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**Predictions of Bioenhancement of
Nonaqueous Phase Liquid Ganglia Dissolution
Using First- and Zero-Order Biokinetic Models
By Eric A. Seagren^{1*}, and Jennifer G. Becker¹**

ABSTRACT:

The bioenhanced dissolution of nonaqueous phase (NAPL) liquid contaminants that occurs as a result of an increased concentration gradient is influenced by several factors, including the biokinetics. This is important because available data suggest that at typical NAPL source zone concentrations, descriptions of dissolution bioenhancement may require kinetic expressions ranging from first- to zero-order. In this work, an analytical model for the bioenhancement factor, E , is developed for NAPL ganglia dissolution with zero-order kinetics, and compared to a model for E with first-order kinetics. The models are analyzed and an illustrative example is provided to demonstrate the importance of using the correct biokinetics when estimating the potential magnitude of the bioenhancement of NAPL ganglia dissolution.

Keywords: Bioenhancement, NAPL pool, dissolution, biokinetics, analytical model

1. Introduction

Mass-transfer limited dissolution of nonaqueous phase liquid (NAPL) contaminants is commonly modeled with a single-resistance model with a linear driving force (e.g., (Miller et al., 1990; Powers et al., 1991; Sleep and Sykes, 1989)):

$$J = k_l (C_s - C) \quad (1)$$

in which: J = dissolution flux [$M_s T^{-1} L^{-2}$], k_l = mass transfer coefficient [LT^{-1}], C_s = aqueous solubility of the chemical [$M_s L^{-3}$], and C = average solute concentration at that point [$M_s L^{-3}$].

This dissolution flux may control contaminant bioavailability and limit *in situ* biodegradation rates (Ramaswami and Luthy, 1997). However, in some cases, NAPL biodegradation rates have been observed that are greater than the abiotic dissolution rate described by Eq. (1). As discussed by Seagren et al. (2002), several possible mechanisms have been postulated for these observations. One of these mechanisms of bioenhancement of NAPL dissolution, and the focus of this work, is the increase in the concentration gradient near the NAPL/water interface by decreasing C in Eq. (1) via *in situ* biodegradation. This mechanism has been studied theoretically for subsurface NAPL contamination in the form of ganglia (Seagren et al., 1993) and pools (Seagren et al., 1994), and demonstrated experimentally, (e.g., (Carr et al., 2000; Cope and Hughes, 2001; Seagren et al., 2002; Yang and McCarty, 2000; Yang and McCarty, 2002)).

As reviewed by Seagren et al. (2002), several factors can influence the degree of bioenhancement of NAPL dissolution that occurs as a result of an increased concentration gradient, including the aqueous-phase concentration near the NAPL source. The dissolved concentration in turn influences the biokinetics and, thus, the magnitude of the bioenhancement effect. For example, when aqueous-phase concentrations are relatively low, the biodegradation can be described by first-order kinetics, while at higher concentrations, zero-order kinetics are

appropriate in the absence of inhibitory effects. Available data suggest that at typical NAPL source zone concentrations, descriptions of dissolution bioenhancement may require kinetic models ranging from first- to zero-order for chlorinated ethene dense NAPLs (DNAPLs) (Nielsen and Keasling, 1999) and petroleum-product light NAPLs (LNAPLs) (Bekins et al., 1998), assuming that the NAPL constituent of interest is the limiting substrate.

Gupta and Seagren (2005) theoretically analyzed the impact of variable-order biodegradation kinetics on the magnitude of bioenhancement of NAPL pool dissolution. The goal of this paper is to extend that work and examine the impact of variable-order biokinetics on the bioenhancement of NAPL ganglia dissolution. In the material that follows, a mathematical model is developed for zero-order kinetics, and compared with a previously developed model for first-order kinetics. Each model is solved for the NAPL ganglia dissolution bioenhancement factor, E , which is the ratio of the ganglia dissolution mass flux with biodegradation to the mass flux without biodegradation. The analysis is performed using analytical models to provide an easily manipulated and intuitively interpretable tool for evaluating the impact of the biokinetics on the degree of bioenhancement of NAPL ganglia. An illustrative example is provided to demonstrate the importance of using the correct biokinetics to estimate the potential magnitude of the bioenhancement of NAPL dissolution.

2. Mathematical Model

2.1. Domain

The interactions of NAPL dissolution, biodegradation, and solute transport are complex; hence, this evaluation is performed using a very simple domain, a saturated, homogeneous, isotropic medium with one-dimensional flow in the x direction. The NAPL is present as residual

saturation of immobilized ganglia uniformly distributed throughout the flow regime. NAPL saturation is described assuming the continuum approach. This scenario is illustrated in Fig. 1.

2.2. Transport of Dissolved NAPL Components

For this analysis, the NAPL water solubility is assumed to be sufficiently low that the solute concentration does not affect the density of the contaminated water or its transport. Therefore, the transport of dissolved NAPL components in saturated, isotropic porous media can be described using the following form of the one-dimensional advection-dispersion-reaction (ADR) equation for a homogeneous medium with steady flow in the x direction:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - \frac{q_x}{nS_w} \frac{\partial C}{\partial x} - R \quad (2)$$

in which: t = time [T], D_x = longitudinal dispersion coefficient [L^2T^{-1}], x = distance in direction of flow [L], q_x = specific discharge [LT^{-1}], n = porosity, S_w = water saturation, and R = source/sink term [$M_sL^{-3}T^{-1}$]. The water saturation accounts for the decrease in the pore volume available for water flow due to NAPL ganglia. The two reaction processes investigated here are NAPL dissolution, R_D , and biodegradation of dissolved NAPL components, R_B .

2.3. Dissolution

To incorporate dissolution as a source term, Eq. 1 is modified according to Miller et al. (1990):

$$R_D = J \frac{A_{na}}{nS_w V} = J \frac{a_{na}}{nS_w} = \frac{k_l a_{na}}{nS_w} (C_s - C) = K_l (C_s - C) \quad (3)$$

in which: A_{na} [L^2] = the interfacial area between the NAPL and aqueous phases, V [L^3] = the total system volume, $a_{na} = A_{na}/V$ = specific NAPL/aqueous phase interfacial surface area [L^{-1}], and $K_l = a_{na}k_l/nS_w$ = the lumped mass-transfer-rate coefficient [T^{-1}].

Use of the lumped mass transfer rate coefficient, K_l , constrains the resulting model to conditions in which a_{na} and S_w are not changing over time (Powers et al., 1991); however, it is generally K_l , rather than k_l , that can be estimated from experimental data. Although quantification of the actual interfacial area is important for obtaining k_l , the heterogeneous nature of the porous media, the time dependence of the interfacial area, and the varying accessibility of different portions of the NAPL ganglia interfacial area to the flowing aqueous phase make estimation of k_l challenging (Miller et al., 1990).

Incorporation of Eq. 3 into the ADR equation (Eq. 2) gives:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - \frac{q_x}{nS_w} \frac{\partial C}{\partial x} + K_l(C_s - C) \quad (4)$$

2.4. Biodegradation

Self-inhibition of the microbes mediating transformation of the dissolved NAPL could limit biodegradation and bioenhancement if inhibitory levels are observed (e.g., (Seagren et al., 2002)); however, in this work it is assumed that the aqueous contaminant concentrations near the NAPL source zone are non-inhibitory. Thus, the differential equations describing biodegradation of a single limiting substrate, e.g., a dissolved NAPL contaminant used as an electron donor or acceptor (R_B), and the linked microbial growth ($R_{biomass}$) are described following Monod kinetics (Monod, 1949):

$$R_B = \frac{dC}{dt} = - \left(\frac{\mu_m X}{Y} \right) \left(\frac{C}{K + C} \right) \quad (5)$$

and

$$R_{biomass} = \frac{dX}{dt} = (\mu_m X) \left(\frac{C}{K + C} \right) \quad (6)$$

where μ_m = maximum specific growth rate (T^{-1}), Y = biomass yield ($M_x M_s^{-1}$), X = biomass concentration ($M_x L^{-3}$), and K = half-saturation constant ($M_s L^{-3}$).

The biomass concentration X is assumed to be constant in time, as has been observed in aquifer sediments, e.g., (Godsy et al., 1992). Consequently, Eq. 6 can be replaced with a constant, and μ_m , X , and Y can be grouped into a new constant, called the substrate utilization rate, $v_m = \mu_m X / Y$ ($M_s L^{-3} T^{-1}$) in Eq. 5. Substituting v_m in Eq. 5 yields (Simkins and Alexander, 1984):

$$R_B = \frac{dC}{dt} = -v_m \left(\frac{C}{K + C} \right) \quad (7)$$

This kinetic model is nonlinear and cannot be solved analytically; however, for low substrate concentrations ($C \ll K$), the Monod model reduces to first-order kinetics with respect to C :

$$R_B = \frac{dC}{dt} = - \left(\frac{v_m}{K} \right) (C) = -K_{B1} C \quad (8)$$

where $K_{B1} = v_m / K$ = the lumped, first-order biodegradation kinetic coefficient (T^{-1}). For high substrate concentrations (i.e., $C \gg K$), Eq. 7 reduces to zero-order kinetics:

$$R_B = -v_m = -K_{B0} \quad (9)$$

For this special case, we renamed v_m as the lumped, zero-order biodegradation kinetic coefficient, K_{B0} ($M_s L^{-3} T^{-1}$).

3. Model Analysis

3.1. Abiotic Conditions

To assess the NAPL dissolution rate under abiotic conditions, it is necessary to solve the governing equation for advection-dispersion and dissolution, Eq. 4. This solution is simplified by assuming quasi-steady-state conditions, which are valid once a steady-state concentration profile has developed in the contaminated region, but before dissolution causes changes in blob size and NAPL saturation that appreciably alter a_{na} or S_w . This assumption was used previously by Powers et al. (1991) in their sensitivity analysis of NAPL blob dissolution. Furthermore, column studies of residual NAPL dissolution have experimentally demonstrated that effluent solute concentrations initially are approximately constant for a number of pore volumes (e.g., (Geller and Hunt, 1993; Imhoff et al., 1994)).

At steady-state, Eq. 4 can be nondimensionalized by defining $x^* = x/L$ (where L = length of the contaminated region through which groundwater is flowing), $C^* = C/C_s$, and the dimensionless parameters Pe and St (Table 1). In nondimensionalized steady-state form, Eq. 4 is:

$$0 = \frac{1}{Pe} \frac{d^2 C^*}{dx^{*2}} - \frac{dC^*}{dx^*} - StC^* + St \quad (10)$$

Solution of Eq. 10 requires specification of two boundary conditions. Assuming the influent stream is uncontaminated, a third-type boundary condition is applied at the inlet boundary ($x = 0$) to ensure conservation of flux,

$$\left(-\frac{1}{Pe} \frac{dC^*}{dx^*} + C^* \right) x^* = 0 \quad (11)$$

To simplify the mathematical analyses, the column domain is assumed to be semi-infinite and a second-type boundary condition is applied at the outlet boundary,

$$\frac{dC^*(\infty)}{dx^*} = 0 \quad (12)$$

Use of the boundary condition in Eq. 12 and the semi-infinite domain approximation has previously been discussed (Nauman and Buffham, 1983; van Genuchten and Parker, 1984). Assuming a semi-infinite domain at the outlet may result in some errors when the analytical solution is used to determine effluent curves from finite columns (van Genuchten and Alves, 1982). Specifically, the semi-infinite solution for Eq. 10 predicts higher solute concentrations near the end of the column when compared to the solution obtained assuming a finite domain ($dC^*/dx^* = 0$), with the difference decreasing as Pe is increased.

As previously presented by Seagren et al. (1993), with the boundary conditions in Eqs. 11 and 12, the analytical solution to Eq. 10 is (van Genuchten and Alves, 1982):

$$C^*(x^*) = 1 - \left(\frac{2}{1 + \sqrt{1 + \frac{4St}{Pe}}} \right) e^{\left(\left(\frac{x^*Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4St}{Pe}} \right) \right)} \quad (13)$$

At steady-state, Eq. 4 can be rearranged and converted to mass rate by integrating both sides of the equation over the volume of the reactor (Seagren et al., 1993):

$$A_X \int_0^L K_L (C_s - C) dx = A_X \int_0^L d \left(v_x C - D_X \frac{dC}{dx} \right) \quad (14)$$

where A_X = domain cross sectional area [L^2]. The right hand side of Eq. 14 is equal to the mass rate out of the domain at $x = L$ minus the mass rate into the domain at $x = 0$. The left hand side is equal to the total mass rate increase in the system due to dissolution and is termed the dissolution

rate, r_d [$M_s T^{-1}$]. Eq. 14 can be nondimensionalized using the previously defined dimensionless parameters to give:

$$St \int_0^1 (1 - C^*) dx^* = \int_0^1 d \left(C^* - \frac{1}{Pe} \frac{dC^*}{dx^*} \right) \quad (15)$$

The left side of Eq. 15 is the dimensionless dissolution rate, r_d' :

$$r_d' = St \int_0^1 (1 - C^*) dx^* \quad (16)$$

Replacing $C^*(x^*)$ in Eq. 16 with the previously developed steady-state relationship in Eq. 13 and integrating yield (Seagren et al., 1993):

$$r_d' = -St \frac{\left(\frac{2}{1 + \sqrt{1 + \frac{4St}{Pe}}} \right)}{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4St}{Pe}} \right) \right)} \left(1 - e^{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4St}{Pe}} \right) \right)} \right) \quad (17)$$

Note that r_d' can be converted to the dimensional dissolution rate, r_d , by multiplying r_d' by $A_x v_x C_s$.

3.2. Biotic conditions: Zero-order kinetics

Adding the lumped zero-order biodegradation term (Eq. 9) to Eq. 4 gives the following equation for a zero-order reaction:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - \frac{q_x}{nS_w} \frac{\partial C}{\partial x} + K_l (C_s - C) - K_{B0} \quad (18)$$

At steady-state, Eq. 18 is rearranged to give the following:

$$0 = D_x \frac{d^2 C}{dx^2} - v_x \frac{dC}{dx} - K_l C + K_l C_s - K_{B0} \quad (19)$$

Eq. 19 is nondimensionalized using x^* , C^* , and three nondimensional coefficients: Pe , St , and $Da_{2,0}$ (Table 1). Another dimensionless parameter that does not appear in Eq. 19, but is useful in interpreting model predictions is $Da_{3,0}$, which is also defined in Table 1. The nondimensional form of Eq. 19 is:

$$0 = \frac{1}{Pe} \frac{d^2 C^*}{dx^{*2}} - \frac{dC^*}{dx^*} - (St C^*) + (St - Da_{2,0}) \quad (20)$$

The analytical solution to Eq. 20, with a third-type inlet boundary condition (Eq. 11) and a semi-infinite domain outlet boundary condition (Eq. 12), is (van Genuchten and Alves, 1982):

$$C^*(x^*) = \left(1 - \frac{Da_{2,0}}{St}\right) + \left(\frac{Da_{2,0}}{St} - 1\right) \left(\frac{2}{1 + \sqrt{1 + \frac{4(St)}{Pe}}} \right) e^{\left(\left(\frac{x^* Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4(St)}{Pe}} \right) \right)} \quad (21)$$

This solution for $C^*(x^*)$ equals zero when $Da_{2,0}$ becomes equal to St . Mathematically, there is no source term and only the sink term (Eq. 9) is relevant when $Da_{2,0} = St$. As $Da_{2,0}$ becomes greater than St , the sink term increases and $C^*(x^*)$ becomes negative. Thus, for all $Da_{2,0} \geq St$, C^* is set equal to zero for all x^* .

The normalized dissolution rate is defined using the same approach applied for the abiotic case. Eq. 19 can be rearranged and converted to mass rate by integrating both sides of the equation over the volume of the reactor:

$$A_x \int_0^L K_l (C_S - C) dx = A_x \int_0^L \left(v_x C - D_x \frac{dC}{dx} \right) dx + A_x \int_0^L K_{B0} dx \quad (22)$$

The right hand side of Eq. 22 is equal to the mass rate out of the domain at $x = L$ minus the mass rate into the domain at $x = 0$ plus the total mass rate decrease in the system due to biodegradation. The left hand side of Eq. 22 is equal to the total mass rate increase in the system

due to dissolution and, as before, is termed the dissolution rate, r_d [$M_s T^{-1}$]. Eq. 22 can be nondimensionalized using the previously defined dimensionless parameters to give,

$$St \int_0^1 (1 - C^*) dx^* = \int_0^1 d \left(C^* - \frac{1}{Pe} \frac{dC^*}{dx^*} \right) + Da_{2,0} \int_0^1 dx^* \quad (23)$$

The left hand side of Eq. 23 is the previously defined dimensionless dissolution rate r'_d (Eq. 16).

Replacing $C^*(x^*)$ in Eq. 16 with the steady-state relationship in Eq. 21 and integrating gives,

$$r'_d = St \left(\frac{Da_{2,0}}{St} \right) + \frac{\left(\frac{Da_{2,0}}{St} - 1 \right) \left(\frac{2}{1 + \sqrt{1 + \frac{4St}{Pe}}} \right)}{\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4St}{Pe}} \right)} \left(1 - e^{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4St}{Pe}} \right) \right)} \right) \quad (24)$$

Again, r'_d can be converted to r_d by multiplying r'_d by $A_x v_x C_s$. As noted above, when

$Da_{2,0} \geq St$, C^* is set equal to zero for all x^* . The maximum dimensionless dissolution rate

occurs when $C^*(0 \leq x^* \leq 1) = 0$ and is defined as,

$$r'_{d \max} = St \int_0^1 (1 - 0) dx^* = St \quad (25)$$

This is reflected in Eq. 24: when $Da_{2,0} = St$, $r'_d = St$. Therefore, for all $Da_{2,0} \geq St$, r'_d is set

equal to $St = r'_{d \max}$. Multiplication of r'_d and $r'_{d \max}$ by $A_x v_x C_s$ yields r_d and $r_{d \max}$, respec-

tively.

The ratio of the dissolution rate with zero-order biodegradation, $r_{d'abiotic}$, to the dissolution rate without biodegradation, $r_{d'abiotic}$, provides the value of E , the bioenhancement factor (Seagren et al. 1994). Therefore, taking the ratio of Eq. (24) to Eq. (17) gives,

$$E = \frac{r_{d' biotic}}{r_{d' abiotic}} = \left(\frac{-Da_{2,0}}{St \frac{\left(\frac{2}{\left(1 + \sqrt{1 + \left(\frac{4St}{Pe} \right)} \right)} \right)}{\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \left(\frac{4St}{Pe} \right)} \right)} \left(1 - e^{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \left(\frac{4St}{Pe} \right)} \right)} \right)} \right)} \right) - \left(\frac{Da_{2,0}}{St} - 1 \right) \quad (26)$$

Example plots of E for zero-order kinetics as a function of $Da_{2,0}$, with $Pe = 0.01, 1.0$, and 100 , are provided in Figure 2a, 2b, and 2c, respectively. These Pe values represent conditions where dispersion is dominant over advection (Figure 2a), dispersion and advection are equivalent in magnitude (Figure 2b), and advection is dominant over dispersion (Figure 2c). Advection is generally expected to be dominant over dispersion, and the trends in Figure 2 are very similar for $Pe \geq 1.0$. For each value of Pe in Figure 2, plots are provided for $St = 0.01, 1$, and 100 . In the absence of biodegradation, these St values represent three different mass-transfer regimes: extreme mass-transfer limitation ($C^*(x^*=1) \rightarrow 0$), intermediate mass-transfer limitation, and local equilibrium ($C^*(x^*=1)=1$), respectively (Seagren et al., 1993).

Figure 2 can be used to delineate several general trends for dissolution bioenhancement with the zero-order kinetics case. At one extreme, when $St = 0.01$ (Figure 2a-c) the advection rate is

so large compared to the mass transfer rate that the system is highly mass transfer-limited, and the dissolution rate is at its maximum because the advection is already keeping the solute concentration low. Under these conditions, biodegradation can have an effect on $C^*(x^*)$ and E at low $Da_{2,0}$ ($\geq 10^{-4}$), but the dissolved concentration in the domain is already so low from advective losses that the overall impact of biodegradation is negligible ($E \leq 1.01$) when $Pe \geq 1.0$, and relatively small ($E = 1.6$) when $Pe = 0.01$. Under the latter condition, although the advection rate is large compared to the mass transfer rate, advection is small relative to dispersion, and biodegradation can have a small effect on $C^*(x^*)$. Therefore, if the system is highly mass-transfer limited, biodegradation has little or no effect on the dissolution rate.

At the other extreme, when $St = 100$ (Figure 2a-c), the mass transfer rate is greater than the advection rate, and biodegradation has little effect on $C^*(x^*)$ and E for $Da_{2,0} < 10^{-2}$. As $Da_{2,0}$ becomes greater than 10^{-2} , the biodegradation rate increases and eventually becomes greater than the advection rate. Under these conditions, $C^*(x^*)$ decreases and the system goes from equilibrium to nonequilibrium. The biodegradation effect increases as $Da_{2,0}$ is increased further, until the maximum bioenhancement possible is reached when $Da_{2,0} = St$, and C^* is set equal to zero for all x^* , as discussed above. The largest impact of biodegradation ($E = 159$) occurs when $Pe = 0.01$, and the competing solute sink advection is small relative to dispersion, with a somewhat smaller bioenhancement effect ($E = 100$) when $Pe \geq 1.0$. The trends at the intermediate value of $St = 1.0$ are similar (Figure 2a-c), and as the magnitude of $Da_{2,0}$ increases to greater than 10^{-2} , the effects of biodegradation on $C^*(x^*)$ and E become observable, plateauing at values intermediate between those at $St = 0.01$ and 100 .

3.3. Biotic Conditions: First-order kinetics

Adding the lumped first-order biodegradation term (Eq. 8) to Eq. 4 gives the following equation for a first-order reaction:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - \frac{q_x}{nS_w} \frac{\partial C}{\partial x} + K_l (C_s - C) - K_{BI} C \quad (27)$$

At steady-state, Eq. 27 is rearranged to give the following:

$$0 = D_x \frac{d^2 C}{dx^2} - v_x \frac{dC}{dx} - (K_l + K_{BI})C + K_l C_s \quad (28)$$

Eq. 28 is nondimensionalized using the same approach as for Eq. 19 and becomes:

$$0 = \frac{1}{Pe} \frac{d^2 C^*}{dx^{*2}} - \frac{dC^*}{dx^*} - (St + Da_{2,l})C^* + St \quad (29)$$

The analytical solution to Eq. 29, with a third-type inlet boundary condition (Eq. 11) and a semi-infinite domain outlet boundary condition (Eq. 12) was previously presented by Seagren et al. (1993). It was integrated following the same approach as outlined above for zero order kinetics to obtain the previously defined dimensionless dissolution rate r_d' :

$$r_d' = St \left(1 - \left(\frac{St}{w} \right) - \frac{\left(\frac{St}{w} \right) \left(\frac{2}{1 + \sqrt{1 + \frac{4w}{Pe}}} \right)}{\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4w}{Pe}} \right)} \left(1 - e^{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \frac{4w}{Pe}} \right) \right)} \right) \right) \quad (30)$$

where $w = St + Da_{2,l}$. In this case, r_d' approaches $St = r_{d\max}'$ when $w \geq 100St$. Again, r_d' can be converted to r_d by multiplying r_d' by $A_x v_x C_s$.

Christ and Abriola (2007) obtained the bioenhancement factor, E , for first-order biokinetics case by dividing Eq. 30, by Eq. (17) to obtain the relationship,

$$E = \frac{r_{d \text{ biotic}}}{r_{d \text{ abiotic}}} = \frac{St(w)^2 - St^2 \left(w - \left(1 - e^{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \left(\frac{4w}{Pe} \right)} \right)} \right) \right)}{w^2 \left(1 - e^{\left(\left(\frac{Pe}{2} \right) \left(1 - \sqrt{1 + \left(\frac{4St}{Pe} \right)} \right)} \right)} \right)} \quad (31)$$

Example plots of E for first-order kinetics as a function of $Da_{2,0}$, with $Pe = 0.01, 1.0$, and 100 , are presented in Figures 3a, 3b, and 3c, respectively, with data provided for $St = 0.01, 1$, and 100 , for each value of Pe in Figure 3. The Pe and St values were selected for the reasons noted above (Seagren et al., 1993).

Several trends for bioenhanced dissolution with first-order biokinetics can be discerned from Figure 3. Similar to the zero-order case, when $St = 0.01$ (Figure 3a-c), the advection rate is so large compared to the mass-transfer rate that the system is very mass-transfer limited. The dissolution rate is at its maximum under these conditions because advection is already keeping the solute concentration (C) low. Under these conditions, biodegradation can have an effect on $C^*(x^*)$ and E at low $Da_{2,1}$ ($\geq 10^{-2}$), but the concentration is already so low from advective losses that the impact of biodegradation is negligible ($E \leq 1.01$) when $Pe \geq 1.0$, and relatively small ($E = 1.6$) when $Pe = 0.01$. Therefore, if the system is very mass-transfer limited, biodegradation has little or effect, no matter how fast the first-order rate.

At the other extreme, when $St = 100$ (Figure 3a-c), biodegradation has little effect on $C^*(x^*)$ and E for $Da_{2,1} < 10^{-2}$. However, as $Da_{2,1}$ becomes greater than 10^{-2} , the biodegradation rate becomes faster than the advection rate. Under these conditions, $C^*(x^*)$ decreases and the system

goes from equilibrium to nonequilibrium. The biodegradation effect increases as $Da_{2,I}$ is increased further, until the maximum bioenhancement is reached at $Da_{2,I} \geq 10^3$. As in the zero-order case, the largest impact of biodegradation ($E = 159$) occurs when $Pe = 0.01$, in which case the competing advective solute sink is small relative to dispersion, with $E = 100$ when $Pe \geq 1.0$. A similar pattern is observed at the intermediate value of $St = 1.0$ (Figure 3a-c). As $Da_{2,I}$ increases to greater than 10^{-2} , the effects of biodegradation on $C^*(x^*)$ and E can be seen, with a maximum bioenhancement factor, E , between the values observed at $St = 0.01$ and 100.

3.4. Comparison of Zero- and First-order kinetics

As demonstrated by the data in Figures 2 and 3, the predictions for E using the zero-order model and the first-order model are equivalent for very small and very large values of $Da_{2,I}$: at the lowest $Da_{2,I}$ values, the biodegradation sink is too small relative to advection to influence the dissolved concentration; and at the highest $Da_{2,I}$ values, the biodegradation sink has maximized dissolution flux by driving the dissolved concentration to zero throughout the domain. However, at intermediate values the bioenhancement factor is quite different for the two models, and inappropriate use of either kinetic model results in large errors in the estimate of the bioenhancement effect. This is not surprising given that for the zero-order model the biodegradation sink term is of constant value (K_{B0}), while in the first-order model it is a function of the K_{B1} value and the dissolved substrate concentration. For this reason, it takes a much larger value of $Da_{2,I}$ to asymptotically approach the maximum bioenhancement with the first-order model than the zero-order model.

Damköhler numbers $Da_{3,I}$ and $Da_{3,0}$ are useful tools for interpreting the differences between the zero-order and first-order curves at the intermediate values of E . For example, for

the zero-order case, when $Da_{2,0} = St$, and $Da_{3,0} = 1$, E is at its maximum because $C^* = 0$ for all x^* , and dissolution cannot be enhanced further. However, in the first-order case, when $Da_{2,1} = St$, and $Da_{3,1} = 1$, E is at an intermediate point between the minimum and maximum values. For example, at $St = 100$ and $Pe = 1.0$ (Figure 3b), there is an inflection point in the E versus $Da_{2,1}$ curve when $Da_{2,1} = St$, and $Da_{3,1} = 1$. For $Da_{3,1} \ll 1$ (i.e., $Da_{2,1} \ll St$), the system is in the biodegradation-limited regime because the maximum biodegradation rate is much slower than the mass-transfer rate. However, when $Da_{3,1} \gg 1$ (i.e., $Da_{2,1} \gg St$), the system is in a dissolution-limited regime because the maximum biodegradation rate is much greater than the maximum mass-transfer rate. When $Da_{3,1}$ becomes greater than 10^4 , or in this case $Da_{2,1} \geq 10^6$, the dissolution rate is at its maximum because $C^* = 0$ for all x^* .

4. Model Application

Application of the model results for calculating the bioenhancement factor with zero- and first-order reactions is illustrated using the experimental column results of Yang and McCarty (2002), which were obtained under conditions similar to those modeled in this study. The initial tetrachloroethene (PCE) DNAPL saturation (S_{No}) was 2%. Four columns were operated: a no substrate control column, and three columns with different electron donor substrates (pentanol, calcium oleate, and olive oil).

The average pore-water velocity, v_x , for this example (Table 2) was estimated by Becker and Seagren (2009) for the experimental conditions of Yang and McCarty (2002), the length of the reactor was taken from Yang and McCarty (2002), and the parameter values needed for estimating the hydrodynamic dispersion, D_x , were assumed as listed in Table 2 (Becker and

Seagren, 2009). These values gave a column $Pe = 87$, indicating the dispersion is rate-limiting compared to advection.

The lumped mass-transfer coefficient, $K_{l,PCE}$, was estimated using the transient mass-transfer coefficient correlation from Powers et al. (1994):

$$Sh' = \frac{K_{l,i} d_{50}^2}{D_0} = 4.13 (Re')^{0.598} \delta^{0.673} U_i^{0.369} \left(\frac{\theta_n}{\theta_{n_0}} \right)^{\beta_4} \quad (32)$$

where Sh' = modified Sherwood number = (mass-transfer rate/diffusion rate), d_{50} = median grain diameter [L], D_0 = aqueous diffusion coefficient [$L^2 T^{-1}$], Re' = Reynolds number =

$v_x \rho_w d_{50} / \mu_w$, ρ_w = water density [$M L^{-3}$], μ_w = water dynamic viscosity [$M L^{-2} T^{-1}$],

$\delta = d_{50} / d_M$ = normalized grain size, d_M = diameter of a "medium" sand grain [L], U_i =

uniformity index = d_{60} / d_{10} ; d_{60} = soil particle size for which 60% of the material by weight is

smaller than that size, d_{10} = soil particle size for which 10% of the material by weight is smaller

than that size, $\theta_n = nS_n$ = volumetric fraction of NAPL in the system, $\theta_{n_0} = nS_{n_0}$ = initial

volumetric fraction of NAPL in the system, and $\beta_4 = 0.518 + 0.114\delta + 0.10U_i$. For this work,

we assumed $d_{50} = 0.08$ cm, and $U_i = 2.42$, and the water and PCE properties listed in Table 2.

Using the estimated value for $K_{l,PCE}$ and the column length and average pore water velocity

(Table 2), St was estimated to equal 80. This value suggests that the dissolution rate is fast

compared to the rate of advection and dispersion of PCE in the column, and is consistent with

Yang and McCarty's (2002) observation that the effluent dissolved PCE concentration

approached the equilibrium concentration in the steady-state control reactor, and during the lag-

period in the electron-donor supplied columns.

The $Da_{2,I}$ and $Da_{2,0}$ values were calculated using the parameters described above, along with the PCE biodegradation kinetics of Haston and McCarty (1999) (Table 2), and assuming an

initial biomass concentration (X_0) of 10 mg VSS/L, based on the inoculum concentration pumped into the columns. Dissolved PCE concentrations in all of the columns were on the order of 700 μ M or greater. Based on this and $K = 0.11$ μ M, the kinetics are expected to be zero-order. The corresponding value of $Da_{2,0}$ is estimated to equal 3.1. Using the estimated values for Pe , St , and $Da_{2,0}$ in Eq. (26), the bioenhancement factor is estimated to equal 4.1. This is very close to the actual dissolution bioenhancement of approximately 3 that was observed in the experiments. Of course, the estimated value of $Da_{2,0}$ and E are dependent on the values of the system parameters that have been assumed. For example, it is likely that the biomass concentration increased in the columns by the time bioenhancement occurred, and because the zero-order prediction for E in this example is at the lower end of the rising portion of the curve (e.g., see Figure 2c), an increase in X will increase the value of $Da_{2,0}$ and E . Thus, if $X = 50$ mg VSS/L, $Da_{2,0}$ is estimated to equal 15.5, and $E = 16.3$. The latter is about 5 times greater than the experimental value, but still a reasonable first estimate, given all of the assumptions made.

In comparison, if first-order kinetics had mistakenly been assumed, as is often done without verification (Bekins et al., 1998), the $Da_{2,1}$ value calculated is 2,525, which, when used with the estimated values for Pe and $Da_{2,1}$ in Eq. (31), results in $E = 77.5$. This estimated bioenhancement based on first-order kinetics is approximately 26 times higher than the effect that was experimentally observed. In this case, the first-order prediction for E is in the region after the curve has plateaued (e.g., see Figure 3c), and the estimate for E is essentially the same (≈ 80) for any biomass concentration > 10 mg/L.

These example calculations illustrate the large errors that can be introduced in the prediction of the bioenhancement factor, E , through inappropriate application of the first- or zero-order approximation. In this case, as expected given the hyperbolic form of the Monod equation, when

dissolved concentrations of the limiting substrate are sufficiently high that the zero-order solution is the correct approximation for the given kinetic parameters (i.e., $C \gg K$), misapplication of the first-order solution for E results in erroneously high values of R_b (Figure 4) and, thus, E . In the above example, bioenhancement was overestimated by a factor of about 25. Conversely, if the first-order approximation is correct ($C \ll K$), the solution using the zero-order approximation over predicts R_b and the bioenhancement effect (Figure 4).

This work completes the development of analytical solutions for bioenhancement factor calculations for first- and zero-order kinetics for NAPL ganglia and pool source zones in simplified domains. The solution for NAPL ganglia source zones with zero-order kinetics is presented in this paper, and the corresponding solution for first-order kinetics is presented in Christ and Abriola (2007) based on the work of Seagren et al. (1993). Solutions for NAPL pool source zones for first- and zero-order kinetics are presented in Seagren et al. (1994), and Gupta and Seagren (2005) and Chu et al. (2003), respectively. Although these solutions are for simplified domains, they provide useful tools for understanding and estimating the potential for bioenhancement under different conditions.

5. Summary and Conclusions

Bioenhancement of NAPL dissolution is impacted by many parameters, including the aqueous-phase concentration near the NAPL source, which in turn influences the biokinetic modeling approach that is appropriate. For example, in the absence of inhibitory effects, when aqueous-phase concentrations are relatively low, the biodegradation can be described by first-order kinetics, while at higher concentrations zero-order kinetics are appropriate. Available data for NAPL source zones, suggest that dissolution bioenhancement may require kinetic models

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4 ranging from first- to zero-order, assuming that the NAPL constituent of interest is the limiting
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6 substrate. Analytical equations describing the degree of bioenhancement, or bioenhancement
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8 factor, E , with NAPL in the form of ganglia, have previously been developed for first-order
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10 kinetics. In this work, a comparable equation was developed for zero-order kinetics. These
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12 analytical models provide easily manipulated and intuitively interpretable tools for evaluating the
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14 impact of the biokinetics on the degree of bioenhancement of NAPL ganglia. An illustrative
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16 example using these analytical solutions for E demonstrates the large errors that can be produced
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18 through inappropriate application of the first- or zero-order approximation.
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Table 1

Definitions of nondimensional coefficients Pe , St , $Da_{2,1}$, $Da_{2,0}$, $Da_{3,1}$, and $Da_{3,0}$, following the notation of Seagren et al. (1993; 1999).

$Pe = \text{Peclet number} = \left(\frac{\text{advection rate}}{\text{dispersion rate}} \right) = \frac{q_x L}{D_x n S_w} = \frac{v_x L}{D_x}$
$St = \text{Stanton number} = \left(\frac{\text{mass-transfer rate}}{\text{advection rate}} \right) = \frac{k_l a_{na} L}{q_x} = \frac{K_l L}{v_x}$
$Da_{2,1} = \text{First-order Damköhler number 2} = \left(\frac{\text{biodegradation rate}}{\text{advection rate}} \right) = \frac{K_{B1} L}{v_x}$
$Da_{2,0} = \text{Zero-order Damköhler number 2} = \left(\frac{\text{biodegradation rate}}{\text{advection rate}} \right) = \frac{K_{B0} L}{C_s v_x}$
$Da_{3,1} = \text{First-order Damköhler number 3} = \left(\frac{\text{biodegradation rate}}{\text{mass-transfer rate}} \right) = \frac{K_{B1}}{K_l}$
$Da_{3,0} = \text{Zero-order Damköhler number 3} = \left(\frac{\text{biodegradation rate}}{\text{mass-transfer rate}} \right) = \frac{K_{B0}}{C_s K_l}$

Note: v_x = average pore water velocity = $q_x / n S_w$.

$D_x = \alpha_x v_x + \tau D_0$, where α_x = longitudinal dispersivity [L], τ = tortuosity factor, and D_0 = aqueous diffusion coefficient [$L^2 T^{-1}$].

Table 2

Parameter values used for illustrative example.

Parameter	Value	Reference
Column Properties		
Average pore water velocity, v_x	0.0009 m/h	(Becker and Seagren, 2009)
Porosity, n	0.30	Assumed
Dispersivity, α_x	0.11 cm	Assumed
Tortuosity factor, τ	0.67	Assumed
Column length, L	0.30 m	(Yang and McCarty, 2002)
Water Properties (at 25°C)		
Dynamic viscosity, μ_w	0.890×10^{-3} N·s/m ²	(Metcalf & Eddy Inc., 1991)
Density, ρ_w	997.0 kg/m ³	(Metcalf & Eddy Inc., 1991)
PCE Properties		
Initial PCE saturation, S_{n0}	0.02	(Yang and McCarty, 2002)
Aqueous diffusion coefficient, D_0	9.0×10^{-6} cm ² /s	(Becker and Seagren, 2009)
Solubility, C_s	150 mg/L	(Verschueren, 1983)
Biokinetic Properties		
Maximum specific substrate utilization rate, $q_{\max} = \mu_m/Y$	2.0 $\mu\text{mol/mg VSS}\cdot\text{d}$	(Haston and McCarty, 1999)
Half-saturation constant, K	0.11 $\mu\text{mol/L}$	(Haston and McCarty, 1999)

FIGURES

Figure 1. One-dimensional domain for development of the mathematical model. Reprinted with permission from Becker, J.G., and E.A. Seagren. 2009. "Modeling the effects of microbial competition and hydrodynamics on the dissolution and detoxification of dense nonaqueous phase liquid contaminants." *Environmental Science & Technology*, 43:870-877. Copyright (2009) American Chemical Society.

Figure 2. An example plot of the bioenhancement factor, E for zero-order kinetics as a function of the zero-order Damköhler No. 2 ($Da_{2,0} = K_{B0}L/C_s v_x$), with $St = 0.01, 1$, and 100 , and: (a) $Pe = 0.01$, (b), $Pe = 1$, and (c) $Pe = 100$.

Figure 3. An example plot of the bioenhancement factor, E for first-order kinetics as a function of the first-order Damköhler No. 2 ($Da_{2,1} = K_{B1}L/v_x$), with $St = 0.01, 1$, and 100 , and: (a) $Pe = 0.01$, (b), $Pe = 1$, and (c) $Pe = 100$.

Figure 4. Conceptual depiction of how misapplication of first- or zero-order approximations of the Monod kinetic model leads to overestimation of bioenhancement effects due to the impacts on the calculated rate of biodegradation (R_B). Calculation of R_B using the full Monod model is given by Eq. 5. The first- and zero-order approximations of R_B are given by Eqs. 8 and 9, respectively.

Figure 1

Figure 2

Figure 3

Figure 4