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Development and application of a screening model for evaluating bioenhanced dissolution in DNAPL source zones

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ABSTRACT

In-situ bioremediation, a widely applied treatment technology for source zones contaminated with dense non-aqueous phase liquids (DNAPLs), has proven economical and reasonably efficient for long-term management of contaminated sites. Successful application of this remedial technology, however, requires an understanding of the complex interaction of transport, mass transfer, and biotransformation processes. The bioenhancement factor, which represents the ratio of DNAPL mass transfer under microbially active conditions to that which would occur under abiotic conditions, is commonly used to quantify the effectiveness of a particular bioremediation remedy. To date, little research has been directed towards the development and validation of methods to predict bioenhancement factors under conditions representative of real sites. This work extends an existing, first-order, bioenhancement factor expression to systems with zero-order and Monod kinetics, representative of many source-zone scenarios. The utility of this model for predicting the bioenhancement factor for previously published laboratory and field experiments is evaluated. This evaluation demonstrates the applicability of these simple bioenhancement factors for preliminary experimental design and analysis, and for assessment of dissolution enhancement in ganglia-contaminated source zones. For ease of application, a set of nomographs is presented that graphically depicts the dependence of bioenhancement factor on physicochemical properties. Application of these nomographs is illustrated using data from a well-documented field site. Results suggest that this approach can successfully capture field-scale, as well as column-scale, behavior. Sensitivity analyses reveal that bioenhanced dissolution will critically depend on *in-situ* biomass concentrations.

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1. Introduction

In-situ bioremediation is an attractive strategy for the economical long-term management of subsurface contamination emanating from dense non-aqueous phase liquid (DNAPL) or low-permeability source zones (e.g., National Research Council, 2004; Scheutz et al., 2010; Stroo et al., 2012). Several studies (McGuire et al., 2006; Sleep et al., 2006; Lebron et al., 2007) have shown that stimulation of indigenous or augmented microorganisms near source zones enhances contaminant dissolution, reducing source longevity and, potentially, contaminant flux. Early efforts to quantify dissolution enhancements due to microbial activity focused on dissolution from fully saturated DNAPL pools (Seagren et al., 1993, 1994; Reitsma and Dai, 2001; Chu et al., 2003, 2004; Gupta and Seagren, 2005). However, source-zone characterization studies have highlighted the importance of quantifying dissolution from complex source zones comprised of both high-saturation pools and low-saturation ganglia (e.g., Lemke and Abriola,

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2006). Thus, there is a need to quantify potential dissolution enhancement from ganglia-contaminated source zone regions.

Enhanced dissolution due to microbial activity (i.e., *bioenhanced* dissolution) is generally defined as the ratio of contaminant mass flux eluting from a DNAPL-contaminated region when microbial activity is present to the contaminant mass flux in the eluate when no microbes are active (Carr et al., 2000; Cope and Hughes, 2001; Yang and McCarty, 2000, 2002; Adamson et al., 2004; Da Silva et al., 2006; Sleep et al., 2006; Amos et al., 2008, 2009; Schaefer et al., 2010). Experimental column results have demonstrated an average two- to six-fold enhancement in the rate of dissolution from residual DNAPL (Christ et al., 2005; Amos et al., 2008), with dissolution enhancement reaching as high as a factor of 20 relative to the abiotic case (e.g., Amos et al., 2009). Variability in the magnitude of bioenhanced dissolution has been attributed to factors that influence the rate of biotransformation such as low pH (e.g., Cope and Hughes, 2001; Adamson et al., 2004) and accumulation of toxic remediation by-products (e.g., Yu et al., 2005; Amos et al., 2007), as well as hydrologic factors such as insufficient contact time and nonuniform saturations (Glover et al., 2007; Amos et al., 2008, 2009). Although these column results provide much-needed insight into the factors controlling dissolution enhancement, they are not readily applicable to the prediction of dissolution enhancement under a wide variety of subsurface site conditions.

Efforts to predict dissolution enhancement due to microbial activity have generally assumed a simple geometry, with a fully saturated DNAPL pool located along the domain boundary. Seagren et al. (1994) were the first to employ a solution to the advection–dispersion–reaction equation (ADRE) in a two-dimensional domain with one-dimensional flow parallel to a DNAPL pool. This study modeled dissolution as a diffusion process away from the fully saturated DNAPL boundary. Using this simplified model, they determined a biotransformation rate threshold, above which dissolution enhancement will take place, and demonstrated that the enhancement scales linearly with biotransformation rate on a log–log plot (Seagren et al., 1994). Chu et al. (2003, 2004) employed a similar mathematical framework to investigate favorable conditions for bioenhanced dissolution in tetrachloroethene (PCE)-contaminated domains. They used their model to explore the influence of electron-donor limitations and bioclogging on microbial enhancements to dissolution and developed a simplified expression to quantify bioenhanced dissolution (Chu et al., 2003). This simplified expression was similar in form to the original expression developed by Seagren et al. (1994), and again assumed dissolution from a DNAPL pool. In a later work, Chu et al. (2004) extended their model to consider multiple pools placed along the domain boundaries to better simulate a more heterogeneous DNAPL-contaminated region. They showed that enhanced dissolution often had an upper bound, due to competition for an electron donor, the effect of toxic byproduct accumulation on dechlorination kinetics, and DNAPL configuration in the source zone (Chu et al., 2004). Follow-up experimental studies using a similar conceptual model (i.e., distinct DNAPL pool zones overlain by uncontaminated groundwater) have likewise demonstrated limitations in enhanced dissolution (Glover et al., 2007; Philips et al., 2011), although Glover et al. (2007) did observe dissolution enhancement factors as high as 13, depending on the sharpness of the interface separating the NAPL contaminated and uncontaminated zones.

Seagren et al. (1993) employed an analytical solution to the one-dimensional ADRE to quantify dissolution enhancements due to microbial activity in ganglia-dominated systems. By comparing solutions that neglected microbial degradation to solutions that included microbial degradation, they were able to predict dissolution enhancement due to microbial activity. Their formulation predicted an effective dissolution rate relative to the maximum rate of dissolution for the given column conditions rather than a bioenhanced dissolution factor. Christ and Abriola (2007), as part of a numerical modeling study of source zone bioremediation, reformulated the Seagren et al. (1993) approach in terms of a bioenhanced dissolution factor to provide a screening-level check on their numerical predictions. However, this approach was only applied to ganglia-dominated geometries with first-order biotransformation kinetics.

In this work, the bioenhanced dissolution factor presented in Christ and Abriola (2007), which is based on an assumption of first-order biotransformation kinetics, is extended to incorporate zero-order and Monod kinetics and used to quantify the expected level of microbially enhanced dissolution under a variety of physicochemical conditions (i.e., transport processes, interphase mass transfer kinetics, and biotransformation kinetics). The bioenhanced dissolution factor is then applied as a simple screening tool and its predictions are compared to published laboratory and field results to demonstrate its utility. Dimensionless contour plots are provided to facilitate application of the bioenhanced dissolution factor and to provide insight into process coupling. Insights are then provided to aid in the assessment of the potential for bioenhanced dissolution at source zones contaminated with DNAPL ganglia.

2. Mathematical model

Dissolution in a one-dimensional, semi-infinite, DNAPL ganglia-contaminated system can be modeled using a steady-state form of an ADRE (e.g., Seagren et al., 1993):

$$\phi S_a D\frac{d^2C}{dx^2}-\phi S_a v\frac{dC}{dx}+k_l\left(C_{eq}-C\right)-R=0 \tag{1}$$

where ϕ is the porosity [L^3/L^3], S_a is the aqueous-phase saturation [L^3/L^3], C is the contaminant concentration in the aqueous phase [M/L^3], D is the macroscale hydrodynamic dispersion coefficient [L^2/T], v is the pore water velocity [L/T], $\hat{K}_l$ is the lumped mass transfer coefficient [1/T], C_{eq} is the equilibrium concentration of the contaminant in the aqueous phase [M/L^3], and R is the biotransformation reaction term [$M/(L^3 \cdot T)$].

The assumption of steady-state bioenhancement processes is an approximation often applied in field remedies. After initial remedy implementation, there will likely be a period of acclimation before a quasi-steady state is reached, and long-term dissolution and/or by-product accumulation will cause further changes later. However, it is assumed that the screening-level approach described herein is appropriate during the extended quasi-steady state period that exists after an initial period of acclimation.