried to quantify this process. Based on laboratory data, numerical studies (e.g. Frind et al., 1999; Zhu and Sykes, 2000a,b) have adopted specific forms of the mass–transfer relationship to simulate field-scale behavior.

Despite the interest in dissolution kinetics, their role in field-scale transport of NAPLs remains unclear. Sale (1998) indicates that under field conditions, the kinetics of NAPL dissolution at the source is often relatively unimportant when compared to the processes that affect NAPL fate and transport as it moves from the source to the CP, thus justifying the use of the local equilibrium assumption (LEA) for mass transfer at the source. Several studies (Pinder and Abriola, 1986; Corapcioglu and Baehr, 1987; Kaluarachchi and Parker, 1990) have used LEA to describe both laboratory and field-scale contaminant behavior. Even when field studies have indicated concentrations lower than the solubility limit, these have been attributed to dilution effects (Feenstra and Cherry, 1988; Rao and Jawitz, 2003).

Numerous mass–transfer correlations of NAPL dissolution have been developed at the laboratory scale; however, the upscaling of these local models to the field-scale remains a challenge due to the heterogeneity of the geological and hydraulic properties of the aquifer, spatial distribution of NAPL pockets in the source zone, as well as the technical and financial difficulties in collecting extensive data for the field-scale models to be used at their full potential. Many of the existing models tend to be quite complicated in nature despite several simplifying assumptions. There exists a need for simple models, especially for use in preliminary evaluations to gain an understanding of the average behavior of the contaminant, or as a screening tool for regulatory purposes (Rao and Jawitz, 2003; Zhu and Sykes, 2004). In this regard, the stream tube modeling approach (Berglund and Cvetkovic, 1996; Berglund, 1997; Ginn, 2002; Jawitz et al., 2005) offers a simpler method that allows for a stochastic description of field-scale solute transport using various local models of choice. Stream tube models neglect transverse mixing among the tubes with the assumption that large-scale variability in velocities dominates field-