

MODELING BIOLOGICALLY REACTIVE TRANSPORT IN POROUS MEDIA

T.P. Clement, Brian S. Hooker, and Rodney S. Skeen
Pacific Northwest Laboratory
Richland, WA 99352
(509)-373-0998

ABSTRACT

A one-dimensional biofilm-based reactive transport model is developed to simulate biologically mediated substrate metabolism and contaminant destruction in saturated porous media. The resulting equations are solved by a finite-difference based, three-level, operator-split approach. The numerical solution procedure is stable, easy-to-code, and computationally efficient. As an example problem, biological denitrification and fortuitous CT destruction processes in one-dimensional porous media is studied. The simulation results of the example problem show that the present model can be successfully used to predict biological processes and nutrient/contaminant transport in saturated porous media.

I. INTRODUCTION

Remediating contaminated aquifers by engineering biological processes has been an attractive option in the past decade. However, methods to design and control these processes *in-situ* are limited by a lack of fundamental understanding of the interactions between microorganisms and subsurface transport. One way to develop this knowledge is to analyze the problem by using computer models. To date, several researchers have studied biological processes in porous media using various types of numerical models.¹⁻³ These models have begun to provide a basis for understanding *in-situ* bioremediation. However, the numerical procedures employed in these models are typically developed to solve a fixed type of microbial kinetics and a fixed number of reacting species. This limits the ability of the models to accommodate other microbial systems. A few researchers have tried to use a reaction-split approach to avoid this limitation.^{4,7} However, none of these models¹⁻⁷ account for the temporal changes in porous media properties caused by biomass growth. These changes can significantly impact flow and transport in porous media.⁸

This work reports a mathematical framework and solution procedure for modeling biologically reactive transport in porous media. The numerical procedure uses a modular approach to solve the transport and reaction equations. The method can accommodate a variable number of reacting species and different types of kinetic expressions. The effects of microbial accumulation on the porous media properties are also described using the method of *Taylor and Jaffe*.⁸ The following sections of this article present the mathematical description of the system, details of the numerical solution procedure, and simulation results for an example problem.

II. MODEL DESCRIPTION

For a one-dimensional, cartesian, reactive-flow system the macroscopic transport equation for each aqueous species is:

$$\frac{\partial}{\partial t}(Rnc) = \frac{\partial}{\partial z}(\alpha q \frac{\partial c}{\partial z}) - \frac{\partial}{\partial z}(qc) \pm r \quad (1)$$

where n is the porosity, c is the aqueous phase macroscopic averaged concentration of the transported species [ML⁻³],

α is the dispersivity [L], q is the Darcy flux [MT^{-1}], R is the retardation factor, and r is the reaction rate that describes the mass of the species reacted per unit volume (bulk volume) per unit time [$ML^{-3}T^{-1}$].

In addition to the transport equations, the mathematical model also includes a set of ordinary differential equations to describe the growth and decay of biomass attached to the solid (biofilm) phase. These differential equations are of the form:

$$\frac{dX^f}{dt} = r^f \quad (2)$$

where r^f is the film-phase reaction rate [T^{-1}], and X^f is the film-phase biomass concentration [M/M]. In subsurface, a significant portion of biomass is attached to the solid phase, hence, it cannot be transported by the flow field. However, there are physical attachment and detachment mechanisms that can exchange microorganisms between aqueous and solid phases.⁹ Analyses of lab-scale experimental data show that first-order expressions reasonably explain attachment and detachment processes in saturated soil columns.⁹ Based on these findings, simple first-order models for attachment and detachment processes are written as:

$$r_{att} = K_{att} X^a \quad (3)$$

$$r_{det} = K_{det} X^f \quad (4)$$

where X^a is the aqueous-phase biomass concentration [ML^{-3}], r_{att} is rate of microbial attachment, r_{det} is the rate of microbial detachment, K_{att} is the microbial attachment coefficient [T^{-1}], and K_{det} is the microbial detachment coefficient [T^{-1}].

Model equations reflecting porosity variations due to biofilm growth are based on the equations developed by Taylor and Jaffe.⁹ These investigators employed a cut-and-random-rejoin-type model to characterize porosity of biofilm coated porous media. This description is given by the relation:

$$n_b = \beta \left(\frac{L_f}{R} \right)^\lambda \left[I_2 \left(\frac{R}{L_f} - 1, \lambda \right) - I_2 \left(\frac{r_{ob}}{L_f}, \lambda \right) \right] \quad (5)$$

In equation 5, the constant β and film thickness L_f are determined from equations:

$$\frac{dL_f}{dX^f} = \frac{\rho_k}{\rho_f S_a} \quad (6)$$

where n_b is the biofilm coated porosity, $r_{ob} = \max [r_s - L_f, 0]$, r_s is the minimum pore radius [L], R is the maximum pore radius [L], λ is the pore size distribution index which gives a measure of uniformity of the porous medium, X^f is a macroscopic averaged biofilm concentration ([M/M], mass of the biofilm per unit mass of the porous medium), ρ_f is the biofilm density [ML^{-3}], and ρ_k is the dry bulk density of the porous medium. The specific surface area of the porous medium S_a is given by:⁹

$$S_a = \frac{2\beta}{L_f} \left(\frac{L_f}{R} \right)^\lambda \left[I_1 \left(\frac{R}{L_f} - 1, \lambda \right) - I_1 \left(\frac{r_{ob}}{L_f}, \lambda \right) \right] \quad (7)$$

Values of I_1 and I_2 are defined by the integral equation:⁹

$$I_n(u, \lambda) = \int_0^u \frac{x^\lambda}{(1+x)^{\lambda+1}} dx \quad (8)$$

This integral is evaluated numerically to compute I_1 and I_2 in equations 5 and 7.

III. EXAMPLE PROBLEM - DENITRIFYING SYSTEM

As an example, we present and solve a mathematical model that describes cometabolic destruction of carbon tetrachloride (CT) under denitrifying conditions. A kinetic model for this system is presented in *Hooker et al.*¹⁰ In this research, kinetic equations developed by *Hooker et al.*¹⁰ are used to model biological growth and contaminant destruction processes in a one-dimensional column. The column is initially assumed to be clean with a small amount of attached biofilm. Nitrate (electron acceptor), acetate (electron donor), and CT (contaminant) are fed to the column. The modeling effort focuses on studying the simultaneous one-dimensional transport and reaction of six mobile components: nitrate, nitrite, acetate, CT, live aqueous-phase biomass, and dead aqueous-phase biomass. This effort also studies the growth and decay of two immobile (attached) components in the biofilm: live film-phase biomass and dead film-phase biomass. Dead and live cells are accounted for in the aqueous and film phases to correctly reflect total aqueous suspended solids and biofilm levels. The dead biomass is assumed to undergo partial solubilization. However, based on experimental observations, the electron acceptor demand exerted by this solubilized fraction is ignored.¹⁰ A detailed summary of reaction and transport model equations for this system is given in the Appendix.

IV. NUMERICAL SOLUTION

Numerical solution of the system of coupled nonlinear partial/ordinary differential equations for the example (equations A-1 to A-8) is accomplished using a three-stage, operator-split, finite-difference method. Since most of our simulations are aimed at studying near-well regions, the transport equations must be solved under advection-dominated flow conditions. The conventional implicit method leads to excessive numerical dispersion and/or instabilities under these conditions. To alleviate numerical dispersion, *Molz et al.*¹ use a Lagrangian approach to solve the advection problem, followed by a fully implicit finite-difference Eulerian scheme to solve the dispersion-reaction problem. This approximation results in a set of nonlinear coupled equations that are solved by an iterative technique.

Several other finite-element models proposed in the literature^{2,3} also use various forms of fully implicit approaches that result in solving a set of nonlinear coupled equations. The disadvantage of such an approach is excessive computing and the loss of code generality. Computer programs generated by these investigators incorporate discretizations for reaction and dispersion problems within a single block of the code. Hence, any future modifications to reaction equations would require extensive modifications to the program. In the present study, we first solve the advection problem by using the Lagrangian approach¹ and then further split the diffusion and reaction parts of the coupled transport equation into two separate levels.^{3,6,7} A finite-difference implementation of this three-level, operator-split approach for coupled reactive-transport equations that accounts for porosity variations is presented below.

For numerical purposes, equation 1 is rewritten in the form:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - V \frac{\partial c}{\partial z} \pm r - \frac{c}{n} \frac{\partial(nR)}{\partial t} \quad (9)$$

where $V = q/nR$ is the retarded pore velocity [LT^{-1}] and $D = \alpha V$ is the effective dispersion coefficient [L^2T^{-1}]. Equation 9 assumes constant Darcy flux and dispersivity values. Since porosity is not constant, the values of D and V will change from node to node. Numerical solution of equation 9 is accomplished by splitting the expression into three levels. At first, the advective part of the transport equation is written as:

$$\frac{\partial c}{\partial t} = -V \frac{\partial c}{\partial z} \quad (10)$$

Equation 10 is solved by tracing back the particles advected to a distance $\Delta t \cdot V$, and updating the concentration from the previous time step $[C]^n$ to $[C]^{n+1}$ (n and $n+1$ are the current and previous time levels, C_i is the

concentration array after an advection step). A simple linear interpolation scheme is used to interpolate the concentrations between the nodes.¹ The advected solution is accomplished for all the six mobile species by individually solving the advective portions of the transport equations. The resulting updated concentration array $[C_i]^{n+1}$ is passed on to the next stage to solve the dispersive portion of the transport equation written as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - \frac{c}{n} \frac{\partial(nR)}{\partial t} \quad (11)$$

A fully implicit finite-difference method is used to solve equation 11 in a Lagrangian view point. The porosity values are estimated explicitly from the previous time level biofilm lengths. Based on this explicit approximation for porosity, a fully implicit finite-difference discretization for equation 11 is written as:

$$\frac{c_i^{n+1} - c_{i1}}{\Delta t} = \frac{D_f}{\Delta z^2} \left[c_{i-1}^{n+1} - \left(2 + \frac{\Delta(nR)}{n\Delta t} \right) c_i^{n+1} + c_{i+1}^{n+1} \right] \quad (12)$$

The resulting set of linear tridiagonal equations are solved by the Thomas algorithm. For the example problem, solution to six independent dispersion equations are accomplished for all the mobile species, and the concentration array $[C_i]^{n+1}$ is updated to $[C_d]^{n+1}$, where C_d is the concentration array after the dispersion step.

As the final stage of this algorithm, solution to the reaction portion of transport equation is accomplished. The reactive part of equation 9 is written as:

$$\frac{dc}{dt} = \pm r \quad (13)$$

After operator splitting, the reactive portion of the transport equation reduces to an ordinary differential equation. Combining the reaction terms for all six mobile species transport equations (A-1 to A-6), and the two ordinary differential equations (A-7 and A-8), results in a coupled set of eight simultaneous, nonlinear, ordinary differential equations. Numerical solution to these differential equations can be accomplished by an explicit, time-marching method. In this study, the fourth-order Runge-Kutta method is used.

Splitting the transport equations in this fashion facilitates grouping reaction terms into a set of ordinary differential equations that can be solved explicitly. This algorithm reduces the coupled, nonlinear, transport equations for the mobile species to a set of independent, linear, advection-dispersion equations. As shown in expressions 10 and 12, these equations can be solved independently for any number of species in a repetitive fashion without nonlinear iterations. Moreover, since the reaction terms are grouped and solved at a separate stage, any modifications to reaction expressions can be done by altering the reactive block of the code alone.

V. MODEL TESTING

Based on the numerical algorithm presented above, a one-dimensional reactive transport model has been developed in FORTRAN 77. To examine the accuracy of the model predictions, results of the numerical code are compared to an analytical solution, and to an experimentally verified model data reported in the literature.^{11,12} In addition, mass balances of various species are computed and verified at every time step to check the validity of the results.

A. Comparison to Analytical Solution

The analytical model used for comparison purpose solves a one-dimensional advection-dispersion equation with first-order reaction:¹¹

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - K_1 c \quad (14)$$

The initial and boundary conditions used are: $t \leq 0, 0 \leq x \leq \infty, c = 0$; $t > 0, x = 0, c = 10 \text{ mg/l}$; and $t > 0, x = \infty, c = 0$. Model parameters used are: $v = 100 \text{ cm/day}$, $\alpha = 1.0 \text{ cm}$, $K_1 = 0$, and 2 day^{-1} , $\Delta x = 0.5 \text{ cm}$, $\Delta t = 0.005 \text{ day}$, and $t = 0.1 \text{ day}$. Solutions for conservative and non conservative contaminant transport problems plotted in Figure 1 show good agreement between analytical and numerical results.

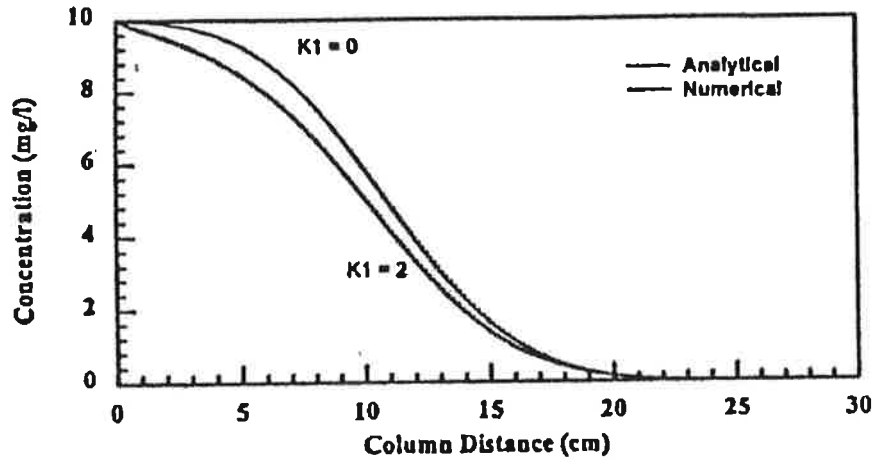


Figure 1. Comparison of Analytical and Numerical Solutions for Conservative and Nonconservative Contaminants

B. Comparison to Published Soil Column Data

Zysset *et al.*¹² present a one-dimensional, finite-element based numerical model for predicting reactive groundwater transport governed by biodegradation. They verified the model performance by reproducing nitrate and sulfate transport observed in laboratory column experiments. The changes in porous medium properties are ignored in the study of Zysset *et al.*¹² In the present research, we resolve the Zysset *et al.*¹² model by using the present numerical procedure and compare the results in Figures 2a and 2b. It can be seen from the figures that there is excellent agreement between the models.

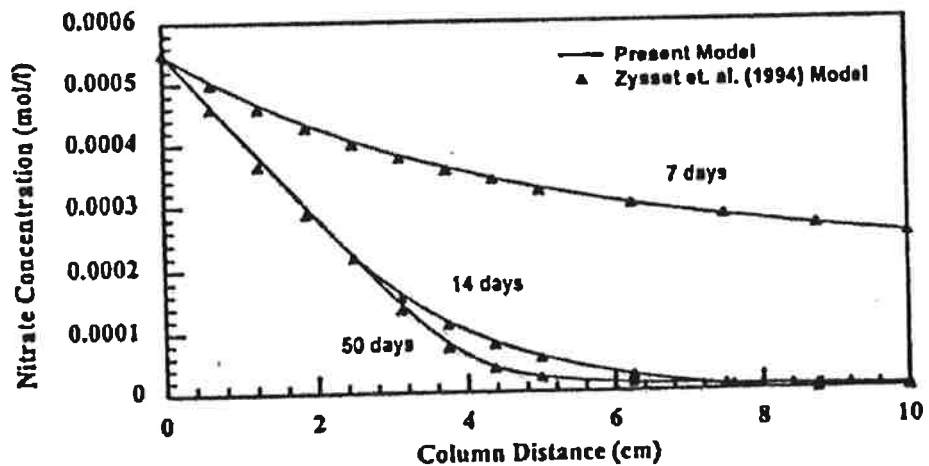


Figure 2a. Comparison to Published Soil Column Data Nitrate Profiles

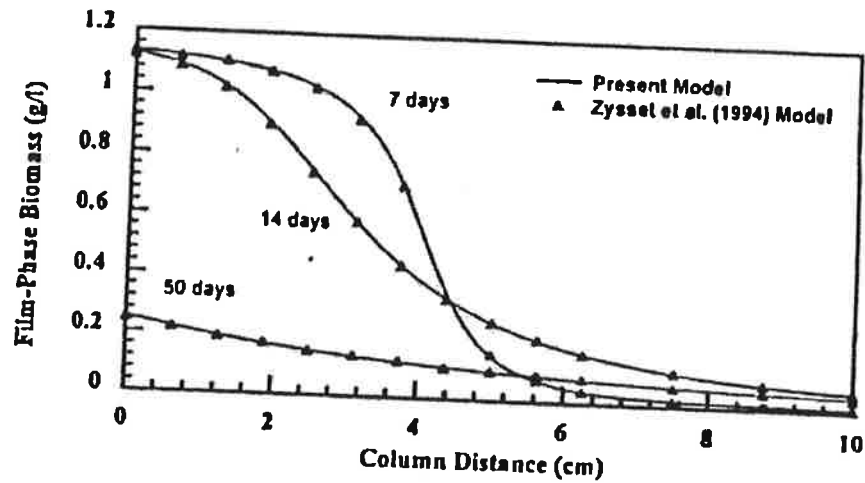


Figure 2b. Comparison to Published Soil Column Data Film-Phase Biomass Profiles

VI. SIMULATION RESULTS FOR THE EXAMPLE PROBLEM

In this section, the mathematical model for the example problem is used to simulate microbial processes in a one-dimensional porous medium column of 20 cm length. Soil parameters used in the simulation are: $n = 0.4$, $\lambda = 2.0$, $r_s = 0$, $R = 0.0414$ cm, $\rho_s = 1600$ g/l, $\rho_r = 39.5$ g/l. Retardation factors for all mobile species are assumed to be unity. A Darcy flux of 200 cm/day corresponding to an initial pore velocity of 500 cm/day is used. All the kinetic parameter values used are reported in *Hooker et al.*¹⁰ The initial and boundary conditions for the problem are:

$$t \leq 0, 0 \leq z \leq \infty, C = 0$$

$$t > 0, z = L, dc/dz = 0$$

$$t > 0, z = 0, C(t) = C_{in}(t); \text{ concentration boundary}$$

where $C_{in}(t)$ is the influent concentration at time t , and L is the length of the soil column.

Model simulations are run for 3 days. The spatial and temporal node sizes used are: $\Delta x = 0.5$ cm and $\Delta t = 0.0001$ day. Figure 3 shows spatial variations in the concentrations of nitrate, nitrite, acetate, and CT at various time intervals. Figure 4 shows the spatial distribution of different forms of biomass within the porous medium. Results in Figure 3 show rapid denitrification leading to almost complete nitrate consumption near the column entrance after 3.0 days of simulation. This is due to considerable biofilm accumulation adjacent to the column entrance, and this effect can be observed from the live biofilm distribution shown in Figure 4. The bioaccumulation process leads to reduced porosity values near the entrance nodes. Longer simulations indicate that after a critical time period (that depends on attachment, detachment, and growth kinetics), the porosity reduction become substantial, and the column is rapidly clogged. This type of entrance clogging phenomenon has been previously observed in laboratory column experiments⁸ and it poses a major problem in operating continuous feed systems.

Figure 3 also shows the fortuitous destruction of CT within the column. Based on the results reported by *Hooker et al.*,¹⁰ rate of CT destruction is directly proportional to biomass concentration, but is inhibited significantly in the presence of nitrate. Observed CT levels reflect minor destruction activity because nitrate is typically present at the column entrance where significant biofilm has developed. The simulation results of this example show the use of the numerical model in predicting the complex interactions between various mobile and immobile components inside a biologically reactive porous medium.

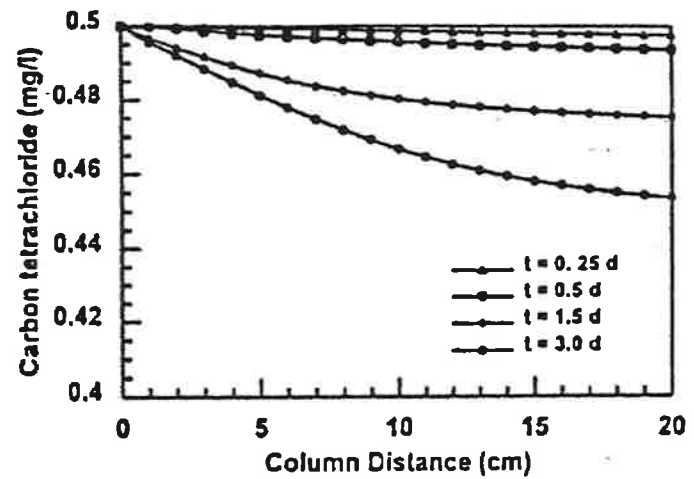
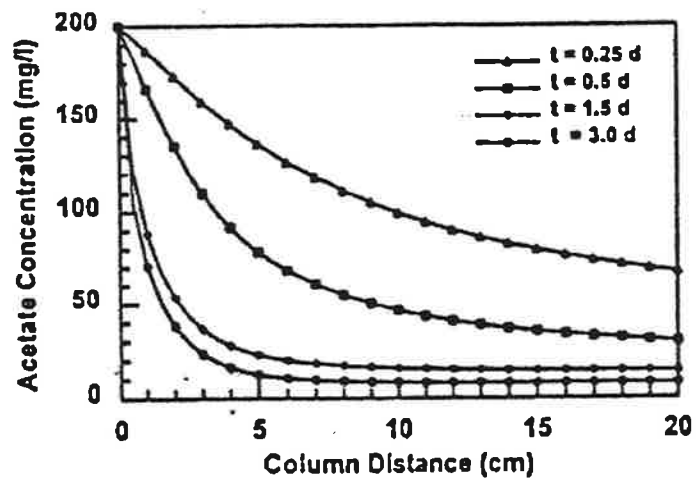
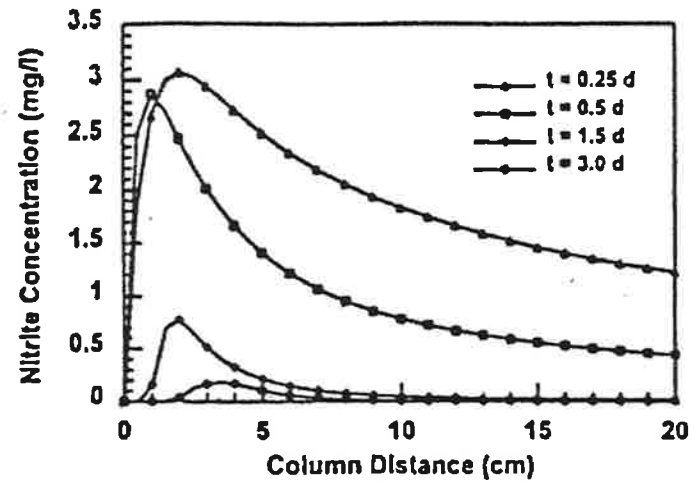
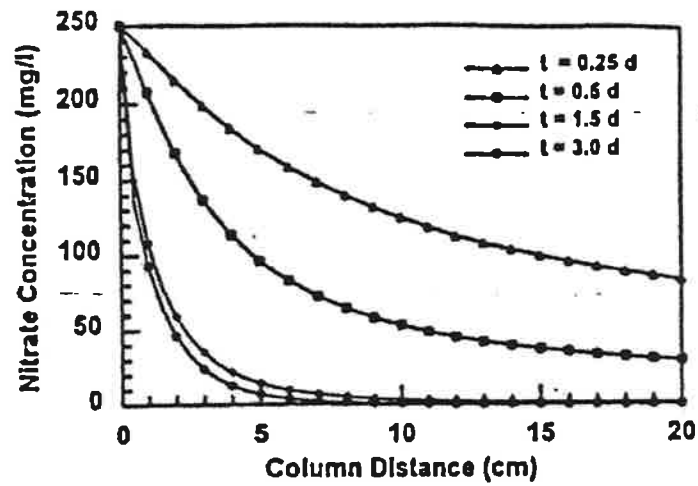


Figure 3. Model Predictions for Nitrate, Nitrite, Acetate, and Carbon Tetrachloride Concentration Profiles in the Column

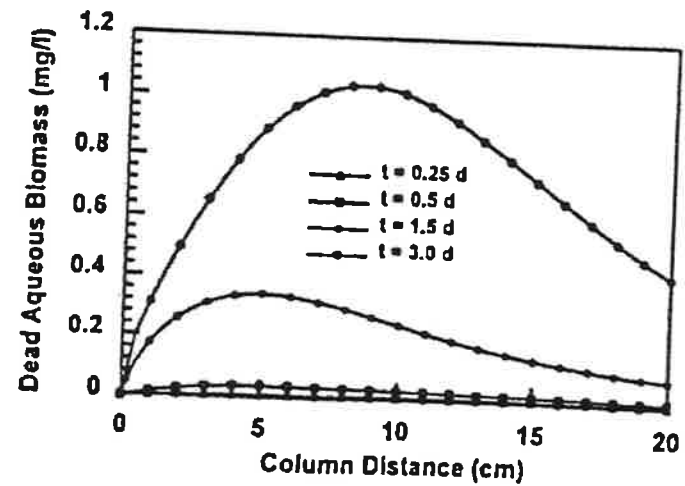
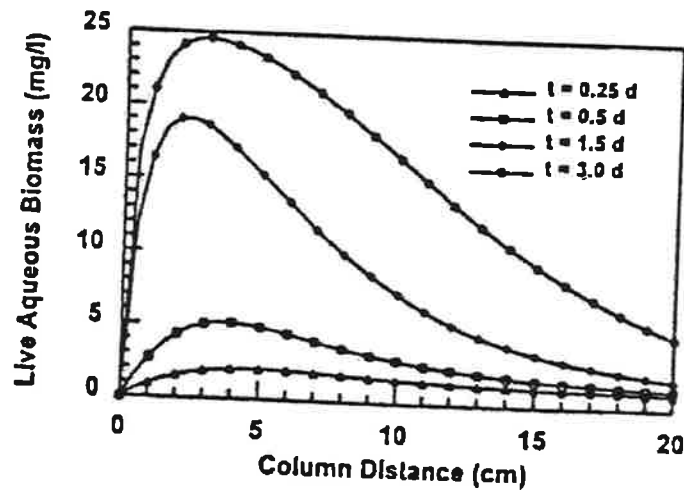
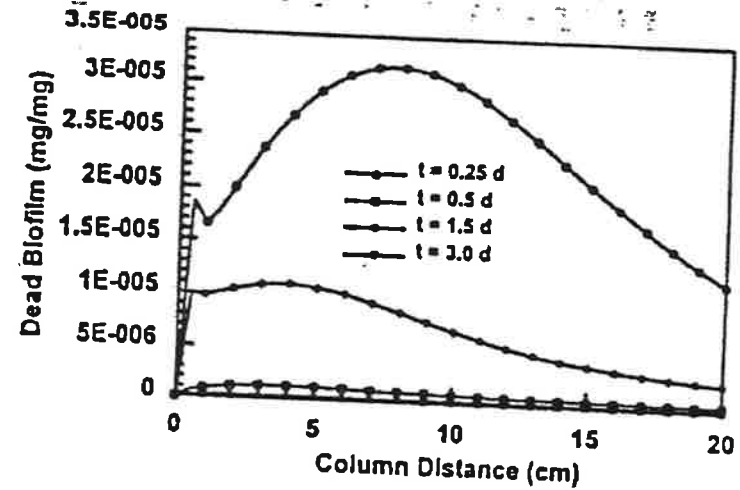
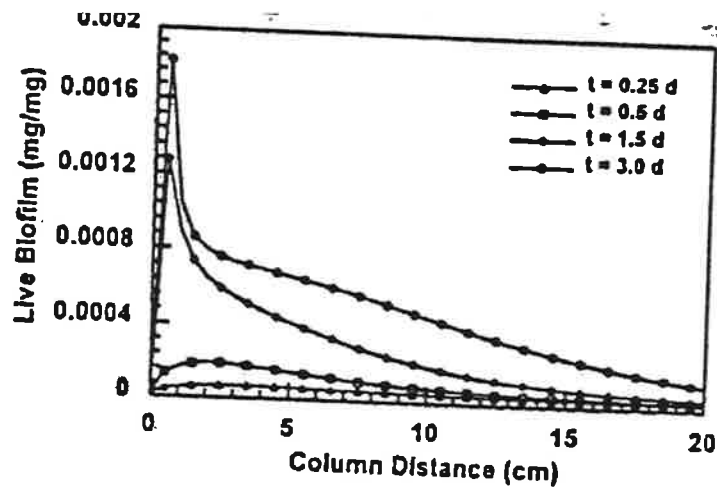


Figure 4. Model Predictions for Live Biofilm, Dead Biofilm, Live Aqueous Biomass, and Dead Aqueous Biomass Concentration Profiles in the Column

VII. SUMMARY AND CONCLUSIONS

This paper presents a one-dimensional, biofilm-based, reactive-transport model to simulate various biologically reactive transport processes in saturated porous media. A finite-difference based three-stage operator-split approach is presented to solve the reactive-transport equations. The numerical solution reproduced an analytical solution, and it also closely modeled an experimentally verified published model data set. The numerical algorithm is stable, easy-to-code, and computationally efficient. As an example problem, biological denitrification and fortuitous carbon tetrachloride destruction processes in a soil column are simulated. The results of this example show that the modeling approaches presented in this study can be successfully used to predict biological processes and nutrient/contaminant transport in saturated porous media.

APPENDIX - SUMMARY OF TRANSPORT AND REACTION EQUATIONS

The governing transport equations with appropriate reaction terms for the six mobile species: nitrate (NO_3^-), nitrite (NO_2^-), acetate (Ac), carbon tetrachloride (CT), live (active) aqueous biomass (X_a^w), and dead (inactive) aqueous biomass (X_i^w), are written as:

$$\frac{\partial}{\partial t}(R_{\text{NO}_3} n[\text{NO}_3]) = \frac{\partial}{\partial z} \left(\alpha q \frac{\partial [\text{NO}_3]}{\partial z} \right) - \frac{\partial}{\partial z} (q[\text{NO}_3]) + n r_{\text{NO}_3}^w + \rho_k r_{\text{NO}_3}^f \quad (\text{A-1})$$

$$\frac{\partial}{\partial t}(R_{\text{NO}_2} n[\text{NO}_2]) = \frac{\partial}{\partial z} \left(\alpha q \frac{\partial [\text{NO}_2]}{\partial z} \right) - \frac{\partial}{\partial z} (q[\text{NO}_2]) + n r_{\text{NO}_2}^w + \rho_k r_{\text{NO}_2}^f \quad (\text{A-2})$$

$$\frac{\partial}{\partial t}(R_{\text{Ac}} n[\text{Ac}]) = \frac{\partial}{\partial z} \left(\alpha q \frac{\partial [\text{Ac}]}{\partial z} \right) - \frac{\partial}{\partial z} (q[\text{Ac}]) + n r_{\text{Ac}}^w + \rho_k r_{\text{Ac}}^f \quad (\text{A-3})$$

$$\frac{\partial}{\partial t}(R_{\text{CT}} n[\text{CT}]) = \frac{\partial}{\partial z} \left(\alpha q \frac{\partial [\text{CT}]}{\partial z} \right) - \frac{\partial}{\partial z} (q[\text{CT}]) + n r_{\text{CT}}^w + \rho_k r_{\text{CT}}^f \quad (\text{A-4})$$

$$\frac{\partial}{\partial t}(n[X_a^w]) = \frac{\partial}{\partial z} \left(\alpha q \frac{\partial [X_a^w]}{\partial z} \right) - \frac{\partial}{\partial z} (q[X_a^w]) + n r_{X_a}^w + \rho_k r_{\text{det}}^f - n r_{\text{att}} \quad (\text{A-5})$$

$$\frac{\partial}{\partial t}(n[X_i^w]) = \frac{\partial}{\partial z} \left(\alpha q \frac{\partial [X_i^w]}{\partial z} \right) - \frac{\partial}{\partial z} (q[X_i^w]) + r_{X_i}^w + \rho_k r_{\text{det}}^f - n r_{\text{att}} \quad (\text{A-6})$$

where ρ_k is the dry bulk density of the porous medium [ML^{-3}], r_i^w represents species production or destruction rate due to biological reactions in the aqueous phase (mass per day per unit liquid volume, $\text{ML}^{-3}\text{T}^{-1}$), r_i^f is the species production or destruction rate due to film-phase biological reaction (mass per day per unit mass of dry porous medium solid, $\text{MM}^{-1}\text{T}^{-1}$), n is the porosity, and R_{NO_3} , R_{NO_2} , R_{Ac} , and R_{CT} are retardation coefficients.

In addition to the six partial differential equations, the mathematical model for the system includes the following two ordinary differential equations that describe the kinetics of attached biofilm components: live film-phase biomass X_a^f , and dead film-phase biomass X_i^f . The reaction rate equations for these biofilm components are written as:

$$\frac{dX_a^f}{dt} = r_{X_a^f} - r_{det} + \frac{nr_{an}}{\rho_k} \quad (A-7)$$

$$\frac{dX_i^f}{dt} = r_{X_i^f} - r_{det} + \frac{nr_{an}}{\rho_k} \quad (A-8)$$

This set of eight equations describes the transient behavior of the biological processes inside the porous medium. The reaction terms in equations A-1 to A-8 use kinetic expressions reported in *Hooker et al.*¹⁰ Both film-phase and aqueous-phase reaction rates use similar expressions, with biomass concentrations corresponding to the phase. Nutrients and contaminant concentrations in the film-phase are assumed to be equal to aqueous phase concentrations.

ACKNOWLEDGMENTS

Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. This work was supported by the U.S. Department of Energy Office of Technology Development, VOC-Arid Integrated Demonstration and In Situ Remediation Integrated Program. Dr. Clement was supported by the Associated Western Universities, Inc., Northwest Division under grant DE-FG06-89ER-7522 with the U.S. Department of Energy.

REFERENCES

- 1) Molz, F.J., M.A. Widdowson, and L.D. Benefield, "Simulation of microbial growth dynamics coupled to nutrient oxygen transport in porous media," *Water Resources Research*, 22, 1207-1216, 1986.
- 2) Kindred, J.S., and M.A. Celia, "Contaminant transport and biodegradation, 2. Conceptual model and test simulations," *Water Resources Research*, 25, 1149-1159, 1989.
- 3) Lindstrom, T.M., "A mathematical model for the one-dimensional transport and fate of oxygen and substrate in a water-saturated sorbing homogeneous porous medium," *Water Resources Research*, 28, 2499-2511, 1992.
- 4) Shouche, M., J.N. Petersen, and R.S. Skeen, "Use of mathematical model for prediction of optimal feeding strategies for in situ bioremediation," *Applied Biochemistry and Biotechnology*, 39, 763-779, 1993.
- 5) Kinzelbach, W., W. Schafer, and J. Herzer, "Numerical modeling of natural and enhanced denitrification processes in aquifers," *Water Resources Research*, 27, 1123-1135, 1991.
- 6) Rifai, H.S., and P.B. Bedient, "Comparison of biodegradation kinetics with an instantaneous reaction model for groundwater," *Water Resources Research*, 26, 637-645, 1990.
- 7) Wheeler, M.F., K.R. Robertson, and A. Chilakapati, "Three-dimensional bioremediation modeling in heterogeneous porous media," *Computational Methods in Water Resources*, Elsevier, Oxford, U.K., IX, vol. 2., 299-315, 1992.
- 8) Taylor, S.W., and P.R. Jaffe, "Substrate and biomass transport in a porous medium," *Water Resources Research*, 26, 2181-2194, 1990.
- 9) Peyton, B.M., R.S. Skeen, B.S. Hooker, R.W. Ludman, A.B. Cunningham, "Evaluation of bacterial detachment rates in porous media," *Applied Biochemistry and Biotechnology*, (in press) 1994.
- 10) Hooker, B.S., R.S. Skeen, and J.N. Petersen, "Biological destruction of CCl₄: II. Kinetic modeling," *Biotechnology and Bioengineering*, 44, 211-218, 1994.
- 11) van Genuchten, M.T., and W.J. Alves, "Analytical solution of the one-dimensional convective-dispersive solute transport equations," *U.S. Department of Agriculture Technical Bulletin*, 1161, Washington D. C., 1982.
- 12) Zysset, A., F. Stauffer, and T. Dracos, "Modeling of reactive groundwater transport governed by biodegradation," *Water Resources Research*, 30, 2423-2434, 1994.