BIOMOC, A Multispecies Solute-Transport Model with Biodegradation

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By Hedeff I. Essaid and Barbara A. Bekins

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PREFACE

This model, BIOMOC, was developed through modifications of an existing transport model (MOC), that was developed originally by Konikow and Bredehoeft (1978). We recommend that this documentation be used in conjunction with the documentation of Konikow and Bredehoeft (1978). Although extensive testing of BIOMOC indicates that this model will yield reliable results for a variety of problems, the user is cautioned that the accuracy and efficiency of the model can be affected significantly for certain combinations of parameter values and boundary conditions. Further discussion of these issues may be found in the Stability Criteria section.

The code and documentation for this model is available for downloading over the Internet from a USGS software repository. The repository is accessible on the World Wide Web (WWW) at http://h2o.usgs.gov/software/. The code may also be obtained via anonymous FTP from the /pub/software directory on the Water Resources Information server (h2o.usgs.gov or 130.11.50.175). Future revisions and updates of the code will be made available for downloading form these same sites.

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BIOMOC, A Multispecies Solute-Transport Model with Biodegradation

By H. I. Essaid and B. A. Bekins

ABSTRACT

A two-dimensional, multispecies reactive solute-transport model with sequential aerobic and anaerobic degradation processes was developed and tested. The model design is general and flexible, permitting simulation of biotransformation reactions for any combination of electron donor and acceptor. In addition, the evolution of redox zones can be simulated, as thermodynamically-favorable electron acceptors are depleted. The code is an extension of the U. S. Geological Survey's Method of Characteristics (MOC) flow and transport model. It allows for multiple particle sets and each particle set is capable of having multiple solute species with similar sorption characteristics. The rate of the degradation reactions can be represented by single-substrate Monod, multiple Monod, or minimum Monod kinetics. Four alternate inhibition formulations account for competitive, noncompetitive, biomass, or Haldane inhibition. Multiple degradation processes and microbial populations can be represented simultaneously. Growth of the biomass is modeled with specified yield and decay values.

The model has been successfully tested against several one-dimensional analytical solutions. These include transient transport with first- and zero-order decay and linear sorption and also steady-state transport with first- and zero-order decay, or Monod degradation. The model results were also compared to results from two other one-dimensional numerical codes.

To illustrate the flexibility of BIOMOC, example applications of the model to two field sites are described. The first example simulates steady-state, one-dimensional, transport and degradation of chlorinated solvents with no biomass growth. In this application, both reductive dehalogenation and aerobic degradation are simulated. The anaerobic reactions are inhibited by the presence of significant levels of dissolved oxygen. The second application is a two-dimensional, transient simulation of the Bemidji, Minnesota crude-oil spill site. In this application, the evolution of redox zones and microbial populations is simulated. Before contamination, aerobic conditions are present in the aquifer. As the plume evolves, the redox conditions change near the oil body from aerobic to manganese-reducing then iron-reducing and finally methanogenic. The results were used to determine the percentage of mass lost by aerobic versus anaerobic degradation and to understand the evolution of the redox zones in a plume.

INTRODUCTION

A promising alternative to traditional pump-and-treat remediation is *in situ* bioremediation, a method that relies on natural and enhanced biodegradation processes at a site (Lee and others, 1988; Madsen, 1991; Bouwer and Zehnder, 1993; Salanitro, 1993; Macdonald and Kavanaugh, 1994). Both aerobic and anaerobic biodegradation processes can be effective at removing organic contaminants from the environment. The availability of electron acceptors determines the sequence of biodegradation processes. Based on the thermodynamics of reactions and redox potential, the theoretical sequence is aerobic degradation, followed by denitrification, manganese and iron reduction, sulfate reduction, and methanogenesis. This sequence may cause zonation of a contaminant plume with different biodegradation processes dominating in each redox zone (Baedecker and Back, 1979; Chapelle and Lovley, 1992; Lyngkilde and Christensen, 1992; Vroblesky and Chapelle, 1994). In addition, halogenated organic compounds may also serve as electron acceptors under sulfate-reducing and methanogenic conditions. Plume evolution is dynamic with the dominant biodegradation processes changing in time and space.

Numerical models that simulate transport and biodegradation processes are useful for integrating information collected in the field and studying the relative importance of simultaneously occurring processes (Borden and others, 1986; Rifai and others, 1988; Chiang and others, 1989; Thierrin and others, 1993). Field sampling limitations make it difficult to develop an accurate mass balance for the contaminant, and thus to distinguish the amount and rate of removal by biodegradation versus dilution and sorption. If sufficient data are available, a numerical model can be used to help answer these questions, estimate removal rates, predict plume evolution, and evaluate factors limiting biodegradation. Essaid and others (1995) summarized the existing models of transport and biodegradation. These models differ in dimensionality, representation of biological growth and contaminant degradation, and the number of processes simulated. Most are limited to specific biodegradation processes that include a maximum of two substrates (carbon sources) and two electron acceptors. Some models include the transport and uptake of substances necessary for microbial growth (for example nitrogen and phosphorous).

This report documents a general and flexible two-dimensional transport and biodegradation model that can handle multiple substrates and microbial populations, sequential terminal electron acceptor use, and cellular nutrient limitation. The governing equations and numerical methods are described. Model results are evaluated by comparison to analytical solutions and other numerical model results. In addition, two example field applications are described to demonstrate the flexibility of the model.

THEORETICAL BACKGROUND AND GOVERNING EQUATIONS

The U.S. Geological Survey's Method of Characteristics (MOC) transport model (Konikow and Bredehoeft, 1978; Goode and Konikow, 1989) was selected as the base for the biodegradation model because a robust transport model is required to handle the steep concentration gradients observed in field data without introducing significant numerical dispersion. In the original MOC code one set of particles was used to simulate transport of a single solute species. Variations of the MOC model exist that handle two concentrations per particle (Sanford and Konikow, 1985) and two particle sets with a single concentration each (Rifai and others, 1988). In this study, the MOC model was expanded to handle multiple particle sets, each particle having multiple solute species concentrations associated

with it. This approach allows solute species having similar sorption characteristics to be represented by a single particle set. This modified version of the MOC code is referred to as BIOMOC.

Flow Equation

The equation describing transient two-dimensional flow of a homogeneous compressible fluid through a nonhomogeneous anisotropic aquifer is:

$$S\frac{\partial h}{\partial t} = \frac{\partial}{\partial x_j}\left(bK_{jk}\frac{\partial h}{\partial x_k}\right) - W \qquad \text{j,k=1,2} \tag{1}$$

where S is the storage coefficient, h is hydraulic head (L), t is time (T), K_{jk} is the hydraulic conductivity tensor (LT^{-1}), b is the aquifer thickness (L), W is the source fluid flux (positive for outflow, negative for inflow) expressed as volumetric flux per unit area (LT^{-1}), and x_j and x_k are cartesian coordinates (L). By Darcy's Law, the average linear flow velocity in the x_j direction (V_j) is given by:

$$V_j = -\frac{K_{jk}}{\varepsilon}\frac{\partial h}{\partial x_j}, \tag{2}$$

where ε is the effective porosity (dimensionless).

Transport Equation

The two-dimensional transport equation solved in the model for each solute species is:

$$R_i\frac{\partial C_i}{\partial t} = \frac{1}{b}\frac{\partial}{\partial x_j}\left(bD_{jk}\frac{\partial C_i}{\partial x_k}\right) - V_j\frac{\partial}{\partial x_j}C_i + \frac{W(C_i - C'_i)}{(\varepsilon b)} - R_i\lambda_i C_i - B_i \qquad \text{j,k=1,2} \tag{3}$$

where C_i is the concentration of the *ith* solute (ML^{-3}), R_i is the retardation factor for the *ith* solute, D_{jk} is the dispersion tensor (L^2T^{-1}), C'_i is the concentration of the *i*th solute in the source fluid (ML^{-3}), λ_i is the first-order decay rate constant (T^{-1}) for the *ith* solute (half life $t_{1/2} = (\ln 2)/\lambda$), and B_i is the biodegradation reaction rate term ($ML^{-3}T^{-1}$) representing the total uptake of the *ith* solute due to all active biodegradation processes. The first-order decay term is multiplied by the retardation factor because both dissolved and sorbed solute are assumed to decay (as in the case of radioactive solutes). However, the biodegradation term is not multiplied by the retardation factor because it is assumed that only the dissolved solute is degraded. Thus, biodegradation is slowed down by sorption.

Biodegradation Terms

Each solute may be involved in several biodegradation processes, such that the total uptake of any solute i is given by the summation of the uptake for all simultaneously occurring biodegradation processes:

$$B_i = \sum_{n=1}^{N} \beta_i^n \nu^n \quad , \tag{4}$$

where N is the total number of biodegradation processes, ν^n is the uptake rate of substrate by biodegradation process n ($ML^{-3}T^{-1}$), and β_i^n is the uptake coefficient of solute i for biodegradation

process n. When the solute is the primary substrate, β_i^n is equal to 1. Otherwise, β_i^n is determined by the stoichiometry of the reaction and is equal to the ratio of the mass of solute i to that of the primary substrate. For example, if for every gram of carbon degraded aerobically, 2.6 gm of dissolved oxygen is consumed, then the uptake coefficient for oxygen is 2.6. The value of β_i^n is negative if solute i is produced by the *nth* biodegradation process and is zero if the solute is not involved in the biodegradation process. An example of how to compute the uptake ratio for each solute is given in the section describing the application to chlorinated solvents.

The literature contains several conceptual models for bacterial growth and contaminant biodegradation (Baveye and Valocchi, 1989; Widdowson, 1991). In the simplest representation, macroscopic fluid substrate, electron acceptor, and cellular nutrient concentrations are used to calculate the growth and uptake. Two alternate representations, the biofilm and microcolony models, include pore scale processes and account for the effect of diffusion into and out of the biophase. BIOMOC is an implementation of the macroscopic approach, and thus, biophase diffusion has been neglected. It has also been assumed that the biomass remains attached to the sediments, and pore clogging by biomass growth is not accounted for in the model.

In general, a variation of Monod kinetics (Monod, 1949) is used to represent the growth and substrate uptake rate. Two different formulations exist for biodegradation processes that involve several solutes. The first formulation, referred to below as the multiple Monod formulation (Molz and others, 1986), assumes that the biodegradation reaction is limited by the concentration of each of the substances involved in the reaction:

$$\nu^n = \frac{V_{max}^n}{I_{nc}} \left\{ \left(\frac{C_1}{K_1^n / I_c + C_1 + I_h} \right) \left(\frac{C_2}{K_2^n / I_c + C_2 + I_h} \right) \cdots \left(\frac{C_m}{K_m^n / I_c + C_m + I_h} \right) \right\} \frac{X_k^n}{I_b}, \tag{5}$$

where V_{max}^n is the asymptotic maximum specific uptake rate of the substrate (T^{-1}), and K^n is the half-saturation constant (ML^{-3}), X_k^n is the biomass concentration of microbial population k responsible for biodegradation process n (ML^{-3}). Although the bacteria are assumed to be attached, for convenience sake, biomass concentration is expressed as mass of bacteria per volume of fluid (equals biomass concentration per bulk aquifer volume divided by porosity). I_{nc}, I_c, and I_b are the noncompetitive, competitive, and biomass inhibition factors, respectively, given by $I = 1 + Q_s / k_s$ where Q_s is the concentration of the inhibiting substance s (ML^{-3}), and k_s is the inhibition constant for that substance (ML^{-3}) (Segel, 1975). An example of noncompetitive inhibition is the inhibition of an anaerobic biodegradation process by the presence of oxygen. Competitive inhibition is used to represent the inhibition of uptake of a secondary substrate when the primary substrate is still present. Biomass inhibition is an empirical means for limiting biomass growth formulated by Kindred and Celia (1989). The biomass inhibition factor for microbial population k is given by $I_b = 1 + X_k / k_{biok}$ where k_{biok} represents the biomass concentration above which the growth of population k becomes limited. This capability may be used to prevent unbounded growth of the microbial population near a continuous source of contaminants. See the Bemidji, MN crude-oil site application for an example of its use. I_h represents inhibition caused by the presence of compounds that are toxic. A modified form of Haldane inhibition (Haldane, 1930), that allows for inhibition by more than one compound (each with concentration C_{ii}), is used where $I_h = \sum C_{ii}^2 / k_{hii}$, is the sum over all inhibiting compounds, and k_{hii} is the Haldane inhibition constant for each ii compound.

The alternative minimum Monod formulation (Kindred and Celia, 1989) assumes that a single solute is limiting the process:

$$\nu^n = \frac{V^n_{max}}{I_{nc}} MIN\left\{\left(\frac{C_1}{K^n_1/I_c + C_1 + I_h}\right), \left(\frac{C_2}{K^n_2/I_c + C_2 + I_h}\right), \ldots, \left(\frac{C_m}{K^n_m/I_c + C_m + I_h}\right)\right\} \frac{X^n_k}{I_b}. \tag{6}$$

Not enough experimental data are available to determine which modified Monod approach is more appropriate for field conditions. Therefore, to preserve generality and flexibility in the model, both formulations have been included as options in BIOMOC.

The metabolism of substrate will result in biomass growth if sufficient cellular nutrients are available. The rate of biomass growth for each population k is given by:

$$\frac{dX_k}{dt} = (P_k - d_k) X_k. \tag{7}$$

where P_k is the specific growth rate for population k (T^{-1}), and d_k is the specific death rate or maintenance constant (T^{-1}). Because microbes are observed to be ubiquitously present in the subsurface, in BIOMOC the biomass concentration is not allowed to decay to less than the initially specified background biomass concentration.

If growth is not limited by cellular nutrient availability, then the specific growth rate is the sum of the specific substrate uptake rates (substrate uptake rate per unit biomass) times the cell-yield coefficients, Y (M bacteria/M substrate), for all M biodegradation processes performed by population k.

$$P_k = \frac{1}{X_k/I_b} \sum_{m=1}^{M} Y^m \nu^m. \tag{8}$$

If growth is cellular nutrient limited and the multiple Monod formulation of equation 5 is used, then:

$$P_k = \frac{1}{X_k/I_b} \sum_{m=1}^{M} Y^m \nu^m \left(\frac{C_{nut}}{K_{nut}/I_c + C_{nut}}\right). \tag{9}$$

If the minimum Monod formulation of equation 6 is used, then:

$$P_k = \sum_{m=1}^{M} Y^m MIN\left[\frac{\nu^m}{X_k/I_b}, \frac{V^m_{max}}{I_{nc}}\left(\frac{C_{nut}}{K_{nut}/I_c + C_{nut}}\right)\right], \tag{10}$$

where Y_{nut} is the cell-yield coefficient of the nutrient (M bacteria/M substrate), C_{nut} is the concentration of the nutrient (ML^{-3}), and K_{nut} is the half saturation constant for the nutrient (ML^{-3}). The net uptake of the nutrient is given by:

$$\nu_{nut} = \sum_{k=1}^{K} \left(\frac{1}{Y_{nut}} P_k X_k - \frac{\Gamma_{nut}}{Y_{nut}} d_k X_k\right), \tag{11}$$

where K is the total number of microbial populations. Γ_{nut} is the nutrient release coefficient and represents the fraction of nutrient incorporated into biomass that becomes available for reuse when microbes die: if $\Gamma_{nut} = 1$ all biomass nutrient is recycled; if $\Gamma_{nut} = 0$ no nutrient is recycled.

Review of Assumptions

A number of assumptions have been made in the development of the above theory and in its application to BIOMOC. These assumptions are summarized below and must be considered during application of the model to a field problem.

1. Flow in only two-dimensions is considered.
1. Darcy's law is valid.
2. Porosity and hydraulic conductivity are constant with time, and porosity is uniform in space.
3. Gradients of fluid density, viscosity, and temperature do not affect the velocity distribution.
4. Fluid and aquifer properties are not affected by the reactions that occur.
5. Ionic and molecular diffusion are neglected.
6. The aquifer is homogeneous and isotropic with respect to longitudinal and transverse dispersivity.
7. Both the dissolved and sorbed solute phases undergo first-order decay as represented by the $R_i\lambda_i C_i$ term in equation 3. Only the dissolved solute undergoes biodegradation as represented by the biodegradation term, B_i, in equations 3 and 4. First-order or zero-order decay of only dissolved solute can be approximated using this term (see Model Evaluation section).
8. There is no microbial transport, and the biomass concentration does not drop below the specified initial concentration.
9. A macroscopic approach has been used to represent biodegradation. Biophase diffusion is neglected.

NUMERICAL METHODS

The details of the numerical methods implemented for solving the flow and transport equations are fully described by Konikow and Bredehoeft (1978). The discretization uses a rectangular, uniformly spaced, block-centered, finite-difference grid. Implicit finite-difference equations are used to solve the flow equation (1). The average linear flow velocities are then calculated and used to solve the transport equation (3) using the method of characteristics and particle tracking.

Initially, particles of each set are distributed uniformly throughout the finite-difference grid. During a time step increment, each particle is moved based on the average linear velocity at the particle location. If there is sorption, the retarded velocity is used. After all the particles have been moved, an average concentration for each grid block is calculated based on the average of the concentrations of the particles located within the block. This new concentration, C_i^*, is the result of advective transport only. Explicit finite-difference approximations are then used to solve for the change in concentration due to hydrodynamic dispersion, fluid sources, and changes in fluid storage using the average of the concentration from the previous time step and the advected concentration, C_i^*. Changes in concentration due to first-order decay processes are calculated directly on particles to preserve accuracy.

All biodegradation terms (equations 5, 6, 8, 9, 10 and 11) are calculated explicitly using the average of the solute concentration from the previous time step and the advected solute concentration (C_i^*) in conjunction with the biomass concentration from the previous time step. Once the biodegradation uptake terms have been calculated for the time step, the amount of biomass growth is determined using the integral of equation (7) (Kindred and Celia, 1989):

$$X_k^{new} = X_k^{old} exp\left[(P_k - d_k)\,\Delta t \right], \tag{12}$$

where X_k^{new} is the biomass concentration of microbial population k at the end of the new time step, X_k^{old} is the biomass concentration of microbial population k from the previous time step, and Δt is the time step size (T). Series expansion of the exponential term in equation (12) shows that this form is slightly more accurate than a finite-difference solution of equation (7).

An immobile set of particles may be specified to facilitate the representation of a solid phase such as iron coatings on sediment grains. These particles do not move and their concentration changes only as a result of biodegradation processes.

Stability Criteria

Explicit solution of the transport equation results in stability criteria that constrain the transport time step increment (Konikow and Bredehoeft, 1978). For dispersion, the following criterion must be satisfied:

$$\Delta t \le Min\,(overgrid) \left[\frac{0.5}{\dfrac{D_{xx}}{(\Delta x)^2} + \dfrac{D_{yy}}{(\Delta y)^2}} \right]. \tag{13}$$

To prevent the change in concentration at a source cell from exceeding the difference between the source concentration (C'_i) and the concentration in the aquifer (C_i) the following criterion must be met:

$$\Delta t \le Min\,(overgrid) \left[\frac{\varepsilon b_{j,k}}{W_{j,k}} \right] . \tag{14}$$

To maintain relatively uniformly spaced particles moving along relatively smooth and continuous pathlines the following accuracy criteria are established:

$$\Delta t \le \left[\frac{\delta \Delta x}{(V_x)_{max}} \right] , \tag{15}$$

$$\Delta t \le \left[\frac{\delta \Delta y}{(V_y)_{max}} \right] , \tag{16}$$

where δ is the maximum fraction of a grid block dimension that a particle will be allowed to move during a transport time increment ($0<\delta\le 1$). The user specifies δ by setting the value of CELDIS in the input file.

The appropriate time increments needed to satisfy the stability criteria in equations (13) through (16) are computed automatically in the model. However, in addition to the above criteria, the biodegradation term is also sensitive to time step size. If the degradation rate is such that the half-life ($t_{1/2}$) is the same order of magnitude as the time increment for a particle move step, accuracy problems may arise. This is because of the explicit method that is used to calculate the biodegradation terms.

To illustrate the effect of time-step size on the stability of the biodegradation term, the transport and first-order decay of a solute were simulated using two approaches: (1) first-order decay and (2) the Monod expression for biodegradation. The Monod expression is approximately the same as first-order decay when $K >> C$:

$$B = V_{max}\left(\frac{C}{K+C}\right) \approx \frac{V_{max}}{K}C \equiv \lambda C \quad , \tag{17}$$

where $t_{1/2} = (ln\ 2)/\lambda$.

First-order decay of a solute is calculated accurately for all time step sizes because it is calculated on a particle-by-particle basis (Goode and Konikow, 1989). On the other hand, the explicit calculation of the Monod biodegradation term is affected by time step size. The simulation results for the two cases are shown in figures 1a and b. When the half-life is close to the time-step size, the solution obtained using the Monod expression oscillates about the solution obtained using first-order decay. When the time step size is cut by a factor of 5, the two solutions converge.

In practice, the user should check the stability of the biodegradation term calculations by running the problem with different time step sizes for the particle move increments. This is achieved by varying CELDIS in the input.

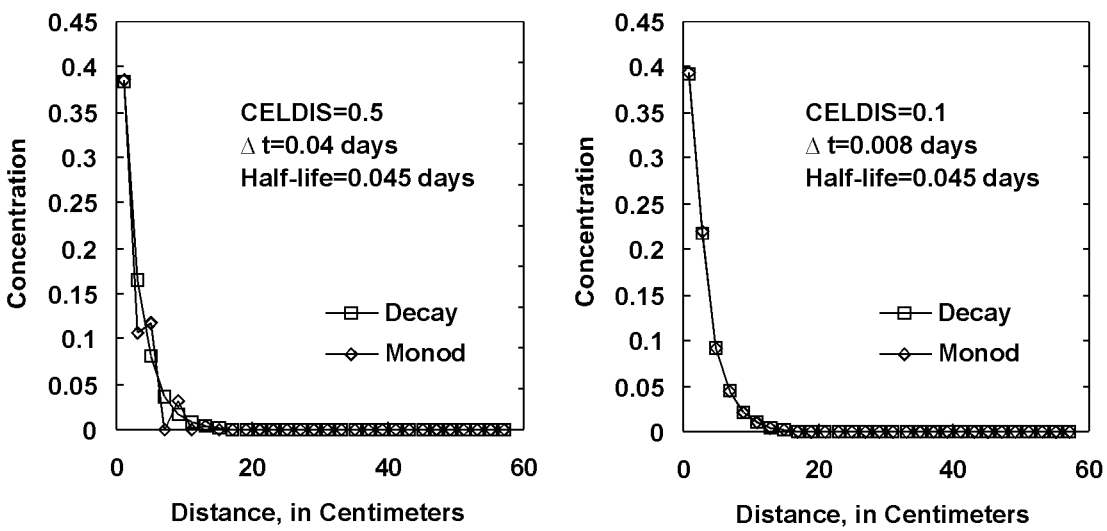

Figure 1. Plots showing the effect of time step size on biodegradation term accuracy.

Boundary and Initial Conditions

BIOMOC is a two-dimensional model. It may be used to simulate a two-dimensional areal aquifer, or a two-dimensional vertical cross-section through an aquifer (figure 2). For a two-dimensional vertical cross-section, the thickness specified in the input is equal to the width of the

slice and should be set to unity. Also, the aquifer hydraulic conductivity instead of transmissivity should be specified, and recharge occurs only in the top active grid blocks.

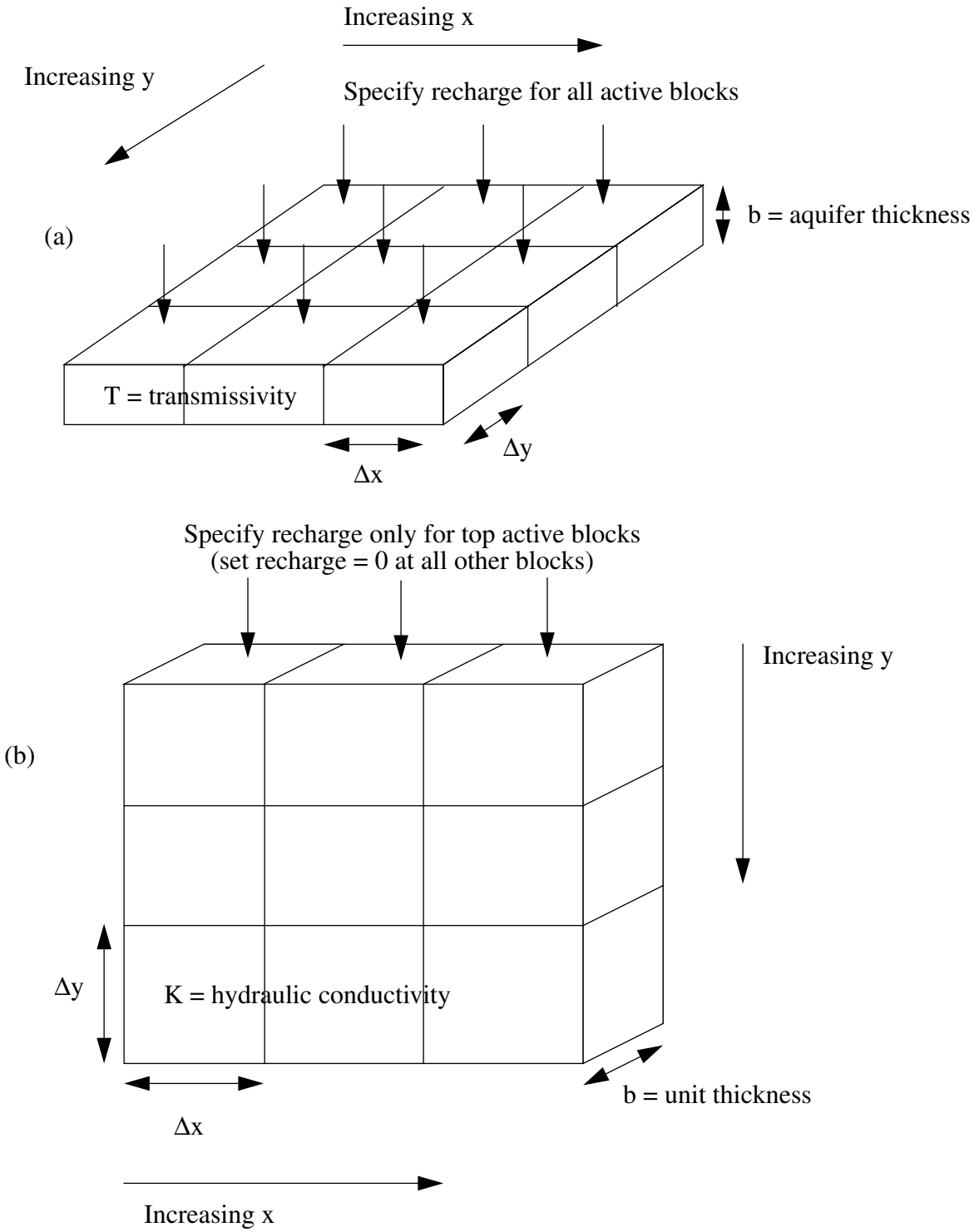

Figure 2. Geometry of (a) a two-dimensional areal simulation and (b) a vertical cross-section simulation illustrating the input parameters that must be specified for each case.

To solve the flow and transport equations, boundary and initial conditions must be specified for each equation. Initial heads must be specified for the transient flow equation, and initial concentrations (solutes and microbes) must be specified for the transport equation. The boundary conditions that can be specified for the flow equation are: no flow, prescribed flux, and a leaky head-dependent boundary that can also be used to set constant-head boundaries. No-flow boundaries are specified by setting the thickness (and hence transmissivity) of nodes to zero to prevent flow across the cell boundaries. BIOMOC requires that the model area be surrounded by a no-flow boundary, and therefore, the outer rows and columns of the finite-difference grid must have zero thickness. Within the model domain, inactive areas may be specified by setting the thickness to zero.

Prescribed flux boundaries may be set by specifying the flux rates for wells in the appropriate nodes (positive for withdrawal, negative for injection). Also, the recharge array may be used for this purpose. At leaky boundaries (for example, leakage through a confining layer or streambed):

$$W(x, y, t) = -\frac{K_z}{m}(H_s - h), \tag{18}$$

where K_z is the vertical hydraulic conductivity of the confining layer (LT^{-1}); m is the thickness of the confining layer (L); and H_s is the hydraulic head above the confining layer (L). K_z/m is defined as the leakance coefficient of the confining layer and has units of (T^{-1}). Constant head nodes may be specified by assigning a high leakance coefficient (such as 1.0 s^{-1}). This causes the head in the aquifer to be essentially equal to the specified value of H_s.

For solution of the transport equation, the solute concentrations in water entering the system across flow boundaries must be specified. If a constant-flux or leaky boundary represents a fluid source, then the chemical concentration of the source fluid (C') must be specified. If the boundary is a fluid sink, the concentration of the fluid leaving the system is equal to the concentration of the water in the aquifer at the location of the sink.

Mass Balance

Fluid and solute mass balances are calculated and reported by BIOMOC at the end of each flow and chemical output step, respectively. Cumulative totals, and rates of, inflows and outflows are reported for fluid flow. For the chemical mass balance, cumulative mass fluxes, mass production and decay, and total dissolved mass are reported. Chemical mass balance errors are estimated by first computing the difference between the net mass flux and the change in mass storage. This difference is then converted to a fractional error by dividing by either: (1) the average of the net flux and the change in mass storage; or (2) the estimated total mass currently in the aquifer (given by the difference between the initial solute mass and the net mass flux). The first method is appropriate when the net flux is large compared to the initial mass in the aquifer. The second method is better when the initial mass is large compared to the net flux. Details of the mass balance calculations are given by Konikow and Bredehoeft (1978).

COMPUTER PROGRAM

General Program Features

The details of the basic subroutines are documented by Konikow and Bredehoeft (1978). To avoid repetition, the discussion below will focus on the general features of the subroutines and their adaptation to handle multiple particle sets and biodegradation terms.

A list of the subroutines is given in table 1 and the general flow of the program is described below.

1. Input data are read into the program in subroutine PARLOD.

2. Particle sets are generated using the subroutine GENPT. The user specifies the number of particle sets to be used and the number of solutes associated with each particle set. Solutes with similar retardation coefficients can be associated with one particle set. An immobile particle set may also be specified to represent material on the sediments that is available for microbial utilization.

3. Subroutines ITERAT and SIP are used to solve the flow equation and determine the head distribution. For steady-state flow cases these subroutines are called only once. For transient flow cases, they are called at the beginning of each time step.

4. Average linear velocities are calculated using subroutine VELO, and stability criteria given in equations (15) and (16) are calculated using the maximum velocity of the particle set with the lowest retardation.

Table 1.--List of BIOMOC subroutines

Name	Purpose
MAIN	Control execution.
PARLOD	Data input and initialization.
ITERAT	Compute head distribution using subroutine SIP.
SIP	Strongly Implicit Procedure solver.
GENPT	Generate or reposition particles.
VELO	Compute hydraulic gradients, velocities, dispersion equation coefficients, and time increment for stable solution of transport equation.
MOVE	Move particles.
CNCON	Compute change in chemical concentrations and mass balance for transport model.
OUTPUT	Print head distribution and compute mass balance for flow model.
CHMOT	Print concentrations, chemical mass balance, and observation well data.
RETARD2	Compute nonlinear retardation factor and correction term for decay of sorbed solute.
SORB2	Compute sorbed concentration corresponding to concentration in solution.
BIO1	Compute biodegradation terms using multiple Monod formulation
BIO2	Compute biodegradation terms using minimum Monod formulation.

5. Subroutine MOVE is called to track the movement of the particle sets. For each particle set, the average linear velocity is adjusted by the retardation factor and moved accordingly. The time interval of the move is determined by the stability criteria and may be less than the time step size for solution of the flow equation.

6. Subroutine CNCON is called from within MOVE to compute the changes in concentrations due to biodegradation, hydrodynamic dispersion, and source fluid mixing for each solute. To calculate the production or loss of each solute by biodegradation, subroutine BIO1 is called when the user specifies multiple Monod kinetics, and subroutine BIO2 is called when the user specifies minimum Monod kinetics. The mass balance for each individual solute is also calculated in CNCON.

7. When time step particle moves are completed, a new time step is begun and procedures 3 through 6 are repeated.

8. If all time steps in a pumping period are completed and if there are multiple pumping periods specified, PARLOD is called to read in the new pumping period specifications and steps 2 through 6 are repeated.

9. The program terminates when the specified simulation time is completed. Frequency of output is controlled by user specified options.

Setting Dimensions

A parameter file (DIMS.INC) has been set up to facilitate changes in problem dimensions (see table 2). To change any problem dimension, the user can simply change the value of the appropriate parameter in this file. For example, to change the maximum number of particle sets from 2 to 5:

```
parameter (NPS=2)
```

should be changed to

```
parameter (NPS=5).
```

A considerable amount of computational effort is used in moving particle sets. For this reason one should try to minimize the number of particle sets by grouping solutes with similar retardation factors onto a single particle set. In addition, computational effort may be minimized by solving the transport problem over a subarea of the flow domain using a transport subgrid.

Input/Output File Information

All input to BIOMOC is specified in the file INPUT.DAT. The specific formats for the input data are given in Appendix C. Any consistent set of length, mass, and concentration units may be used to specify input parameters. Time units should be seconds unless the input format specifies otherwise (for example the pumping period length, PINT, is in years). Many output files are generated during a BIOMOC simulation. These files are explained below.

1. BIOMOC.OUT: This file contains the general input and output information. The head distribution and fluid mass balance are reported in this file. Also, particle movement information and chemical mass balances are printed here.

2. BIOVEL.OUT: This is the file to which flow velocities are written if the user requests this option.

3. BIOPROF.OUT: This file contains the concentrations of all solutes and microbes along row 2 of the grid, for each chemical output interval. This corresponds to concentrations at the water table in a vertical cross-section simulation, or along the flow line of a one-dimensional simulation.

4. BIOOBS*n*.OUT: This file gives the time history of concentrations (solutes and microbes) at the *nth* observation well. The time (second column) is reported in units of days.

Table 2.--Example DIMS.INC file used for setting up problem dimensions.

```
c  flow x-dimension
     parameter (NXD=220)
c  flow y-dimension
     parameter (NYD=3)
c transport x-dimension
     parameter (NXC=210)
c transport y-dimension
     parameter (NYC=3)
c  maximum number of particles
     parameter (NPTS=95000)
c  maximum number of particle sets
     parameter (NPS=2)
c  maximum number of solutes
     parameter (NSL=5)
c  maximum number of microbial populations
     parameter (NMC=1)
c  maximum number of microbial processes
     parameter (NPR=5)
c  maximum number of observation points
     parameter (NOB=5)
c  maximum number of profiles
     parameter (NPF=15)
c  maximum number of concentrations per particle set
     parameter (NPC=5)
```

5. BIOHEAD.OUT: This is the file to which heads are written if the user requests this option.

6. BIOCON*n*.OUT: This is the file to which final concentrations of the *nth* solute are written at the end of the simulation.

7. BIOPOP*n*.OUT: This is the file to which final concentration values of the *nth* microbial population are written at the end of the simulation.

By default, BIOMOC is set up to handle a maximum of five BIOOBS*n*.out files, fifteen BIOCON*n*.OUT files, and four BIOPOP*n*.OUT files. These may be changed by editing the dimensions in line:

```
      character*15 fname(5),fcname(15),fpname(4)    ,
```

and adding the necessary file names to lines:

```
      data fname/'bioobs1.out','bioobs2.out','bioobs3.out',
     &'bioobs4.out','bioobs5.out'/
```

```
 data fcname/'biocon1.out','biocon2.out','biocon3.out',
&'biocon4.out','biocon5.out','biocon6.out','biocon7.out',
&'biocon8.out','biocon9.out','biocon10.out','biocon11.out',
&'biocon12.out','biocon13.out','biocon14.out','biocon15.out'/
 data fpname/'biopop1.out','biopop2.out','biopop3.out',
&'biopop4.out'/             .
```

MODEL EVALUATION

To illustrate that BIOMOC correctly solves the governing equations in the model, several one-dimensional test cases are presented. The first set of tests compares BIOMOC with analytical solutions for one-dimensional transport having various reaction formulations. The second test compares BIOMOC results to experimental and modeling results presented by Chen and others (1992) for toluene and benzene degradation. The third test is a comparison to results obtained using the one-dimensional model of Kindred and Celia (1989) to simulate aerobic biodegradation and denitrification with cellular nutrient limitation.

One-Dimensional Transport with Linear Sorption, Decay, and Biodegradation

Several analytical solutions are available for special cases of the equation describing one-dimensional transport of a single solute with linear sorption, first-order decay, and biodegradation with no biomass growth. For this case, the applicable governing equation solved by BIOMOC is:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - R\lambda C - V_{max}\left(\frac{C}{K+C}\right) \quad . \tag{19}$$

In this equation it is assumed that both the dissolved and sorbed solute undergo first-order decay (as in the case of a radioactive substance), however, only the dissolved solute undergoes biodegradation.

Analytical solutions for transient and steady-state first- and zero-order decay and steady-state Monod degradation are presented and used to evaluate model performance. These analytical solutions may also be used to fit field data and obtain estimates of field biodegradation rates for simple flow systems and simple degradation pathways.

The analytical solutions presented below all have a constant-concentration (C_o) boundary condition at the inlet boundary. BIOMOC does not represent constant-concentration boundaries. Instead, in the BIOMOC simulations shown, an influx of water with a constant concentration of C_o was used to represent the boundary. In some cases, this resulted in a simulated constant concentration at the inlet grid block that was slightly less than C_o. For these cases, the simulated concentration was used for C_o in the analytical solution.

1. Transient zero-order production and first-order decay with dispersion and linear sorption (van Genuchten and Alves, 1982)

An analytical solution for the transient transport equation with first-order decay of dissolved solute and zero-order production has been developed by Selim and Mansell (1976) and is reported in van Genuchten and Alves (1982). The governing equation for this case is:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda C + \gamma \quad , \tag{20}$$

where γ is a zero-order decay term, and the first-order decay term, λ, is not multiplied by the retardation factor because it is assumed that sorbed solute does not decay. The initial and boundary conditions are given by:

$C = C_i$ at $t = 0$ for all x,
$C = C_0$ at $x = 0$, $t > 0$,

and

$$\frac{\partial C}{\partial x} = 0 \qquad \text{at } x = L \text{ for all } t.$$

The solution is:

$$C(x, t) = \left(C_i - \frac{\gamma}{\lambda}\right)A(x, t) + \left(C_o - \frac{\gamma}{\lambda}\right)B(x, t) \quad , \tag{21}$$

where:

$$\begin{aligned} A(x, t) = \exp\left(\frac{-\lambda t}{R}\right)\Bigg\{ & 1 - \frac{1}{2}erfc\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] - \frac{1}{2}\exp\left(\frac{vx}{D}\right)erfc\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right] \\ & - \frac{1}{2}\left[2 + \frac{v(2L - x)}{D} + \frac{v^2 t}{DR}\right]\exp\left(\frac{vL}{D}\right)erfc\left[\frac{R(2L - x) + vt}{2(DRt)^{1/2}}\right] \\ & + \left(\frac{v^2 t}{\Pi DR}\right)^{1/2}\exp\left[\frac{vL}{D} - \frac{R}{4Dt}\left(2L - x + \frac{vt}{R}\right)^2\right]\Bigg\} \end{aligned} \quad , \tag{22}$$

$$B(x, t) = B_3(x, t) / B_4(x) \quad , \tag{23}$$

$$\begin{aligned} B_3(x, t) = & \frac{1}{2}\exp\left[\frac{(v - u)x}{2D}\right]erfc\left[\frac{Rx - ut}{2(DRt)^{1/2}}\right] + \frac{1}{2}\exp\left[\frac{(v + u)x}{2D}\right]erfc\left[\frac{Rx + ut}{2(DRt)^{1/2}}\right] \\ & + \frac{(u - v)}{2(u + v)}\exp\left[\frac{(v + u)x - 2uL}{2D}\right]erfc\left[\frac{R(2L - x) - ut}{2(DRt)^{1/2}}\right] \\ & + \frac{(u + v)}{2(u - v)}\exp\left[\frac{(v - u)x + 2uL}{2D}\right]erfc\left[\frac{R(2L - x) + ut}{2(DRt)^{1/2}}\right] \\ & - \frac{v^2}{2\lambda D}\exp\left(\frac{vL}{D} - \frac{\lambda t}{R}\right)erfc\left[\frac{R(2L - x) + vt}{2(DRt)^{1/2}}\right] \end{aligned} \quad , \tag{24}$$

$$B_4(x) = 1 + \left(\frac{u - v}{u + v}\right)\exp\left[-\frac{uL}{D}\right] \quad , \tag{25}$$

and

$$u = v\left(1 + \frac{4\lambda D}{v^2}\right)^{1/2} \quad . \tag{26}$$

For the special case of K>>C, the Monod kinetics term on the right-hand-side of (19) simplifies to $(V_{max}/K)\,C$, a first-order decay term. If there is no sorption (R=1), and V_{max}/K is set equal to λ, the decay term in (19), $R\lambda C$, and the Monod term are equivalent. Numerically, however, these two terms are evaluated very differently in BIOMOC. The first-order decay term is evaluated by decaying the concentrations of the particles directly, leading to an accurate solution. However, the Monod kinetics terms are calculated using the block concentrations obtained by averaging particle concentrations. Furthermore, the term is evaluated explicitly using the average of the concentration from the previous time step and the advected concentration. To test the accuracy of the explicit evaluation of the Monod term, a simulation was conducted with R=1 and Monod parameters such that $K>>C$ and $V_{max}/K = \lambda$. The parameters used in the simulation are given in table 3. Because BIOMOC does not provide for constant concentration boundaries, a constant influx concentration boundary was used. Figure 3 shows that even though the Monod calculations are performed explicitly, there is excellent agreement between the numerical and analytical solutions.

Table 3.--Parameters used in transient zero-order decay, first-order decay, and first-order decay with sorption simulations.

	Zero-Order Decay	First-Order Decay	First-Order Decay with Retardation
L (cm)	200	200	200
Δx (cm)	2	2	2
D (cm^2/d)	37.5	37.5	37.5
v (cm/d)	25	25	25
C_i (mg/L)	0	0	0
C_o (mg/L)	1	1	1
$t_{1/2}$ (d)	1e+08	4.5	4.5
λ (d^{-1})	7e-09	0.154	0.154
γ (d^{-1})	-0.154	0	0
R	1	1	2
V_{max} (d^{-1})	1.54e-02	1.54e+02	1.54e+02
K (mg/L)	0.0001	1000	1000
Y	0	0	0
X (mg/L)	1	1	1
t (d)	4	4	4

When there is retardation due to linear sorption the numerical solutions obtained using decay and the Monod expression are no longer equivalent. For first-order decay, it is assumed in BIOMOC that the solute sorbed onto the solids also decays at the rate λ. However, for the biodegradation term it is assumed in BIOMOC that only solute in solution is biodegraded. Thus, the resulting concentrations are higher than for the first-order decay simulation. The difference between the two solutions is illustrated in figure 3. For field simulations in which both retardation and degrdation are significant, use of the BIOMOC biodegradation term more accurately represents the processes because only the dissolved phase is subject to biodegradation.

For the special case of $K << C$, the Monod kinetics term on the right-hand-side of equation 19 simplifies to V_{max}, a zero-order decay term equivalent to $-\gamma$ in equation 20. A comparison of the analytical solution and the numerical solution for this special case is given in figure 3 and the parameters used in the model simulation are given in table 3. There is excellent agreement between the numerical and analytical solutions.

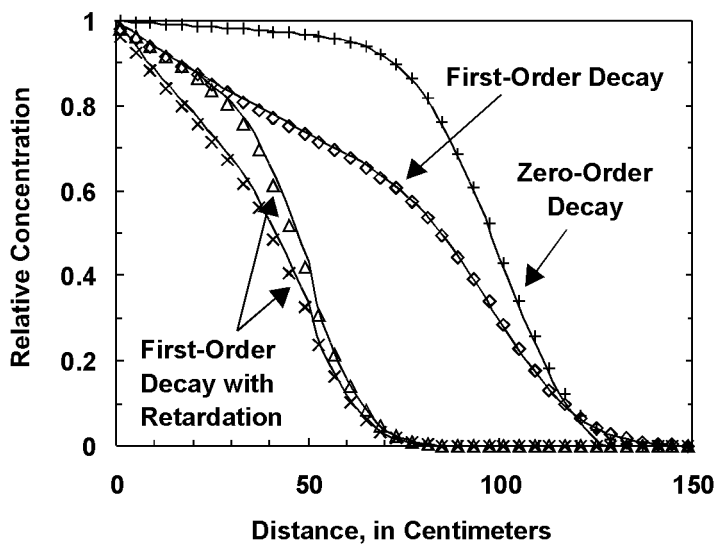

Figure 3. Comparison of analytical (lines) and numerical (points) solutions for transient zero-order decay (+), first-order decay (◊), first-order decay of dissolved phase with retardation (Δ), and first-order decay of dissolved and sorbed phase with retardation (X). For the numerical solutions, only the values at the odd-numbered nodes are shown.

2. Steady-state zero-order production and first-order decay with dispersion and linear sorption (van Genuchten and Alves, 1982)

An analytical solution for the steady-state transport equation with first-order decay and zero-order production has been developed by van Genuchten and Alves (1982). The governing equation is:

$$0 = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \lambda C + \gamma \quad , \tag{27}$$

with boundary conditions:

$$C = C_0 \text{ at } x = 0,\ t > 0,$$

and

$$\frac{\partial C}{\partial x} = 0 \qquad \text{at } x = L.$$

The solution is:

$$C(x) = \frac{\gamma}{\lambda} + \left(C_o - \frac{\gamma}{\lambda} \right) A(x) \qquad , \tag{28}$$

where:

$$A(x) = \frac{\exp\left[\frac{(v-u)x}{2D}\right] + \left(\frac{u-v}{u+v}\right)\exp\left[\frac{(v+u)x}{2D} - \frac{uL}{D}\right]}{1 + \left(\frac{u-v}{u+v}\right)\exp\left[-\frac{uL}{D}\right]} \qquad , \tag{29}$$

and

$$u = v\left(1 + \frac{4\lambda D}{v^2}\right)^{1/2} \qquad . \tag{30}$$

Figure 4 shows a comparison between the analytical and numerical solutions for a case with zero-order decay only, and a case with first-order decay. The parameters used for these solutions are given in table 4. In both cases the agreement between the two solutions is excellent. For the zero-order decay case there is a slight deviation from the analytical solution at the downgradient edge of the front.

3. Steady-State Monod kinetics with no dispersion (Parlange and others, 1984)

Parlange and others (1984) presented an analytical solution to equation (19) for the case of Monod degradation with no dispersion and no decay:

$$x = \frac{v}{V_{max}}\left[K\ln\left(\frac{C_o}{C}\right) + C_o - C \right] , \tag{31}$$

with boundary conditions:

$$C = C_0 \text{ at } x = 0,$$

and

$$\frac{\partial C}{\partial x} = 0 \qquad \text{at } x = L.$$

This solution may be used to calculate the distance x corresponding to a given concentration *C(x)*. To evaluate the full Monod kinetics term calculation in equation (19), this analytical solution was compared to the numerical solution obtained using the parameters given in table 5. The analytical and numerical solutions agree well as shown in figure 5.

Table 4.--Parameters used in steady-state zero-order decay and first-order decay simulations.

	Zero-Order Decay	First-Order Decay
L (cm)	200	200
Δx (cm)	2	2
D (cm^2/d)	37.5	37.5
v (cm/d)	25	25
C_o (mg/L)	0.939	0.924
$t_{1/2}$ (d)	1e+07	1
λ (d^{-1})	7e-08	0.693
γ (d^{-1})	-0.5	0
V_{max} (d^{-1})	5.01e-01	6.93e+02
K (mg/L)	0.0001	1000
Y	0	0
X (mg/L)	1	1
t (d)	183	183

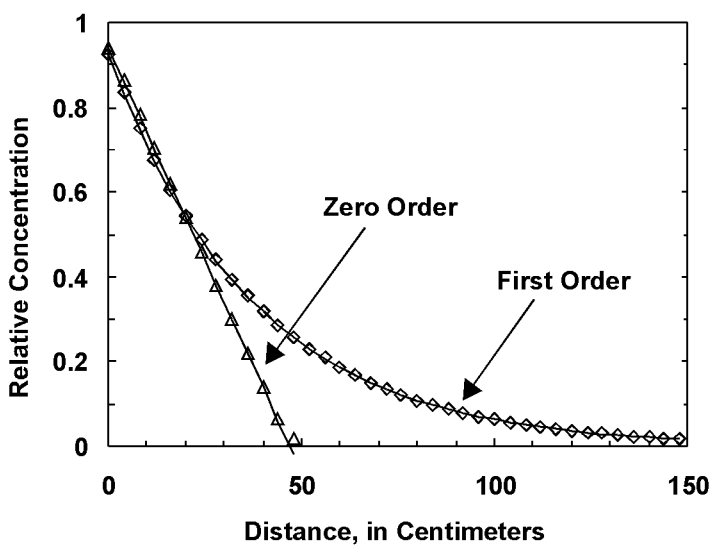

Figure 4. Comparison of analytical (lines) and numerical (points) solutions for steady-state zero-order decay (Δ) and first-order decay (◊). For the numerical solutions, only the values at the odd-numbered nodes are shown.

Table 5.--Parameters used in steady-state Monod kinetics simulation.

	Monod Kinetics
L (m)	200
Δx (m)	1
v (m/d)	0.1
C_o (mg/L)	1
V_{max} (d^{-1})	4.77e-03
K (mg/L)	0.5
Y	0
X (mg/L)	1
t (d)	1826

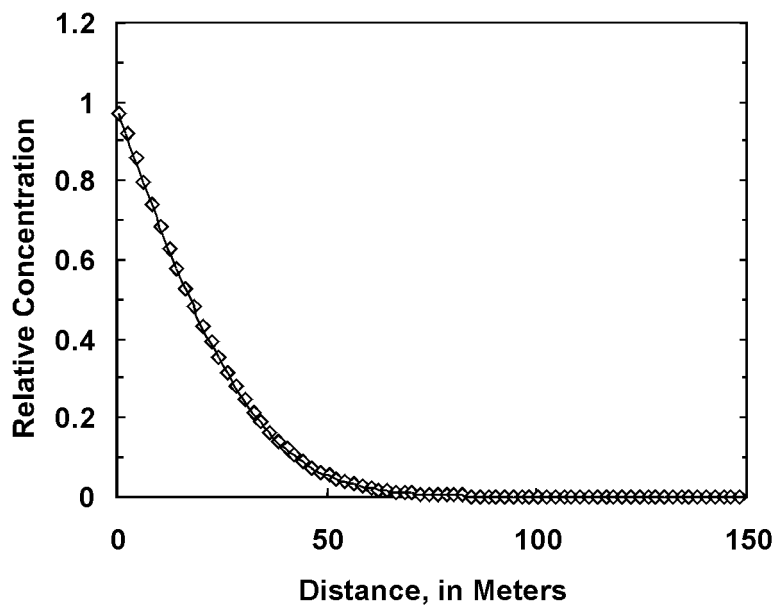

Figure 5. Comparison of analytical (line) and numerical (points) solutions for steady-state Monod kinetics. For the numerical solution, only the values at the even numbered nodes are shown.

Aerobic Biodegradation and Transport of Toluene and Benzene

Chen and others (1992) presented experimental and simulation results for toluene and benzene transport and biodegradation in a continuous flow, water saturated, soil column. A constant composition solution of toluene (20 mg/L), benzene (20 mg/L), and hydrogen peroxide (132.7 mg/L) was fed to the column. Effluent samples were analyzed for toluene and benzene concentrations an a mathematical model was used to predict the effluent concentrations. Model parameters were independently estimated using laboratory measured and literature values (table 6). The modeling approaches used by Chen and others (1992) differ significantly from those in BIOMOC. They used the multiple Monod formulation, but represented the biomass as attached microcolonies with biophase diffusion. The governing equations were solved using the Galerkin finite-element method and a set iterative solution scheme.

Table 6.--Parameters used in the simulation of aerobic degradation of toluene and benzene.

Z-direction grid spacing	0.01 m	
Column length	0.56 m	
Porosity	0.38	
Average linear velocity	0.33 m/d	
Longitudinal dispersivity	0.0224 m	
Simulation time	10 d	
Time step size	0.005 d	
Aerobic degradation of toluene		
V_{max}	9.9 d^{-1}	
K_{tol}	17.4 mg/L	
K_{DO}	0.1 mg/L	
Y	0.5 mg/mg	
β_{tol}	1.0	
β_{DO}	2.19	
Initial toluene degrading biomass, X_o		0.82 mg/L
Toluene-degrading biomass death rate, d_k		0.1 d^{-1}
Aerobic degradation of benzene		
V_{max}	8.3 d^{-1}	
K_{tol}	12.2 mg/L	
K_{DO}	0.1 mg/L	
Y	0.5 mg/mg	
β_{tol}	1.0	
β_{DO}	2.15	
Initial benzene degrading biomass, X_o		0.21 mg/L
Benzene-degrading biomass death rate, d_k		0.1 d^{-1}

Figure 6 shows the experimental data, the simulation results obtained by Chen and others (1992), and those obtained using BIOMOC with the multiple Monod formulation. The Chen and others model underpredicted toluene concentrations and BIOMOC gave a slight over-prediction. Chen and others found that their initial experimental estimate of benzene degrading biomass underpredicted benzene concentrations. They reduced the initial benzene degrading biomass by a factor of four in order to fit the experimental data (results shown in figure 6). Using the modified biomass estimate of Chen and others, benzene concentrations are overpredicted by BIOMOC, except at late times (figure 6). A good fit between BIOMOC and the experimental data can be obtained by reducing the experimental estimate of initial benzene degraders by only a factor of two (not shown). Thus, the difference in the two models is within the range of uncertainty in the benzene degrading biomass estimates.

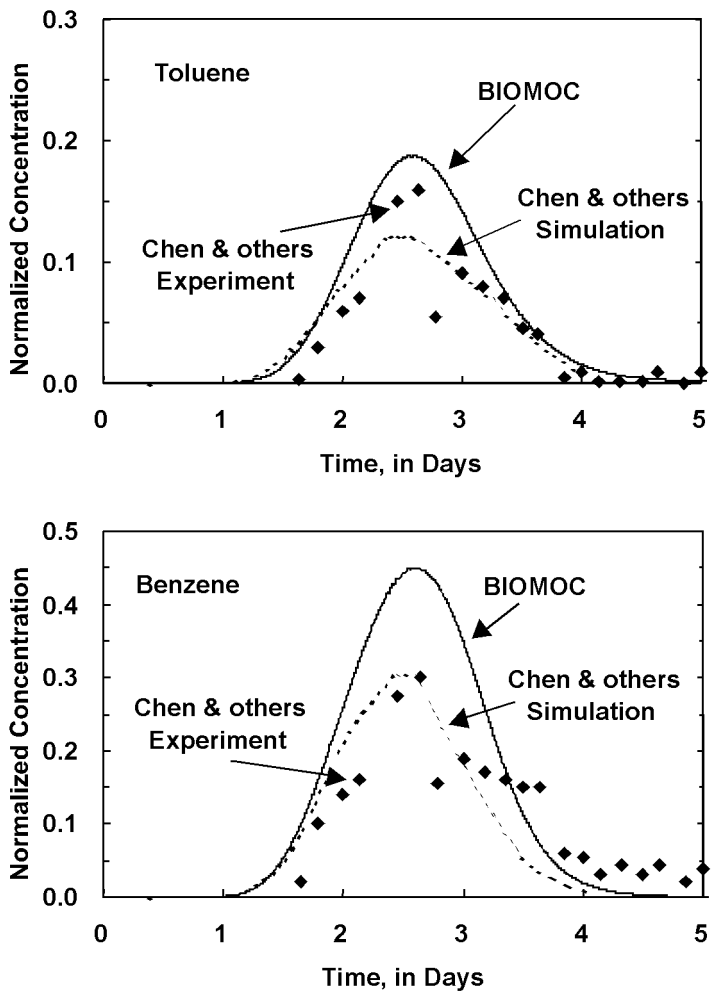

Figure 6. Experimental and simulation results of Chen and others (1992) and BIOMOC results for aerobic degradation of toluene and benzene.

Aerobic Biodegradation and Denitrification of a Substrate with Cellular Nutrient Limitation

The model of Kindred and Celia (1989) (referred to as KC in the following discussion) was chosen for evaluation purposes because it is the most comprehensive in terms of biodegradation processes, and because of its accurate numerical method. The numerical method uses weight functions that adapt to the changing character of the nonlinear governing equations, thus providing very accurate results for reactive transport problems (Celia and others, 1989). The biodegradation reaction terms in the KC model are calculated using the macroscopic approach and the minimum Monod formulation. The minimum Monod formulation, as implemented by Kindred and Celia (1989), was used in the BIOMOC comparison simulations.

The test simulation included aerobic degradation of a substrate followed by denitrification, with cellular nutrient limitation (represented by availability of elemental nitrogen). Noncompetitive inhibition was used to suppress denitrification while dissolved oxygen was present. The KC model assumes that cellular nutrients incorporated into the biomass are released by decay and that the biomass can decay to less than the initial background concentration. To be consistent with the KC model, a modified form of BIOMOC that included these assumptions was used for this comparison. The flow and transport parameters used are given in table 7. A uniform, steady flow was used with initial substrate, dissolved oxygen, nitrate, and elemental nitrogen concentrations of 0, 3, 2, and 0.01 mg/L, respectively. At the inlet, the substrate, dissolved oxygen, nitrate, and nitrogen concentrations were fixed at 10, 3, 2, and 0.01 mg/L, respectively. The right hand boundary condition for all solute concentrations was $dC/dx=0$.

The results, plotted in figure 7, show good agreement with some slight differences, mainly near the inlet where concentration changes are rapid and the difference in bacterial growth calculations between the two models becomes apparent. BIOMOC uses the average of the concentration from the previous time step and the concentration at the current time step after advection of the particles (C_i^*) to explicitly calculate the biodegradation reaction terms and the biomass growth. The KC model uses extrapolated concentration values for the current time step to calculate the biodegradation reaction terms, and then uses the average of the extrapolated value and the new time step concentration value to calculate the biomass growth. The minor difference between the two solutions suggests that the computational savings gained by using an explicit approximation for these terms in BIOMOC is justified.

Table 7.--Parameters used in the simulation of aerobic degradation and denitrification with cellular nutrient limitation.

X-direction grid spacing	2 m	
Porosity	0.38	
Hydraulic conductivity,	1×10^{-4} m/s	
Average linear velocity	1.0 m/d	
Longitudinal dispersivity	0.2 m	
Simulation time	68 d	
Time step size	0.2 d	
Aerobic degradation of substrate		
V_{max}	1.0 d^{-1}	
K_{sub}	0.1 mg/L	
K_{DO}	0.14 mg/L	
Y	0.25 mg/mg	
β_{sub}	1.0	
β_{DO}	2.0	
Initial aerobic biomass, X_o		0.2 mg/L
Aerobic biomass inhibition constant, k_{bio}		1.0 mg/L
Aerobic biomass death rate, d_{aer}		0.01 d^{-1}
Nitrate reduction of substrate:		
V_{max}	1.0 d^{-1}	
K_{sub}	0.1 mg/L	
$K_{nitrate}$	0.1 mg/L	
Y	0.2 mg/mg	
β_{sub}	1.0	
$\beta_{nitrate}$	2.0	
Noncompetitive inhibition constant, $k_{nc\ DO}$		0.001 mg/L
Nitrogen uptake:		
K_{nut}	0.01 mg/L	
Y_{nut}	7.0 mg/mg	
Initial nitrate-reducing biomass, X_o		0.1 mg/L
Nitrate-reducing biomass inhibition constant, k_{bio}		1.0 mg/L
Nitrate-reducing biomass death rate, d_{nit}		0.01 mg/L

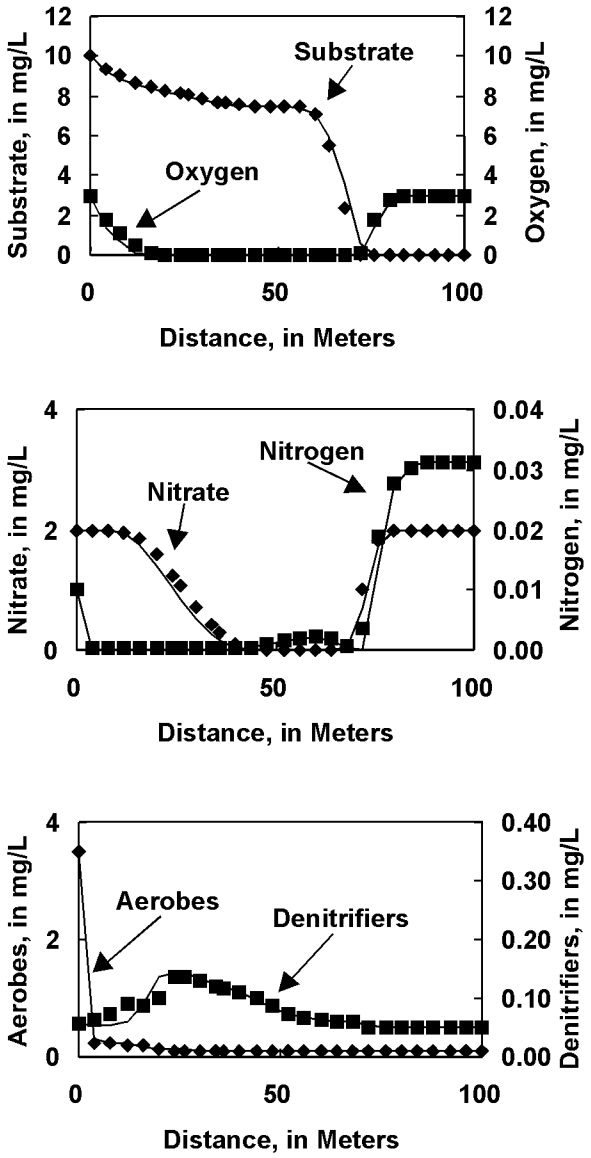

Figure 7. Simulation results obtained using BIOMOC (lines) and the model of Kindred and Celia (1989) (symbols) for aerobic degradation and nitrate reduction with cellular nutrient limitation.

EXAMPLE APPLICATIONS

To demonstrate the flexibility of BIOMOC and illustrate its use, two example applications of the model are described. The first example simulates steady-state, one-dimensional, transport and degradation of chlorinated solvents with no biomass growth at a site located on Dover Air Force Base, Delaware. In this application, both reductive dehalogenation and aerobic degradation are simulated. The anaerobic reactions are inhibited by the presence of significant levels of dissolved oxygen. The second application is a two-dimensional, transient simulation of the Bemidji, Minnesota

crude-oil spill site. In this application, the evolution of redox zones and microbial populations is simulated.

The first step in applying BIOMOC to a field problem is to characterize the flow at the site and to define the geometry and boundary conditions of the system. In addition, a conceptual model of the biodegradation at the site must be developed. This includes defining the active biodegradation processes by specifying the substrates, reactants, products, and the microbial population mediating each process.

Following conceptual model development, estimates of flow, transport, and biodegradation parameters must be made. These may be based on a combination of field measurements and observations, laboratory values, and/or literature values. As with any model, there may be considerable uncertainty involved in estimating parameters and this should be taken into account in the interpretation of model results.

Application to Chlorinated Solvents

Over the past ten years, documentation of the biological transformation of chlorinated solvents in the environment has been steadily accumulating. The various reactions that can occur were reviewed by Vogel et al. (1987). Under strictly anaerobic conditions, tetrachloroethene (PCE), trichlorethene (TCE), dichlorethene (DCE), and vinyl chloride (VC) can be degraded by reductive dehalogenation (Vogel and McCarty, 1985). Under aerobic conditions, degradation of a primary substrate may result in cometabolic epoxidation of these compounds. More recently, VC and DCE have also been demonstrated to degrade when present as the sole carbon source (Davis and Carpenter, 1990; Klier and others, *in press*). The ideal conditions for natural attentuation of chlorinated solvents occur when either co-contaminants or natural organic carbon are present near the source to drive the initial steps of reductive dehalogenation (Wiedemeier et al., 1996). Once the initial contaminants are converted to less chlorinated compounds such as VC and DCE, these compounds will degrade if oxygen is present downgradient of the source area. In this example, the BIOMOC model is used to understand how an ideal zonation of anaerobic and aerobic conditions is established and maintained in an aquifer in which natural remediation of chlorinated solvents is occurring. The losses due to cometabolic transformation processes have been neglected. However, it is possible to account for these using the method given by Semprini et al. (1991) with the competitive inhibition capabilty of BIOMOC.

This example application is based on data from a site located on Dover Air Force Base where natural attenuation of chlorinated solvents is occurring. Using the model it was possible to analyze several important issues. First, because reductive dehalogenation reactions produce some contaminants as they consume others, it is necessary to model both the production and consumption of each compound. As a result of the full accounting provided by the model, it is possible to obtain the true transformation rate of each species rather than the net disappearance rate. Second, the reductive dehalogenation reactions occur only when dissolved oxygen (DO) concentrations are very low and a suitable electron donor is present. Using the model it is possible to determine the mechanism by which low dissolved oxygen conditions are maintaned near the source area and also whether adequate concentrations of an electron donor are present to drive the reductive dehalogenation. Finally, it was possible to examine the source of the dissolved oxygen that drives oxidation of the less chlorinated compounds downgradient of the source area.

Site Description

A complete description of the site may be found in a report by the U.S. Army Corps of Engineers and Dames and Moore (1994). Figure 8 shows time-averaged data from a one-dimensional flowline beginning immediately under landfill LF15 and including wells located 138 m, 218 m, and 313 m downgradient, respectively. The presence of DCE, VC, and methane in samples from below LF15 indicates that the original waste PCE and TCE are partially transformed by reductive dehalogenation in the landfill before entering the ground water.

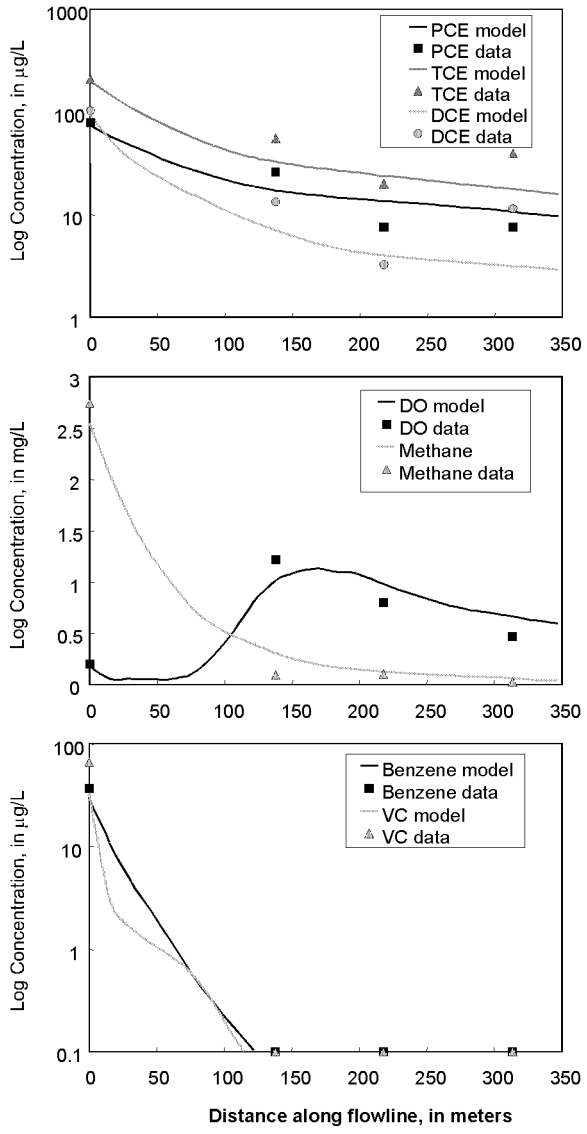

Figure 8. Comparison of modeled and observed concentrations of chlorinated aliphatics and other compounds along a simulated flowline at Dover AFB. The observed values are averages over four years.

Within the ground water, a complex zonation of aerobic and anaerobic conditions prevails. Samples from the well at 138 m have non-detectable VC and benzene concentrations and DO values of about 1 mg/L which is about one-third of the background value. In addition, the concentrations of methane and the chlorinated degradation products have declined. The presence of higher DO, and the absence of VC and benzene indicates that aerobic transformation processes are important between the landfill and this location. Presumably the source of the DO is recharge water that enters the aquifer along a swale that runs between the two sites. Farther downgradient, along the same flowline, at 218 m and 313 m, the concentrations of methane, DO, TCE, PCE, and DCE decline slowly. From these data is appears that influx of DO from recharge becomes less important and that DO levels decrease as methane and DCE are oxidized. In this area low average DO levels may coexist with anaerobic pockets in which reductive dehalogenation of PCE and TCE are coupled to oxidation of methane. These data provide a conceptual framework and constrain a one-dimensional model of the aerobic and anaerobic biotransformation processes acting on the contaminants downgradient of LF15.

The Conceptual Model

The redox conditions along a hypothetical flow path are anaerobic below the LF15 source area and evolve to slightly aerobic by the first monitoring well. By the third and fourth well, dissolved oxygen has again declined. Although the field conditions in the aquifer downgradient of LF15 are complex, a simple conceptual model serves to illustrate some of the important processes. Seven solutes and two microbial populations are accounted for in the model. The solutes are: PCE, TCE, DCE, VC, benzene, methane, and DO. These participate in seven biological transformation reactions: three anaerobic and four aerobic. In the three anaerobic reactions, methane oxidation is coupled to reductive dechlorination of PCE, TCE, and DCE. This reaction can also be coupled to other organic compounds that are present in the ground water such as benzene, low molecular weight fatty acids, and toluene. In the present model, methane is used because it has been detected in relatively high concentrations at the source area and it is also present in the downgradient wells. The model uses noncompetitive inhibition to slow the rate of reductive dehalogenation in the presence of significant DO concentrations. In the four aerobic reactions, DO is consumed during the oxidation of DCE, VC, benzene, and methane. The first microbial population consists of strict anaerobes that perform the three reductive dehalogenation reactions. The second microbial population consists of aerobic heterotrophs that perform the four aerobic transformations. Degradation by cometabolic processes was not accounted for in this conceptual model.

The model simulates concentrations along a hypothetical one-dimensional flow tube that starts below LF15 and extends 457 m downgradient. The concentrations of PCE, TCE, DCE, and VC in the influx from the landfill are set to the average of the observed concentrations from 1988, 1989, 1994, and 1995. The concentration of benzene is set to the 1995 value because this is the highest benzene concentration ever observed below this landfill. The DO and methane concentrations are also set to the 1995 values because this is the first year that these concentrations were measured. Recharge water with a DO concentration of 10 ppm enters the model flowline betwen the landfill and 198 m downgradient. This roughly corresponds to the location of a swale that overlies the flowpath in this area. The model was run for a period of eight years. This is a sufficient amount of time for the contamination front to migrate completely across the model length. Thus the results represent a steady-state simulation of the contaminant concentrations.

The above conceptual model was varied to test several alternate hypotheses. The source of dissolved oxygen in the ground water downgradient of the landfill was tested with two possible

scenarios. In the first, dissolved oxygen entered only with the recharge water. In the second, a small amount of dissolved oxygen was present in the water below the landfill and dissolved oxygen was also supplied with the recharge water. Two possible electron donors for reductive dehalogenation were tested. These were benzene and methane. Finally, the amount of DCE transformed by aerobic versus anaerobic degradation was varied by adjusting the model concentration of dissolved oxygen that inhibits reductive dehalogenation. In this example, the results from the best conceptual model will be presented and the shortcomings of these alternate scenarios will be discussed.

Model Parameter Estimates

Flow and transport parameters

The values for the specified heads, the hydraulic conductivity and the recharge rate were based on estimates made by U.S. Army Corps of Engineers and Dames and Moore (1994). At the landfill end the flow boundary condition is set to a constant head of 3.66 m while at the downgradient boundary the head is set to 2.13 m. The hydraulic conductivity is set to 27 m/day and the recharge rate over the first 198 m of the flow path is set to 39.4 cm/yr. The porosity is a uniform value of 0.3. These values result in an average linear velocity of about 0.335 m/day, which is consistent with estimates of the velocity in the aquifer. Longitudinal dispersion is set to 0.3 m and transverse dispersivity is 0.003 m. The model also includes the effect of linear sorption, and the values for k_d were estimated using an organic carbon fraction of 250-350 mg/kg and octanol-water partition coefficients from the literature. Because of the low organic carbon fraction, only a minimal amount of the contaminants are sorbed to the aquifer material.

Biodegradation kinetics parameters

Initial first-order rates were estimated from the field data. Because the first-order degradation model is an approximation to the full Monod kinetics model, it is necessary to convert the first-order rate constants to Monod kinetics parameters for use in the BIOMOC model. The formula relating a first-order rate to the Monod kinetics parameters is: $k \sim V_{max}/K$ where k is the first-order rate constant (d^{-1}), V_{max} is the maximum specific substrate utilization rate (µg/L-d), and K is the half-saturation constant (µg/L). This expression has an approximation error of less than one percent when the value of K is at least one hundred times that of the maximum simulated concentrations. Thus, in all cases, the value of K was set to 10,000 µg/L to ensure that the Monod reaction kinetics in the code are approximately equivalent to first-order kinetics. In addition, the dependence on the microbial population is disabled by setting the biomass value for both microbial populations to 1.0 with a yield, of Y=0. In this way, the reaction rate represents the ability of the aquifer to transform the contaminants. A noncompetitive inhibition expression is used to inhibit reductive dechlorination in the presence of DO. The effect of this expression is to slow the reaction rate when the concentration of DO is significant relative to the preset value of the inhibition constant. The inhibiting oxygen concentrations for the reductive dechlorination of PCE to TCE and TCE to DCE are set to $k_{nc}DO$=800 µg/L. The inhibiting oxygen concentration for the DCE to VC transformation is set to $k_{nc}DO$=100 µg/L.

Uptake coefficients

The uptake coefficients for the reactions are computed from the reaction stoichiometries and the molecular weights. The following procedure was used to determine the model inputs. The reaction converting PCE to TCE is derived by coupling the half-reaction for the reductive dechlorination of PCE given by McCarty and Wilson (1992):

$$CCl_2 = CCl_2 + H^+ + 2e^- \rightarrow CHCl = CCl_2 + Cl^-$$

to the half-reaction for the oxidation of methane:

$$CH_4 + 2H_2O \rightarrow CO_2 + 8e^- + 8H^+$$

The net reaction is:

$$4CCl_2 = CCl_2 + CH_4 + 2H_2O \rightarrow 4CCl_2 = CCl + CO_2 + 4HCl$$

The same method yields the following reactions for the reductive dechlorination of TCE and DCE coupled to methane oxidation:

$$CHCl = CHCl + 2O_2 \rightarrow 2CO_2 + 2HCl$$
$$2CH_2 = CHCl + 5O_2 \rightarrow 4CO_2 + 4HCl + 2H_2O \quad .$$

Next the oxidation of DCE, VC, benzene, and methane are coupled to the reduction of DO:

$$C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \, .$$

These reactions are used to derive the uptake ratios of reactants and products for input to the BIOMOC program. Each reaction has a primary solute that has an uptake ratio of β=1. For the remaining solutes involved in the reaction, the uptake ratios, β_i, are derived using the formula:

$$\beta_i = \frac{\alpha_i \times MW_i}{\alpha_1 \times MW_1} \tag{32}$$

where α is the stoichiometric coefficient of the solute in the reaction and MW is the molecular weight. The subscript 1 refers to the primary solute for the reaction and the subscript *i* refers to the solute for which the uptake ratio is being computed. The uptake ratios used for the seven modeled reactions are shown in table 8. A positive value indicates that the compound is consumed and a negative value indicates production. Other model parameters used in the simulation are listed in table 9. Table 10 lists the section of the BIOMOC input file that specifies the biodegradation parameters to illustrate how the biodegradation processes and parameters of this example are setup in the model input.

Model Results

Figure 8 shows the model results and the data from the four wells along the flowline. The results in the plot represent a one-dimensional, steady-state solution to the equations. This is achieved after about 7 years. The PCE front takes the longest to migrate across the model domain because it is retarded by a factor of about 1.5. Focusing first on the model DO curve, the DO entering the left boundary and with the recharge is consumed between 0 and 122 m by the oxidation of VC and benzene. When the DO is low, then the reductive dehalogenation reactions can take place. Thus where DO is low between 1 and 122 m, the rate of PCE, TCE, and DCE reduction is fastest. The production of VC by the reduction of DCE causes the VC curve to flatten in this section. Beyond 122 m, DO builds back up because benzene and VC are no longer present in significant concentrations and DO is continuing to enter with the recharge water until 198 m. The DO increase causes the rate of

Table 8.--Uptake coefficient used in the chlorinated solvent example.

Reaction	β_{PCE}	β_{TCE}	β_{DCE}	β_{VC}	$\beta_{benzene}$	$\beta_{methane}$	β_{DO}
$PCE \rightarrow TCE$	1	-0.792	0	0	0	0.0241	0
$TCE \rightarrow DCE$	0	1	-0.738	0	0	0.0304	0
$DCE \rightarrow VC$	0	0	1	-0.644	0	0.0412	0
$DCE \rightarrow CO_2$	0	0	1	0	0	0	0.660
$VC \rightarrow CO_2$	0	0	0	1	0	0	1.29
$benzene \rightarrow CO_2$	0	0	0	0	1	0	3.1
$methane \rightarrow CO_2$	0	0	0	0	0	1	4.0

reduction of PCE and TCE to slow down because they are inhibited by the presence of DO. However, the methane continues to be oxidized and this keeps the DO values at an intermediate level of about 800 µg/L, allowing the reduction of PCE and TCE to continue at a slow rate. The reduction of DCE slows to a negligible amount because the inhibition concentration is set to 100 µg/L. At this point, however, the oxidation of DCE can occur so that any DCE produced by TCE reduction is oxidized and the DCE values continue to drop with distance.

Several alternate scenarios were tested but, in each case, problems with the results suggest that the final scenario presented above better represents the processes occurring in the field. In one alternate scenario, dissolved oxygen was not present in the ground water entering the model boundary at the landfill and was supplied only with the recharge water. The simulation results, in this case, showed that the VC did not degrade by the second monitoring well at 138 m. Based on the fact that VC has never been detected in this well, the modeling suggests that the oxygenated backgound water that mixes with the anaerobic infiltration below that landfill is an important source of DO. In another scenario, benzene was used as an electron donor instead of methane. However, because benzene is not present in the second monitoring well, it is not available to drive reductive dehalogenation downgradient of this well. Methane, however, is present in the wells farther downgradient. Thus with methane as the electron donor it is possible to simulate continued slow reductive dehalogenation over the section from 213 to 457 m. Finally, the amount of DCE transformed by aerobic versus anaerobic degradation was varied by adjusting the concentration of dissolved oxygen in the model that inhibits reduction of DCE to VC. In the final modeling scenario, the reduction of DCE to VC was allowed to proceed only when DO was around 100 ppb or lower. If the reaction is allowed to proceed at higher DO concentrations (up to 800 ppb), then VC accumulates in the downgradient part of the model. Because VC has never been detected in this area, the model results indicate that the reduction of DCE to VC reaction should be inhibited at DO concentrations of 100 ppb or higher. The continued transformation of DCE in the downgradient part of the model where DO concentrations are above the inhibiting concentration occurs by aerobic degradation.

Table 9.-- Model parameters used in the chlorinated solvent example.

X-direction grid spacing		3.0 m
Total length		457 m
Porosity		0.30
Average linear velocity		0.34 m/d
Longitudinal dispersivity		0.3 m
Simulation time		8.0 yr
Time step size		2.7 d
Anaerobic Biotransformation of PCE to TCE		
	V_{max}	17.3 d^{-1}
	K_{PCE}	10,000 µg/L
	K_{meth}	0.1 µg/L
	Y	0.0 µg/µg
	$K_{nc}DO$	800 µg/L
Initial PCE degrader biomass, X_o		1.0 µg/L
PCE degrader biomass death rate, d_k		0.0 d^{-1}
The parameters for the other anaerobic reactions are identical to those for PCE except:		
TCE to DCE	V_{max}	30 d^{-1}
DCE to VC	V_{max}	53 d^{-1}
	$K_{nc}DO$	100 µg/L
Aerobic Biotransformation of DCE to CO_2		
	V_{max}	70 d^{-1}
	K_{DCE}	10,000 µg/L
	K_{DO}	0.1 µg/L
	Y	0.0 µg/µg
Initial aerobic DCE degrader biomass, X_o		1.0 µg/L
aerobic DCE degrader biomass death rate, d_k		0.0 d^{-1}
The parameters for the other aerobic reaction are identical to those for DCE except:		
VC to CO_2	V_{max}	518 d^{-1}
benzene to CO_2	V_{max}	100 d^{-1}
methane to CO_2	V_{max}	35 d^{-1}

Table 10.-- Biodegradation model parameters, and their description, from the BIOMOC input file for the chlorinated solvent example. Solutes one through seven are: PCE, TCE, DCE, VC, benzene, dissolved oxygen, and methane, respectively. Microbial populations one and two are: anaerobes that perform reductive dehalogenation and aerobes, respectively. Biodegradation processes one through seven are: reductive dehalogenation of PCE, TCE, and DCE, and oxidation of DCE, VC, benzene, and methane, respectively. (*is* is an index for solutes involved in a particular biodegradation process, *ks* is an index for all solutes simulated, *ib* is an index for microbial population, *nc* is an index for all solutes acting with a given inhibition type on a biodegradation process. Other parameters are defined in Appendix B)

```
    7                                        [nproc]
  2 2.00e-04 1 0.0 0 1 0 [nsproc(1)][vmax(1)][iz(1)][yield(1)][ncomp(1)][nnc(1)][nhal(1)]
    1  10000.    7   0.1                     [ksproc(1,is)][hfk(1,is)]
    6 800.                                   [ksnc(1,nc)][facnc(1,nc)]
    1. -0.792 0.0 0.0 0.0 0.0 0.0241         [upcoef(1,ks)]
  2 3.50e-04 1 0.0 0 1 0 [nsproc(2)][vmax(2)][iz(2)][yield(2)][ncomp(2)][nnc(2)][nhal(2)]
    2  10000.    7   0.1                     [ksproc(2,is)][hfk(2,is)]
    6 800.                                   [ksnc(2,nc)][facnc(2,nc)]
    0.0 1.0 -0.738 0.0 0.0 0.0 0.0304        [upcoef(2,ks)]
  2 6.13e-04 1 0.0 0 1 0 [nsproc(3)][vmax(3)][iz(3)][yield(3)][ncomp(3)][nnc(3)][nhal(3)]
    3  10000.    7   0.1                     [ksproc(3,is)][hfk(3,is)]
    6 100.                                   [ksnc(3,nc)][facnc(3,nc)]
    0.0 0.0 1.0 -0.644 0.0 0.0 0.0412        [upcoef(3,ks)]
  2 8.10e-04 2 0.0 0 0 0 [nsproc(4)][vmax(4)][iz(4)][yield(4)][ncomp(4)][nnc(4)][nhal(4)]
    3  10000.    6   0.1                     [ksproc(4,is)][hfk(4,is)]
    0.0 0.0 1.0 0.0 0.0 0.660 0.0            [upcoef(4,ks)]
  2 6.00e-03 2 0.0 0 0 0 [nsproc(5)][vmax(5)][iz(5)][yield(5)][ncomp(5)][nnc(5)][nhal(5)]
    4  10000.    6   0.1                     [ksproc(5,is)][hfk(5,is)]
    0.0 0.0 0.0 1.0 0.0 1.28  0.0            [upcoef(5,ks)]
  2 1.16e-03 2 0.0 0 0 0 [nsproc(6)][vmax(6)][iz(6)][yield(6)][ncomp(6)][nnc(6)][nhal(6)]
    5  10000.    6   0.1                     [ksproc(6,is)][hfk(6,is)]
    0.0 0.0 0.0 0.0 1.0 3.10 0.0             [upcoef(6,ks)]
  2 4.00e-04 2 0.0 0 0 0 [nsproc(7)][vmax(7)][iz(7)][yield(7)][ncomp(7)][nnc(7)][nhal(7)]
    6  0.1    7   10000.                     [ksproc(7,is)][hfk(7,is)]
    0.0 0.0 0.0 0.0 0.0 4.00 1.00            [upcoef(7,ks)]
    0                                        [numnut]
    0.0e-06    0.0e-06                       [death(ib)]
    0     0.00    0.00                       [nzinhib][zinhibfac]
0 1.0000                                     [z1]
0 1.0000                                     [z2]
```

Simulation of the Bemidji, Minnesota Crude-Oil Spill Site

Petroleum hydrocarbons represent the largest class of contaminants in found in groundwater. It is well established that much of the soluble fraction of a non-aqueous petroleum hydrocarbon source biodegrades under both anaerobic and aerobic conditions. However, both the rate of degradation and the specific compounds that can be degraded depend strongly on the aquifer redox conditions. Commonly, insufficient oxygen is present in the native groundwater to mineralize the contaminant fluxes from the source and the core of the plume is anaerobic. For this reason, a model that accounts

for all of the potential electron acceptors is necessary to evaluate the biodegradation capacity of an aquifer.

In this example, BIOMOC was used to evaluate the relative contribution of aerobic and anaerobic biodegradation processes to natural attenuation of a petroleum hydrocarbon plume. Using the model, it was possible to account for the variation in degradation rates between aerobic and anaerobic processes and between different classes of dissolved organic carbon. The model also provided an accounting of each type of electron acceptor and thus could be used to determine when the background supply was exhausted. This section describes how BIOMOC was used to simulate the important degradation processes observed at a crude-oil spill study site. Further details of this example are given by Essaid and others (1995).

Site Description

On August 20, 1979, a buried oil pipeline located in a pitted and dissected glacial outwash plain near Bemidji, Minnesota, broke, spilling about 1.7×10^6 liters (11,000 barrels) of crude oil. An estimated 1.2×10^6 liters (7,800 barrels) of the spilled oil were removed by pumping from surface pools, trenching, burning, and excavation of soil (Hult, 1984). The oil collected in topographic depressions and trenched areas where large volumes of oil infiltrated into the subsurface, forming two main bodies of oil floating on the water table. The subsurface oil bodies provide a long-term, continuous source of hydrocarbon components that dissolve in, and are transported with, the flowing ground water.

Evidence for microbial degradation of the petroleum hydrocarbons at the site has been documented in several studies (Lovley and others, 1989; Hult and others, 1991; Hiebert and Bennett, 1992; Bennett and others, 1993; Eganhouse and others, 1993; Baedecker and others, 1993; Cozzarelli and others, 1994; Eganhouse and others, 1996). Five geochemical zones in the ground water (figure 9) have been identified along a section through the northern oil body (Baedecker and others, 1989; Baedecker and others, 1993; Bennett and others, 1993). Zone 1 consists of oxygenated uncontaminated native ground water. The native water is very low in nitrate, ammonia, and sulfate. Zone 2, which is below the area sprayed by oil, is characterized by reduced oxygen concentrations and the presence of refractory high molecular-weight hydrocarbons. Zone 3, beneath and immediately downgradient from the separate-phase oil body, is anoxic and contains high concentrations of hydrocarbons, dissolved manganese and iron, and methane. Zone 4 makes a transition from anoxic conditions to fully oxygenated conditions, where concentrations of hydrocarbons decrease rapidly as a result of aerobic degradation. Zone 5 consists of oxygenated water downgradient from the oil body with slightly elevated concentrations of dissolved inorganic and organic constituents.

Ground-water samples from numerous wells along this section have been analyzed over time (Baedecker and others, 1993; Bennett and others, 1993; Eganhouse and others, 1993). Total dissolved organic carbon (TDOC) is made up of two operationally defined fractions: volatile dissolved organic carbon (VDOC) and nonvolatile dissolved organic carbon (NVDOC) (Baedecker and others, 1993). Figure 10 shows the temporal evolution of concentrations since 1979 at a well located 36 m downgradient from the center of the oil body. VDOC and NVDOC concentrations initially increased and then achieved steady concentrations. Mn^{2+} increased, peaking after eight years and then decreased suggesting that the Mn available for reduction was being depleted. Fe^{2+} concentrations began to increase after eight years following the drop in Mn^{2+}, and peaked in 11 years, suggesting iron reduction. Likewise methane concentration abruptly increased after eight years and then leveled off suggesting the onset of methanogenesis.

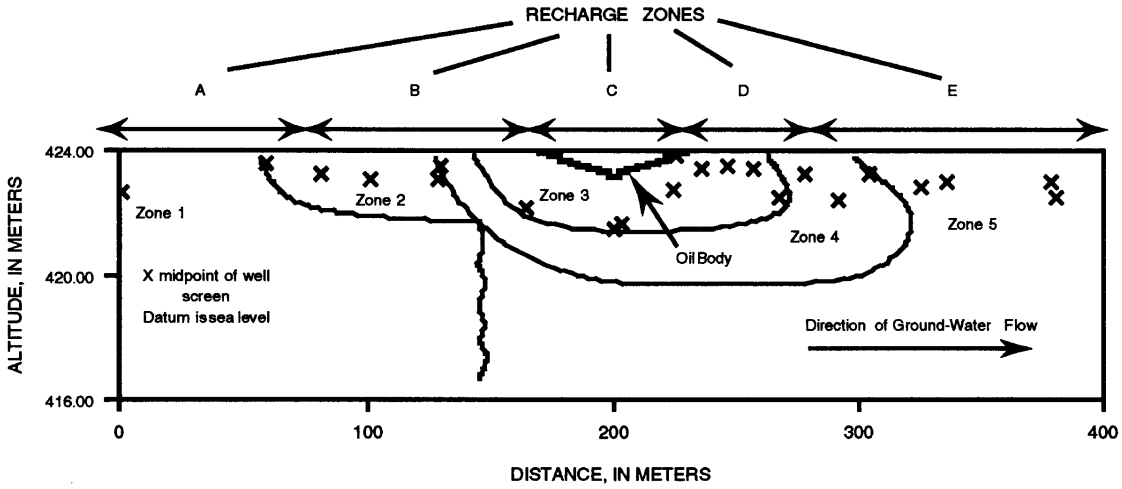

Figure 9. The simulated two-dimensional cross section at the Bemidji, Minnesota, site, showing the recharge zones used in the model simulation (table 12), the discrete representation of the oil body, and the geochemical zones of the ground-water plume: Zone 1 - oxygenated uncontaminated native ground water; Zone 2 - ground water with reduced oxygen concentrations and refractory high molecular weight hydrocarbons; Zone 3 - anoxic ground water with high concentrations of hydrocarbons, dissolved manganese, iron, and methane; Zone 4 - transition from anoxic to fully oxygenated conditions with rapid decrease in concentrations of hydrocarbons; Zone 5 - oxygenated water with slightly elevated concentrations of dissolved inorganic and organic constitutents. (modified from Baedecker and others (1993)).

The Conceptual Model

Because the field conditions at the Bemidji site are complex, a simplified conceptual model was developed to make the simulations tractable. Seven mobile solutes (VDOC, NVDOC, DO, Nitrogen, Mn^{2+}, Fe^{2+}, and CH_4), two solid-phase concentrations (Mn^{4+} and Fe^{3+}), and three microbial populations (aerobes, Mn/Fe reducers, and methanogens) were modeled. Table 11 summarizes the eight biodegradation processes represented in the model and the solutes involved in each process. TDOC was split into two degradable fractions—volatile dissolved organic carbon (VDOC) and nonvolatile dissolved organic carbon (NVDOC). Each DOC fraction undergoes aerobic degradation, Mn reduction, Fe reduction, and methanogenesis. The model accounts for the transport and consumption or production of: dissolved oxygen (DO); the cellular nutrient nitrogen (N); dissolved manganese (Mn^{2+}) produced by reduction of solid phase manganese (Mn^{4+}); dissolved iron (Fe^{2+}) produced by reduction of solid phase iron (Fe^{3+}); and methane (CH_4) produced by methanogenesis. Aerobic degradation takes place first, with oxygen noncompetitively inhibiting anaerobic processes. In addition, iron reduction is noncompetitively inhibited by solid phase manganese. Thus, as oxygen is consumed and an anoxic zone develops, the Mn/Fe reducers and methanogens begin to grow and release dissolved Mn, dissolved Fe, and methane. The multiple Monod formulation of equation (3) was used because this formulation is more common in the literature than the minimum Monod formulation.

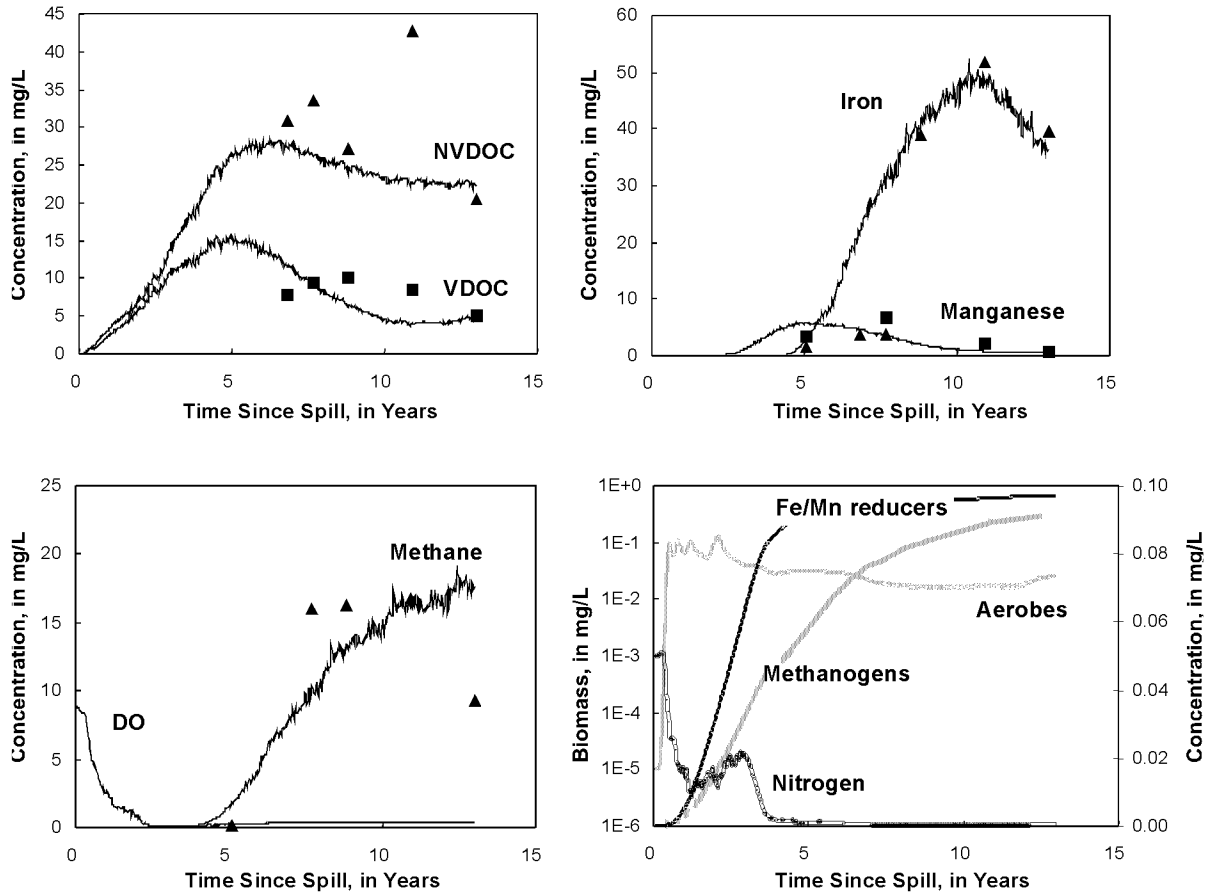

Figure 10. Changes in simulated (lines) and observed (symbols) concentrations with time since 1979 at a location 36 m downgradient from the center of the oil body: (a) volatile and nonvolatile dissolved organic carbon (VDOC and NVDOC, respectively); (b) dissolved manganese (Mn^{2+}) and dissolved iron (Fe^{2+}); (c) dissolved oxygen (DO) and methane; and (d) nitrogen, aerobes, Mn/Fe reducers, and methanogens.

Table 11.--Biodegradation processes, the solutes involved in each process, and the microbial population responsible for each process in the Bemidji simulation (Aerobic = aerobic biodegradation, Mn red. = Mn reduction, Fe red. = Fe reduction, Meth. = methanogenesis, X = consumed, ++ = produced, I = inhibits, A = aerobes, Mn/Fe = manganese and iron reducers, M = methanogens).

	VDOC	NVDOC	DO	N	Mn^{2+}	Fe^{2+}	CH_4	Mn^{4+}	Fe^{3+}	Microbe
VDOC:										
Aerobic	X		X	X						A
Mn red.	X	++	I_{nc}	X	++			X		Mn/Fe
Fe red.	X	++	I_{nc}	X		++		I_{nc}	X	Mn/Fe
Meth.	X		I_{nc}	X			++			M
NVDOC:										
Aerobic		X	X	X						A
Mn red.		X	I_{nc}	X	++			X		Mn/Fe
Fe red.		X	I_{nc}	X		++		I_{nc}	X	Mn/Fe
Meth.		X	I_{nc}	X			++			M

Table 12.--Initial and recharge water concentration in milligrams per liter for the Bemidji, Minn., example (Recharge zones A through E are shown in figure 9).

Solute	Initial Concentration mg/L	Recharge Zone Concentration				
		A	B	C	D	E
VDOC	0.0	0.0	0.0	70.0	0.0	0.0
NVDOC	0.0	0.0	20.0	80.0	0.0	0.0
DO	9.0	9.0	9.0	0.0	4.5	9.0
N	0.05	0.05	0.05	0.24	0.05	0.05
Mn^{2+}dissolved	0.0	0.0	0.0	0.0	0.0	0.0
Fe^{2+} dissolved	0.0	0.0	0.0	0.0	0.0	0.0
Methane	0.0	0.0	0.0	0.0	0.0	0.0
Mn^{4+} solid	100.	0.0	0.0	0.0	0.0	0.0
Fe^{3+} solid	1500.	0.0	0.0	0.0	0.0	0.0

A vertical cross-section of unit width parallel to the direction of ground-water flow along the sampling transect was simulated from the time of the spill in 1979 until September 1992 (figure 9). Steady-state flow and isothermal conditions (9° C) were assumed. The average organic carbon content of the aquifer is only 0.09%, resulting in retardation factor estimates that lie within the range of uncertainty in the velocity estimates. Therefore, sorption processes were neglected. Also, the change in water-table elevation over time was neglected.

The simulated section (8 m deep, 400 m wide) is shown in figure 9. A spatial discretization of 2 m horizontally and 0.1 m vertically, and a temporal discretization of 10.3 days were used. Constant heads of 424.0 m and 422.6 m were specified at the upgradient and downgradient lateral boundaries, respectively. The bottom boundary condition was no flow, and a temporally constant rate of recharge was specified across the top of the aquifer. Within the oil body, the oil in the pore space reduces the flow of water through this zone. As a first approximation, the hydraulic conductivity and recharge rate were reduced to 25 percent of the aquifer values in the zone of the oil body.

Table 12 lists the initial and recharge water concentrations used for each solute. The initial system was a clean aquifer with fully oxygenated water. The background dissolved organic carbon concentration (2.0 mg/L) was neglected because it was assumed to be a nondegradable, naturally occurring fraction. The initial solid phase iron concentration was 1,500 mg/L of bulk aquifer volume (17 mmole/kg sediment) based on a background value measured by Lovley and others (1989) and an initial solid phase Mn concentration of 100 mg/L bulk aquifer volume was assumed.

VDOC and NVDOC from the oil body entered the aquifer with the recharge water. In the spray zone (recharge zone B), all of the volatile and some of the nonvolatile components appear to have been degraded in the unsaturated zone (Baedecker and others 1993). The recharge water in the spray zone was assumed to be fully oxygenated, and the observed reduction in DO concentration in the ground water was assumed to be due to aerobic degradation of NVDOC occurring in the saturated zone. In the zone of the oil body (recharge zone C), it was assumed that both volatile and nonvolatile carbon fractions entered the aquifer (Eganhouse and others, 1993). Hult and others (1991) have shown that biodegradation above the water table depletes the oxygen resulting in an anoxic unsaturated zone in the vicinity of the oil. Therefore, it was assumed that there was no oxygen in the

recharge water near the oil body (zone C), and that oxygen was partially depleted in the recharge water downgradient of the oil body (zone D). In order to maximize the amount of nitrogen available for cell growth, the total measured nitrogen concentration in the aquifer (nitrate plus ammonia forms) was assumed to be available for cell growth. In the background zones this was 0.05 mg/L. Measured concentrations in the oil zone were much higher than in background water (either due to nitrogen sources in the oil body or from breakdown of biomass) and the recharge water in zone C was assigned a concentration of 0.24 mg/L.

Model Parameter Estimates

Most of the transport and biodegradation parameters needed to simulate the Bemidji plume have not been measured at the site. Literature values, theoretical estimates, and field biomass measurements were used to obtain reasonable estimates of parameter values used in the simulation.

Flow and Transport Parameters

Estimates of permeability (Essaid and others, 1993; Dillard, 1993) and measurements of velocity (White, 1991) have been made at the site; however, the values range over several orders of magnitude. Average values of physical properties obtained from these studies were used in the simulations. The porosity was 0.38, the hydraulic conductivity was 1×10^{-4} m/s, the water table gradient was 0.0035, and the recharge rate was 0.126 m/yr. These values result in an average linear velocity of 0.09 m/d. A longitudinal dispersivity of 0.1 m and a transverse dispersivity of 0.001 m were assumed.

Biodegradation Kinetics Parameters

When available, literature values were used to help constrain the model parameters. The literature contains numerous measurements of Monod kinetic parameters for aerobic degradation of hydrocarbons (e.g. MacQuarrie and others, 1990; Alvarez and others, 1991). Reported asymptotic maximum specific uptake rate (V_{max}) values range from 0.01 to 9.9 d^{-1}, half saturation constant (K) values range from 0.03 to 15.9 mg/L, and yields (Y) range from 0.01 to 1.56 gm cells/gm carbon. Unfortunately, most studies of anaerobic degradation of hydrocarbons have been limited to estimates of first-order biodegradation rates rather than full Monod kinetics parameters (e.g. Wilson and others, 1990; Cozzarelli and others, 1994; Wilson and others, 1994; and Albrechtsen, 1994). Without knowing the biomass concentrations in these experiments, it is impossible to estimate Monod kinetics parameters from these first-order rates. Edwards and Grbić-Galić (1994) reported kinetic parameters for methanogenic degradation of toluene by enriched cultures. Their values, expressed in terms of carbon uptake, were $V_{max} = 0.19$ d^{-1}, $K = 0.25$ mg/L, and $Y = 0.01$ gm cells/gm carbon.

Yield Estimates

To limit the range of possible kinetic parameters that could be used in the model, theoretical growth yields for the degradation of benzene, toluene, ethylbenzene, and xylene (BTEX compounds) were computed using the stoichiometric and thermodynamic model presented by McCarty (1971). The computational method is outlined by McFarland and Sims (1991) together with a comment on adjusting the calculations for nonstandard conditions given by Walton and Smith (1992).

The reaction free energies were first computed using unit activities at a pH of 7.0. The free energies of formation for water and carbon dioxide were taken from Thauer and others (1977). The aqueous free energies of the BTEX compounds were computed from the gaseous state values given in Reid and others (1985) using values for Henry's constants from Montgomery and Welkom (1990). Reaction stoichiometries and free energies for the electron acceptor half-reactions were taken from McFarland and Sims (1991). The nitrogen source was assumed to be ammonia and because of the highly hostile environment in the field, a low efficiency of energy transfer (0.2) was assumed to be representative of field conditions (Battley, 1987).

Uptake Coefficients

Data from microcosm studies (Cozzarelli and others, 1994) were used to determine the uptake coefficients for the manganese and iron reduction of hydrocarbons. It was found in this study that only a fraction of the solid phase manganese and iron used by the microbes is released as dissolved Mn^{2+} and Fe^{2+}. There is field evidence that the rest is precipitated as a solid phase (Baedecker and others, 1992). Eganhouse and others (1993) examined the downgradient profiles of VDOC and NVDOC and concluded that some of the VDOC is being degraded to NVDOC as an intermediate step in the anoxic zone. For this reason, in the model, half of the VDOC that is degraded by Mn/Fe reduction is converted to NVDOC (β_{NVDOC} = -0.5). Stoichiometric relations were used to determine the uptake coefficients for the other biodegradation processes.

Initial Biomass Estimates

In August, 1994, samples were collected from a background location, and two locations downgradient from the oil body (39 and 52 m from the center of the oil body) for microbial biomass determinations. The Most Probable Number (MPN) method was used to enumerate microorganisms in water and sediment samples capable of degradation under differing redox potentials. In order to obtain estimates of initial concentrations of aerobes, Mn/Fe reducers, and methanogens, biomass concentrations were calculated from the MPN numbers assuming a cell dry weight of 2×10^{-10} mg (McCarty, 1985). Background concentrations were on the order of 10^{-5} mg/L for aerobes, and 10^{-7} to 10^{-6} mg/L for Fe reducers and methanogens (Essaid and others, 1995).

Calibrated Model Results

Comparisons to the observed spatial and temporal variations in solute concentrations were used to calibrate the model. The yield estimates obtained using an efficiency of 0.2 were used as initial guesses and V_{max} and K values were adjusted. The parameters used in the model (table 13) were obtained by trial and error adjustment of initial guesses. Table 13 reports the values for VDOC biodegradation kinetics. The parameters for the NVDOC were identical, except that V_{max} and Y were 75 percent of the values for VDOC. This is based on the observation in the field that the VDOC fraction is degraded more easily than the NVDOC fraction (Eganhouse and others, 1993). Inhibition factors were obtained by calibration. Table 14 lists the section of the BIOMOC input file that specifies the biodegradation parameters to illustrate how the biodegradation processes and parameters of this example are setup in the model input.

Table 13.--Biodegradation parameters used in the Bemidji, Minn., simulation for VDOC. The parameters for NVDOC are the same except for V_{max} and Y which are 75 percent of the VDOC values. The footnotes give the basis for the estimates.

Aerobic degradation of VDOC:	
[1]$Vmax$	0.5 d-1
[1]K_{VDOC}	1.0 mg/L
[1]K_{DO}	1.0 mg/L
[2]Y	0.27 mg/mg
[3]β_{VDOC}	1.0
[3]β_{DO}	2.6
Manganese reduction of VDOC:	
[1]V_{max}	0.065 d-1
[1]K_{VDOC}	1.0 mg/L
[1]$K_{Mn^{4+}}$	15 mg/L
[2]Y	0.21 mg/mg
[4]$k_{nc\ DO}$	0.8 mg/L
[3]β_{VDOC}	1.0
[3]β_{NVDOC}	-0.5
[3]$\beta_{Mn^{4+}}$	12.
[3]$\beta_{Mn^{2+}}$	-2.1
Iron reduction of VDOC:	
[1]V_{max}	0.065 d-1
[1]K_{VDOC}	1.0 mg/L
[1]$K_{Fe^{3+}}$	50 mg/L
[2]Y	0.063 mg/mg
[4]$k_{nc\ DO}$	0.8 mg/L
[4]$k_{nc\ Mn^{4+}}$	0.001 mg/L
[3]β_{VDOC}	1.0
[3]β_{NVDOC}	-0.5
[3]$\beta_{Fe^{3+}}$	24.
[3]$\beta_{Fe^{2+}}$	-4.3
Methanogenic degradation of VDOC:	
[1]V_{max}	0.19 d-1
[1]K_{VDOC}	0.25 mg/L
[2]Y	0.03 mg/mg
[4] $k_{nc\ DO}$	0.8 mg/L
[3]β_{VDOC}	1.0
[3]β_{CH4}	-0.83
Nitrogen uptake:	
[1]K_{nut}	0.001 mg/L
[3]Y_{nut}	7.0 mg/mg

Microbial Populations:

	Aerobes	Mn/Fe Reducers	Methanogens
[4]k_{bio} mg/L	0.35	0.35	0.30
[5]X_o mg/L	0.00001	0.000001	0.000001
[1]d_k d^{-1}	0.02	0.0002	0.0

1. Initial guesses based on reported literature values, with adjustment during calibration.
2. Based on yield estimate calculations.
3. Based on stoichiometry and results of microcosm experiments.
4. Calibrated.
5. Based on field measurements.

Table 14.--Biodegradation parameters, and their description, from the BIOMOC input file for the Bemidji, Minn., simulation. Solutes one through nine are: volatile- and nonvolatile-dissolved organic carbon (VDOC and NVDOC), dissolved oxygen, nitrogen, dissolved manganese, dissolved iron, methane, solid phase manganese, and solid phase iron, respectively. Microbial populations one through three are: aerobes, manganese/iron reducers, and methanogens, respectively. Biodegradation processes one through eight are: aerobic degradation of VDOC; manganese reduction, iron reduction, and methanogenesis coupled to oxidation of VDOC; aerobic degradation of NVDOC; manganese reduction, iron reduction, and methanogenesis coupled to oxidation of NVDOC, respectively. (*is* is an index for solutes involved in a particular biodegradation process, *ks* is an index for all solutes simulated, *ib* is an index for microbial population, *nc* is an index for all solutes acting with a given inhibition type on a biodegradation proces, other parameters are defined in Appendix B)

```
    8                                   [nproc]
  2 5.80e-06 1 0.27 0 0 0 [nsproc(1)][vmax(1)][iz(1)][yield(1)][ncomp(1)][nnc(1)][nhal(1)]
    1   1.    3   1.                   [ksproc(1,is)][hfk(1,is)]
    1. 0. 2.625 0. 0. 0. 0. 0. 0.      [upcoef(1,ks)]
  2 7.50e-07 2 0.21 0 1 0 [nsproc(2)][vmax(2)][iz(2)][yield(2)][ncomp(2)][nnc(2)][nhal(2)]
    1   1.    8  15.                   [ksproc(2,is)][hfk(2,is)]
    3   0.805                          [ksnc(2,nc)][ksfac(2,nc)]
    1. -0.5 0. 0.0 -2.1 0. 0. 12. 0.   [upcoef(2,ks)]
 2 7.50e-07 2 0.063 0 2 0 [nsproc(3)][vmax(3)][iz(3)][yield(3)][ncomp(3)][nnc(3)][nhal(3)]
    1   1.    9  50.                   [ksproc(3,is)][hfk(3,is)]
    3   0.805   8 0.001                [ksnc(3,nc)][ksfac(3,nc)]
    1. -0.5 0. 0. 0. -4.3 0. 0. 24.    [upcoef(3,ks)]
 1 2.18e-06 3 0.03 0 1 0 [nsproc(4)][vmax(4)][iz(4)][yield(4)][ncomp(4)][nnc(4)][nhal(4)]
    1   0.25                           [ksproc(4,is)][hfk(4,is)]
    3   0.805                          [ksnc(4,nc)][ksfac(4,nc)]
    1. 0. 0. 0. 0. 0. -0.83 0. 0.      [upcoef(4,ks)]
 2 4.35e-06 1 0.203 0 0 0 [nsproc(5)][vmax(5)][iz(5)][yield(5)][ncomp(5)][nnc(5)][nhal(5)]
    2   1.    3   1.                   [ksproc(5,is)][hfk(5,is)]
    0. 1. 2.625 0. 0. 0. 0. 0. 0.      [upcoef(5,ks)]
 2 5.63e-07 2 0.158 0 1 0 [nsproc(6)][vmax(6)][iz(6)][yield(6)][ncomp(6)][nnc(6)][nhal(6)]
    2   1.    8  15.                   [ksproc(6,is)][hfk(6,is)]
    3   0.805                          [ksnc(6,nc)][ksfac(6,nc)]
    0. 1. 0. 0. -2.1 0. 0. 12. 0.      [upcoef(6,ks)]
 2 5.63e-07 2 0.047 0 2 0 [nsproc(7)][vmax(7)][iz(7)][yield(7)][ncomp(7)][nnc(7)][nhal(7)]
    2   1.    9  50.                   [ksproc(7,is)][hfk(7,is)]
    3   0.805  8   0.001               [ksnc(7,nc)][ksfac(7,nc)]
    0. 1. 0. 0. 0. -4.3 0.0. 14.       [upcoef(7,ks)]
 1 1.64e-06 3 0.023 0 1 0 [nsproc(8)][vmax(8)][iz(8)][yield(8)][ncomp(8)][nnc(8)][nhal(8)]
    2   0.25                           [ksproc(8,is)][hfk(8,is)]
    3   0.805                          [ksnc(8,nc)][ksfac(8,nc)]
    0. 1. 0. 0. 0. 0. -0.83 0. 0.      [upcoef(4,ks)]
    1                                  [numnut]
    4   7.   .001   0.                 [ksnut][yieldnut][hfknut][relcoef]
    2.32e-07     2.32e-09   0.00e-11   [death(ib)]
    1     0.35    0.35  0.30           [nzinhib][zinhibfac(ib)]
0 .00001                               [z(1)]
0 .000001                              [z(2)]
0 .000001                              [z(3)]
```

Figure 10 presents the observed and simulated concentrations at a well that is 36 m downgradient from the center of the oil body. The observed and simulated VDOC and NVDOC concentrations match quite well (figure 10a). The temporal variation in DO, Mn^{2+}, Fe^{2+}, and methane concentrations are shown in figures 10b and 10c. The simulation captures the general evolution of the plume with time, but does not match the observed concentrations exactly. Figure 10d shows the influence of nutrient limitation on biomass growth. At early time, there is considerable growth of aerobic biomass with a rapid decrease in nitrogen concentrations as the nitrogen is incorporated into the new biomass. As aerobic biomass growth slows, due to biomass inhibition, the uptake of nitrogen is less than the influx of nitrogen, and the nitrogen concentration increases. Then, as Mn/Fe reducers and methanogens begin to grow substantially, the nitrogen concentration drops and eventually approaches 0 mg/L. This causes a slowing in the biomass growth because of the limited influx of nitrogen, in addition to slowing of growth by biomass inhibition.

CONCLUSIONS

The model described in this report can simulate the two-dimensional transport and biotransformation of multiple reacting solutes. The program is general and flexible allowing for any combination of electron donor and acceptor species. A number of mathematical expressions for biological transformation rates from the literature have been included as options in the code. These include single, multiple, and minimum Monod kinetics and competitive, noncompetitive, and substrate inhibition. The inhibition formulations are particularly useful for modeling the transitions between redox zones within contaminant plumes. The kinetic parameters can be formulated to simulate zero-order or first-order approximations to Monod kinetics. The growth and decay of several microbial populations performing the transformations is also accounted for. The microbial growth can be either disabled, limited by a prescribed maximum value, or limited by the availability of a specified nutrient.

The accuracy of the numerical results has been evaluated by comparison with analytical solutions and with other numerical codes. In these cases there was good agreement between the BIOMOC results and the other solution methods. The code has been applied to two example problems. The first example is a one-dimensional steady-state simulation of the transformation of chlorinated solvents. The second example is a two-dimensional transient simulation of a crude-oil spill site. The descriptions of these examples serve as useful illustrations of the steps involved in formulating a conceptual model and assembling the many input parameters.

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APPENDIX A: NOTATION

b	thickness of aquifer or width of the vertical cross-section through the aquifer, L.
B_i	biodegradation reaction term, $ML^{-3}T^{-1}$.
C_i	concentration of the *ith* solute, ML^{-3}.
C'_i	concentration of the *i*th solute in the source fluid, ML^{-3}.
C^*_i	new concentration at each model block resulting from advective transport, ML^{-3}.
C_{nut}	concentration of a nutrient, ML^{-3}.
C_o	total solution concentration of two exchanging ions, L^{-3}.
D_{jk}	dispersion tensor, L^2T^{-1}.
d_k	death rate or maintenance constant, T^{-1}.
H_s	head in aquifer overlying confining layer, L.
I_b	biomass inhibition factor, dimensionless.
I_c	competitive inhibition factor, dimensionless.
I_h	Haldane inhibition factor, dimensionless.
I_{nc}	noncompetitive inhibition factor, dimensionless.
K^n	half-saturation constant, ML^{-3}.
k_{bio}	biomass inhibition constant, ML^{-3}.
k_c	competitive inhibition constant, ML^{-3}.
k_h	Haldane inhibition constant, ML^{-3}.
k_{nc}	noncompetitive inhibition constant, ML^{-3}.
K_d	linear sorption distribution coefficient, L^3M^{-1}.
K_z	Vertical hydraulic conductivity of confining layer, LT^{-1}.
k_{nc}	noncompetitive inhibition constant, ML^{-3}.
K_{nut}	half saturation constant for a nutrient, ML^{-3}.
k_s	inhibition constant for substance *s*, ML^{-3}.
m	thickness of confining layer, L.
P_k	specific rate of production of population *k* biomass, T^{-1}.
Q_s	concentration of inhibiting substance *s*, ML^{-3}.
R_i	retardation factor for the *ith* solute, dimensionless.
t	time, T.
$t_{1/2}$	first-order decay half-life, in seconds, T.
V_j	average linear velocity of the fluid, LT^{-1}.
V^n_{max}	maximum specific uptake rate of substrate for biodegradation process *n*, T^{-1}.
W	source fluid flux, LT^{-1}.
x_j	spatial coordinate, L.
X^n_k	biomass concentration of microbial population *k* performing degradation process *n*, ML^{-3}.
X_o	initial biomass concentration, ML^{-3}.
Y	cell-yield coefficient, M cells/M substrate.
Y_{nut}	cell-yield coefficient of a nutrient, M bacteria/M nutrient.
β^n_i	uptake coefficient of solute *i* for biodegradation process *n*, dimensionless.
Γ_{nut}	nutrient release coefficient, dimensionless.
Δt	time step size, T.

ε	effective porosity, dimensionless.
ν_{nut}	nutrient uptake rate, $ML^{-3}T^{-1}$.
ν^{n}	uptake rate of substrate by biodegradation process *n,* $ML^{-3}T^{-1}$.
ρ_b	aquifer bulk density, ML^{-3}.

APPENDIX B: DEFINITION OF SELECTED PROGRAM VARIABLES

AAQ	area of aquifer in model
ANFCTR	anisotropy factor (ratio of T_{yy} to T_{xx})
AOPT	iteration parameters
AREA	area of one cell in finite-difference grid
BETA	longitudinal dispersivity of porous medium
BIOUP	biodegradation reaction term, B_i
CELDIS	maximum distance across one cell that a particle is permitted to move in one step (as fraction of width of cell)
CLKCN	concentration of leakage through confining layer or streambed
CMSIN	mass of solute recharged into aquifer
CMSOUT	mass of solute discharged from aquifer
CNCNC	change in concentration due to dispersion and sources
CNCPCT	change in concentration as percentage of concentration at node
CNOLD	concentration at node at end of previous time increment
CNREC	concentration of well withdrawal or injection, C'_i
CNRECH	concentration in fluid source
COMPINHIB	competitive inhibition factor, I_c
CONC	concentration in aquifer at node
CONINT	concentration in aquifer at start of simulation
CPROF	concentration profile at water table
C1	CONC at node (IX,IY)
DALN	longitudinal dispersion coefficient
DDRW	drawdown
DEATH	death rate or maintenance constant, d_k
DELQ	volumetric rate of leakage across a confining layer or streambed
DELS	rate of change in ground-water storage
DERH	change in head with respect to time
DISP	dispersion equation coefficients
DISTX	distance particle moves in x-direction during time increment
DISTY	distance particle moves in y-direction during time increment
DK	linear sorption distribution coefficient, K_d
DLTRAT	ratio of transverse to longitudinal dispersivity
DTRN	transverse dispersion coefficient
FACCOMP	competitive inhibition constant, k_c
FACHAL	Haldane inhibition constant
FACNC	noncompetitive inhibition constant, k_{nc}
FCTR	multiplication or conversion factor
FLMIN	solute mass entering modeled area during time step
FLMOT	solute mass leaving modeled area during time step
GRDX	hydraulic gradient in x-direction
GRDY	hydraulic gradient in y-direction
GROW	specific rate of production of population k biomass, P_k
HALINHIBFAC	haldane inhibition factor
HC	head from column computation

HFK	half-saturation constant, K^n
HFKNUT	half saturation constant for a nutrient, K_{nut}
HI	initial head in aquifer
HK	computed head at end of time step
HMIN	minimum iteration parameter
HR	head from row computation in subroutine ITERAT; elsewhere HR represents head from previous time step
IBIO	biodegradation flag
IMOB()	particle mobility flag
IMOV	particle movement step number
INT	pumping period number
IPRNT	print control index for hydrographs
IREACT	reaction type specifier
ITMAX	maximum permitted number of iteration
IXOBS	x-coordinate of observation point
IYOBS	y-coordinate of observation point
IZ	index of microbe population involved in biodegradation process
KOUNT	iteration number
KP	particle set index
KPS	particle set solute index
KS	solute index
KSCOMP	number of solutes competitively inhibiting a biodegradation process
KSHAL	number of solutes causing Haldane inhibition of a biodegradation process
KSNC	number of solutes noncompetitively inhibiting a biodegradation process
KSNUT	nutrient solute index
KSPROC	index for solutes involved in a biodegradation process
LIMBO	array for temporary storage of particles
N	time step number
NCA	number of aquifer nodes in model
NCINHIB	noncompetitive inhibition factor, I_{nc}
NCODES	number of node identification codes
NCOMP	number of solutes competitively inhibiting a biodegradation process
NCONC	number of solutes per particle set
NHAL	number of solutes causing Haldane inhibition of a biodegradation process
NITP	number of iteration parameters
NMOV	number of particle movements (or time increments) required to complete time step
NNC	number of solutes noncompetitively inhibiting a biodegradation process
NODEID	node identification code
NP	total number of active particles in grid
NPCELL	number of particles in a cell during time increment
NPMAX	maximum number of available particles
NPMP	number of pumping periods or simulation periods
NPNT	number of time steps between printouts
NPOP	number of microbe populations
NPROC	number of biodegradation processes
NPSET	number of particle sets

NPTPND	initial number of particles per node
NREC	number of pumping wells
NSOL	number of solutes
NSPROC	number of solutes involved in a biodegradation process
NTIM	number of time steps
NTIME	time for water table profile
NUMNUT	number of nutrients
NUMOBS	number of observation wells
NX	number of nodes in x-direction
NY	number of nodes in y-direction
NZCRIT	maximum number of cells that can be void of particles
NZERO	number of cells that are void of particles at the end of a time increment
PARAM	iteration parameter for current iteration
PART	concentration of solutes associated with particle set.
PARTXY	particle x- and y-coordinates. Also note that the signs of coordinates are used as flags to store information on original location of particle.
PERM	hydraulic conductivity
PINT	pumping period in years
POROS	effective porosity, ε
PUMP	cumulative net pumpage
PYR	total duration of pumping period (in seconds)
QNET	net water flux
QSTR	cumulative change in volume of water in storage
REC	point source or sink; negative for injection, positive for withdrawal, W
RECH	diffuse recharge or discharge; negative for recharge, positive for discharge
RELCOEF	nutrient release coefficient, Γ_{nut}
RF	retardation factor, R_i
RN	range in concentration between regenerated particle and adjacent node having lower concentration
RHOB	aquifer bulk density, ρ_b
RP	range in concentration between regenerated particle and adjacent node having higher concentration
S	storage coefficient (or specific yield)
SLEAK	rate of leakage through confining layer or streambed
STORM	change in total solute mass in storage (by summation)
STORMI	initial mass of solute in storage
SUMC	summation of concentrations of all particles in a cell
SUMIO	change in total solute mass in storage (from inflows-outflows)
SUMT	total elapsed time (in seconds), t
SUMTCH	cumulative elapsed time during particle moves (in seconds)
TDEL	current time step, Δt
THALF	decay half-life, in seconds, $t_{1/2}$
THCK	saturated thickness of aquifer, b
TIM	length of specific time step (in seconds)
TIMD	elapsed time in days
TIMY	elapsed time in years

TIMV	length of time increment for particle movement (in seconds)
TIMX	time step multiplier for transient problems
TINIT	size of initial time step for transient flow problems (in seconds)
TITLE	problem description
TMCN	computed concentrations at observation points
TMOBS	elapsed times for observation point records
TMRX	transmissivity coefficients (harmonic means on cell boundaries; forward values are stored)
TMWL	computed heads at observation points
TOL	convergence criteria
TOTLQ	cumulative net leakage through confining layer or streambed
TRAN	transverse dispersivity of porous medium
UP	uptake of primary substrate or nutrient in a biodegradation process, ν^n; ν_{nut}
UPCOEF	uptake coefficient of solute *i* for biodegradation process *n*, β_i^n
UPTAKE	uptake rate of substrate by biodegradation process *n*, ν^n; ν_{nut}
VMAX	maximum value of VX (in subroutine VELO)
VMAX	asymptotic maximum specific uptake rate of the substrate
VMAY	maximum value of VY
VMGE	magnitude of velocity vector
VMXDB	maximum value of VXBDY
VMYBD	maximum value of VYBDY
VPRM	initially used to read transmissivity (or hydraulic conductivity) values at nodes; then after line B2270, VPRM equals leakance factor for confining layer or streambed. If VPRM≥0.09, then the program assumes that the node is a constant-head boundary and is flagged for subsequent special treatment in calculating advective transport.
VX	velocity in x-direction at a node, V_j
VXBDY	velocity in x-direction on a boundary between nodes
VY	velocity in y-direction at a node, V_j
VYBDY	velocity in y-direction on a boundary between nodes
WT	initial water-table or potentiometric elevation, or constant head in stream or source bed, H_s
XDEL	grid spacing in x-direction
XOLD	x-coordinate of particle at end of previous time increment
XPROF	distance for water table profile
XVEL	velocity of particle in x-direction
YDEL	grid spacing in y-direction
YIELD	cell-yield coefficient, *Y*
YIELDNUT	cell-yield coefficient of a nutrient, Y_{nut}
YOLD	y-coordinate of particle at end of previous time increment
YVEL	velocity of particle in y-direction
Z	biomass concentration, X_k^n
ZINHIB	biomass inhibition constant, k_{bio}
ZINHIBFAC	biomass inhibition factor, I_b
ZINIT	initial biomass concentration, X_o
ZPROF	biomass concentration for water table profile

APPENDIX C: DATA INPUT FORMATS

Line	Column	Format	Variable	Definition
1	1-80	10A8	TITLE	Description of problem
2		FREE	NTIM	Maximum number of flow time steps in a pumping period
		FREE	NPMP	Number of pumping periods. Note that if NPMP>1, then data set 22 must be completed
		FREE	NX	Number of nodes in x direction, if NX<0 then a transport subgrid must be specified in a following data set
		FREE	NY	Number of nodes in y direction
		FREE	NPMAX	Maximum number of particles
		FREE	NPNT	Flow time-step interval for printing hydraulic and chemical output data
		FREE	NITP	Number of iteration parameters
		FREE	NUMOBS	Number of observation points to be specified in data set 1
		FREE	ITMAX	Maximum allowable number of iterations
		FREE	NREC	Number of pumping or injection wells to be specified in data set 2
		FREE	NPTPND	Initial number of particles per node (options= 4,5,8,9,16)
		FREE	NCODES	Number of node identification codes to be specified in data set 7
		FREE	NPNTMV	Particle movement interval (IMOV) for printing chemical output data (Specify 0 to print only at end of a flow time step)

Line	Column	Format	Variable	Definition
		FREE	NPNTVL	Option for printing computed velocities (0=do not print; 1=print for first time step; 2=print for all time steps)
		FREE	NPNTD	Option for printing computed dispersion equation coefficients (option definition same as for NPNTVL)
		FREE	NPDELC	Option for printing computed changes in concentration (0=do not print; 1=print)
		FREE	NPNCHV	Option to write velocity data to unit 7 (option definition same as for NPNTVL)
3		FREE	IBIO	Biodegradation options, 0=no biodegradation; 1=multiple Monod; 2= minimum Monod
		FREE	NSOL	Total number of solute species
		FREE	NPOP	Total number of microbe populations
		FREE	NPSET	Total number of particle sets
4 to npset+3	1-5	I5	IREACT(kp)	Particle set *kp* reaction type: -1=decay only, 0=no reaction, 1=linear sorption and optional decay
	6-10	I5	NCONC(kp)	Number of solutes associated with particle set *kp*
	11-15	I5	IMOB(kp)	Flag indicating mobility of particle set, 0=mobile, 1=immobile
npset+4		FREE	MX	Grid index for lower x limit of transport subgrid (this parameter should be included only if NX<0)
		FREE	MY	Grid index for lower y limit of transport subgrid (this parameter should be included only if NY<0)
		FREE	MMX	Grid index for upper x limit of transport subgrid (this parameter should be included only if NX<0)
		FREE	MMY	Grid index for upper y limit of transport subgrid (this parameter should be included only if NY<0)

Line	Column	Format	Variable	Definition
npset+5	1-5	G5.0	PINT	Pumping period in years
	6-10	G5.0	TOL	Convergence criteria
	11-15	G5.0	POROS	Effective porosity
	16-20	G5.0	BETA	Longitudinal dispersivity
	21-25	G5.0	S	Storage coefficient (set S=0 for steady flow problems)
	26-30	G5.0	TIMX	Time increment multiplier for transient flow problems (TIMX is disregarded if S=0)
	31-35	G5.0	TINIT	Size of initial time step in seconds (TINIT is disregarded if S=0)
	36-40	G5.0	XDEL	Width of finite-difference cell in x direction
	41-45	G5.0	YDEL	Width of finite-difference cell in y direction
	46-50	G5.0	DLTRAT	Ratio of transverse to longitudinal dispersivity
	51-55	G5.0	CELDIS	Maximum cell distance per particle move (value between 0 and 1.0)
	56-60	G5.0	ANFCTR	Ratio of T_{yy} to T_{zz}
npset+6 to 2npset+5		FREE	THALF(kp)	For IREACT(kp)=-1, decay only, THALF in seconds For IREACT(kp)=0, do not insert line
		FREE	DK(kp), RHOB(kp), THALF(kp)	For IREACT(kp)=1, linear sorption and optional decay. For no decay, specify THALF(kp)=0.

Data set	Number of lines	Format	Variable	Definition
1	NUMOBS	2I5	IXOBS, IYOBS	x and y coordinates of observation points (this data set is eliminated if NUMOBS = 0)
2	NREC	2I5, (10G10.2)	IX,IY,FCTR, CNREC(ks), ks=1,NSOL	x and y coordinates of pumping (+) or injection (-) wells, pumping rate, and if an injection well, the concentration of each solute in the injected water (this data set is eliminated if NREC=0)
3	1	I1,G10.0	INPUT, FCTR	[1]Parameter card for VPRM
	NY	8E10.3	VPRM	Transmissivity (or hydraulic conductivity in a vertical cross-section) data, for an anisotropic aquifer read in values of T_{xx} (K_{xx}) and T_{yy} (K_{yy}) will be calculated using ANFCTR
4	1	I1,G10.0	INPUT, FCTR	[1]Parameter card for THCK
	NY	20G3.0	THCK	Saturated thickness (or unit width in a vertical cross-section) of aquifer
5	1	I1,G10.0	INPUT, FCTR	[1]Parameter card for RECH
	NY	20G4.1	RECH	Diffuse recharge (-) or discharge (+)
6	1	I1,G10.0	INPUT, FCTR	[1]Parameter card for NODEID
	NY	20I1	NODEID	Node identification matrix (used to define boundary conditions and stresses)
7	NCODES	I2,3g10.2, I2,9g10.2/ (34x, 9g10.2)	ICODE, FCTR1, FCTR2(1), FCTR3, OVERRD, fctr2(ks), ks=2,nsol	Instructions for using NODEID array. When NODEID=ICODE, program sets leakance=FCTR1, CNRECH(ks)=FCTR2(ks), and if OVERRD≠0, RECH=FCTR3. Set OVERRD=0 to preserve values of RECH specified in data set 5.
8	1	I1,G10.0	INPUT, FCTR	[1]Parameter card for WT
	NY	1X, 10F12.0	WT	Initial water-table or potentiometric elevation, or constant head in stream or source bed

Data set	Number of lines	Format	Variable	Definition
				Repeat data set 19 for each solute
9	1	I1,G10.0	INPUT, FCTR	[1]Parameter card for CONC(ks)
	NY	20G4.0	CONC(ks)	Initial concentration of solute *ks* in aquifer
				The biodegradation parameters in data sets 10 through 21 should be included only if IBIO>0
10	1	FREE	NPROC	Number of simulated biodegradation processes
				Repeat data sets 11-16 for each biodegradation process *iproc*:
11		FREE	NSPROC(iproc)	Number of solutes undergoing microbial uptake in process *iproc*
		FREE	VMAX(iproc)	Asymptotic maximum specific uptake rate V_{max} of process *iproc*
		FREE	IZ(iproc)	Index of microbe population performing process *iproc*
		FREE	YIELD(iproc)	Yield of process *iproc*
		FREE	NCOMP(iproc)	Number of solutes competitively inhibiting process *iproc*
		FREE	NNC(iproc)	Number of solutes noncompetitively inhibiting process *iproc*
		FREE	NHAL(iproc)	Number of solutes causing Haldane inhibition of process *iproc*
				Repeat data set 12 for each solute undergoing microbial uptake in process *iproc* *(is=1,nsproc)*. The first solute listed must be the substrate used in process *iproc*:
12		FREE	KSPROC(iproc,is)	Solute index
		FREE	HFK(iproc,is)	Half saturation constant for solute *ksproc*
				Repeat data set 13 for each solute competitively inhibiting process *iproc* *(nc=1,ncomp(iproc))*

Data set	Number of lines	Format	Variable	Definition
13		FREE	KSCOMP (iproc,nc)	index of solute competitively inhibiting process *irpoc*
		FREE	FACCOMP (iproc,nc)	competitive inhibition constant for solute *kscomp(iproc,nc)*
				Repeat data set 14 for each solute noncompetitively inhibiting process *iproc (nc=1,nnc(iproc))*
14		FREE	KSNC(iproc,nc)	index of solute noncompetitively inhibiting process *iproc*
		FREE	FACNC (iproc,nc)	noncompetitive inhibition constant for solute KSNC(iproc,nc)
				Repeat data set 15 for each solute causing haldane inhibition of process *iproc (nc=1,NHAL(iproc))*
15		FREE	KSHAL (iproc,nc)	index of solute causing Haldane inhibition of process *irpoc*
		FREE	FACHAL (iproc,nc)	Haldane inhibition constant for solute KSHAL(iproc,nc)
16		FREE	UPCOEF (iproc,ks), ks=1,NSOL	Uptake coefficient for each solute *ks:* =0 for solutes not involved in process *iproc*; >0 for solutes consumed in process *iproc*; <0 for solutes produced in process *iproc.*
17		FREE	NUMNUT	Number of cellular nutrients
				Repeat data set 18 for each cellular nutrient *inn (inn=1,NUMNUT)*
18		FREE	KSNUT(inn)	Nutrient solute index
		FREE	YIELDNUT(inn)	Nutrient yield
		FREE	HFKNUT(inn)	Nutrient half saturation constant
		FREE	RELCOEF	Nutrient release coefficient
19		FREE	DEATH(ib), ib=1,NPOP	Death rate of each microbe population *ib*
20		FREE	NZINHIB	Biomass inhibition flag: =0 no biomass inhibition: =1 biomass inhibition.

Data set	Number of lines	Format	Variable	Definition
		FREE	ZINHIBFAC(ib), ib=1,NPOP	Biomass inhibition constants for *ib=1,NPOP*
				Repeat data set 21 for each microbe population *ib (ib=1,NPOP)*
21	1	I1,G10.0	INPUT, FCTR(ib)	[1]Parameter card for biomass concentration
		20G4.0	Z(ib)	Biomass concentration for microbe population *ib* (biomass concentration will never drop below Z(ib))
				This data set allows time step parameters, print options, and pumpage data to be revised for each pumping period of the simulation. Data set 22 is only used if NPMP>1. The sequence of lines in data set 22 must be repeated for each pumping period after the first (NPMP-1)
22a	1	I1	ICHK	Parameter to check whether any revisions are desired. Set ICHK=1 if data are to be revised, and then complete data set 22b and c. Set ICHK=0 if data are not to be revised for the next pumping period, and skip rest of data set 22.
22b	1	10I5, 3G5.0	NTIM, NPNT, NITP, ITMAX, NREC, NPNTMV, NPNTVL, NPNTD, NPDELC, NPNCHV, PINT, TIMX, TINIT	Parameters to be revised for next pumping period; the parameters were previously defined in the description of data lines 2 and 3. Only include this card if ICHK=1 in previous line.
22c	NREC	2I5, (10G10.2)	IX,IY,FCTR, CNREC(ks), ks=1,NSOL	Revision of previously defined data set 2. Include only if ICHK=1 and NREC>0 in previous lines.

1. The parameter line must be the first line of the indicated data sets. If INPUT=0, the data set has a constant value, which is defined by FCTR and there is no need for further input. If INPUT=1, the data set varies in space, and the full data set must be specified as described in the subsequent input lines. In this case, FCTR is a multiplication factor for the values read in the data set.

APPENDIX D: INPUT DATA FOR TEST PROBLEM

The input file for the test problem Aerobic Biodegradation and Transport of Toluene and Benzene (see Model Evaluation section) is listed below to illustrate a sample INPUT.DAT file for BIOMOC.

```
1-D T, B, and O transport with aerobic degradation, from chen et al.
    1    1   58    3 95000    1   10    1  500    1   16    1  360    1    0    0    0
    1    3    2    3
    1    1    0
    1    1    0
    0    1    0
.01815.e-6 0.38 2.24  0.0  0.0  0.0   1.   1. .010 0.10  1.0
   0.139   1.64    0.
   0.093   1.64    0.
   57    2
    2    2  -1.45e-4      20.0      20.0     132.7      0.00
1 20.00E+08     VPRM Hydraulic conductivity


 0.000e+00 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11 0.500e-11
 0.500e-11 0.000e+00


1   1.0         THCK Thickness


  0  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1
  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1
  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  0


0  0.0          RECH Recharge
1  1.0          NODEID Node identification matrix
```

```
00000000000000000000
00000000000000000000
000000000000000010



 1  0.100    00.0       0.0 0           0.0       9.0      0.05
0   1.0        WT Initial head
0   0.0        CONC(1) Initial concentration of solute 1
0   0.0        CONC(2) Initial concentration of solute 2
0   8.5        CONC(3) Initial concentration of solute 3
    2                           [nproc]

 2 1.146e-04 1 0.5 0 0 0  [nsproc(1)][vmax(1)][iz(1)][yield(1)][ncomp(1)][nnc(1)][nhal(1)]

    1  17.4    3   0.1                     [ksproc(1,is)][hfk(1,is)]

    1. 0.   2.19  0.0                      [upcoef(1,ks)]

  2 9.606e-05 2 0.5 0 0 0 [nsproc(2)][vmax(2)][iz(2)][yield(2)][ncomp(2)][nnc(2)][nhal(2)]

    2  12.2    3   0.1                     [ksproc(2,is)][hfk(2,is)]

    0. 1.   2.15                           [upcoef(2,ks)]

    0                                      [numnut]

    1.157e-06    1.157e-06                 [death(ib)]

    0     0.25    0.25  0.25      [nzinhib][zinhibfac]
0 0.8200                          [z1]
0 0.2100                          [z2]
```

APPENDIX E: SELECTED OUTPUT FOR TEST PROBLEM

Selected sections of the output file BIOMOC.OUT for the test problem Aerobic Biodegradation and Transport of Toluene and Benzene (see Model Evaluation section) are given below. The input file for this problem is given in Appendix D.

```
1U.S.G.S. METHOD-OF-CHARACTERISTICS MODEL FOR SOLUTE TRANSPORT IN GROUND WATER
01-D T, B, and O transport with aerobic degradation, from chen et al.

0                    I N P U T     D A T A
0                      GRID DESCRIPTORS

            NX    (NUMBER OF COLUMNS)  =    58
            NY    (NUMBER OF ROWS)     =     3
            XDEL  (X-DISTANCE (L UNITS)) =     1.0
            YDEL  (Y-DISTANCE (L UNITS)) =     1.0
0                      TIME  PARAMETERS

            NTIM   (MAX. NO. OF TIME STEPS)       =      1
            NPMP   (NO. OF PUMPING PERIODS)       =      1
            PINT   (PUMPING PERIOD IN YEARS)      =       .018
            TIMX   (TIME INCREMENT MULTIPLIER)    =       .00
            TINIT  (INITIAL TIME STEP IN SEC.)    =      0.
0             HYDROLOGIC AND CHEMICAL PARAMETERS

            S       (STORAGE COEFFICIENT)       =       .000000
            POROS   (EFFECTIVE POROSITY)        =       .380
            BETA    (LONGITUDINAL DISPERSIVITY) =      2.2
            DLTRAT  (RATIO OF TRANSVERSE TO
                    LONGITUDINAL DISPERSIVITY)  =       .01
            ANFCTR  (RATIO OF T-YY TO T-XX)     =      1.000000

            nsol    (No. of solutes)           =       3
            npop    (No. of microbial pop.)     =       2
            ibio    (0=no degradation, 1=mult.
                    Monod, 2=min. Monod)     =       1

            npset    (No. of particle sets)       =      3
            No. of concentrations per particle set:

                 nconc( 1)= 1
                 nconc( 2)= 1
                 nconc( 3)= 1
0                    EXECUTION PARAMETERS

            NITP   (NO. OF ITERATION PARAMETERS) =   10
            TOL    (CONVERGENCE CRITERIA - SIPP) =   .50E-05
            ITMAX  (MAX.NO.OF ITERATIONS - SIP)  =     500
            CELDIS (MAX.CELL DISTANCE PER MOVE
                       OF PARTICLES - M.O.C.)    =     .100
            NPMAX  (MAX. NO. OF PARTICLES)       =  95000
            NPTPND (NO. PARTICLES PER NODE)      =    16
0     *** ONE-DIMENSIONAL *** WILL USE ONLY 1 ROW OF PARTICLES
            USE 2 PARTICLES FOR NPTPND = 4 OR 5
            USE 3 PARTICLES FOR NPTPND = 8 OR 9
            USE 4 PARTICLES FOR NPTPND = 16
1
0                      PROGRAM OPTIONS

            NPNT   (TIME STEP INTERVAL FOR
                    COMPLETE PRINTOUT)       =     1
            NPNTMV (MOVE INTERVAL FOR CHEM.
                    CONCENTRATION PRINTOUT)  =   360
            NPNTVL (TIME STEP INTERVAL FOR
                    VELOCITY PRINTOUT; 0=NEVER;
                    -1=FIRST TIME STEP;
                    -2=LAST TIME STEP)       =     1
            NPNTD  (PRINT OPTION-DISP.COEF.
                    0=NO; 1=FIRST TIME STEP;
                    2=ALL TIME STEPS)        =     0
            NUMOBS (NO. OF OBSERVATION WELLS
                    FOR HYDROGRAPH PRINTOUT) =     1
            NREC   (NO. OF PUMPING WELLS)    =     1
            NCODES (FOR NODE IDENT.)         =     1
            NPNCHV (TIME STEP INTERVAL FOR
                    VELOCITY PRINTOUT ON
                    FILE UNIT 7; 0=NEVER;
                    -1=FIRST TIME STEP;
                    -2=LAST TIME STEP)       =     0
            NPDELC (PRINT OPT.-CONC. CHANGE) =     0
            IREACT (REACTION SPECIFIERS):


            Particle Set    1:
```

```
                REACTION - LINEAR SORPTION

                  RHOB    (BULK DENSITY)                =  1.64000E+00
                  DK      (DISTRIBUTION COEFFICIENT)    =  1.39000E-01
                  RF      (RETARDATION FACTOR)          =  1.59989E+00


            Particle Set    2:


                REACTION - LINEAR SORPTION

                  RHOB    (BULK DENSITY)                =  1.64000E+00
                  DK      (DISTRIBUTION COEFFICIENT)    =  9.30000E-02
                  RF      (RETARDATION FACTOR)          =  1.40137E+00


            Particle Set    3:


                REACTION - NONE

1              STEADY-STATE FLOW

     TIME INTERVALS (IN SEC) FOR SOLUTE-TRANSPORT SIMULATION
     .57119E+06

0          LOCATION OF OBSERVATION WELLS

                NO.     X     Y

                 1     57     2

0          LOCATION  OF  PUMPING  WELLS

           X   Y   RATE(IN CFS)   SOLUTE CONC. (1,2,....,NSOL)

           2   2    -.145E-03  .200E+02  .200E+02  .133E+03

0          AREA OF ONE CELL =    1.000
0          X-Y SPACING:
               1.0000
               1.0000
1TRANSMISSIVITY MAP (L**2/SEC)

    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
1AQUIFER THICKNESS (L)

    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00
   1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00
   1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00
   1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00
   1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00
   1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00  1.00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
1DIFFUSE RECHARGE AND DISCHARGE (L/SEC)

    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
```

```
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
1HYDRAULIC CONDUCTIVITY MAP (L/SEC)

    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02
   1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02  1.00E-02   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
0          NO. OF FINITE-DIFFERENCE CELLS IN AQUIFER =       56

          AREA OF AQUIFER IN MODEL  =   56.000       L**2


          NZCRIT   (MAX. NO. OF CELLS THAT CAN BE VOID OF
                    PARTICLES;  IF EXCEEDED, PARTICLES ARE REGENERATED)   =    1

1NODE IDENTIFICATION MAP


   0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
   0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
   0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
   0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  1  0
   0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
   0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
0     NO. OF NODE IDENT. CODES SPECIFIED =  1
0          THE FOLLOWING ASSIGNMENTS HAVE BEEN MADE:
     CODE NO.     LEAKANCE     SOURCE SOLUTE CONC.(1,2,...,NSOL            RECHARGE
0        1         .100E+00  .000E+00  .000E+00  .900E+01
1VERTICAL HYDRAULIC CONDUCTIVITY/THICKNESS (L/(L*SEC))

    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00  1.00E-01   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
    .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00   .00E+00
1WATER TABLE

    0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.
    0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.
    0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.
    0.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.
    1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.
    1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   1.   0.
    0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.
    0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.
    0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.   0.
1HEAD DISTRIBUTION - ROW
 NUMBER OF TIME STEPS =     0
        TIME(SECONDS) =   .00000E+00
        TIME(DAYS)    =   .00000E+00
        TIME(YEARS)   =   .00000E+00

     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
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    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000
   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000
   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000
   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000
   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000
   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000   1.0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
```

Initial microbial mass:

Population 1

```
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00
 .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00
 .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00
 .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00
 .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00
 .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .820E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
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Population 2

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 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00
 .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00
 .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00
 .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00
 .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00
 .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .210E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
 .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00  .000E+00
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```
        There are   2  degradation processes active

        Process   1 depends on solutes    1   3
        With half saturation constants of    17.4       .100
        Maximum uptake rate =   .115E-03
        Microbial population   1
        Yield coefficient    .500
        Uptake coefficients:  =1 for primary substrate
                  >0 for solutes consumed, <0 for solutes produced
                  =0 for solutes not involved in process
                  Solute   1 Uptake coefficient =    1.00
                  Solute   2 Uptake coefficient =    .000E+00
                  Solute   3 Uptake coefficient =    2.19

        Process   2 depends on solutes    2   3
        With half saturation constants of    12.2       .100
        Maximum uptake rate =   .961E-04
        Microbial population   2
        Yield coefficient    .500
        Uptake coefficients:  =1 for primary substrate
                  >0 for solutes consumed, <0 for solutes produced
                  =0 for solutes not involved in process
                  Solute   1 Uptake coefficient =    .000E+00
                  Solute   2 Uptake coefficient =    1.00
                  Solute   3 Uptake coefficient =    2.15

        Solute

    Microbe population  1:
        death rate constant      .116E-05  nzinhib=  0,  zinhibfac=  .00

    Microbe population  2:
        death rate constant      .116E-05  nzinhib=  0,  zinhibfac=  .00
```

```
1CONCENTRATION

 NUMBER OF TIME STEPS =     0
        TIME(SECONDS) =   .00000E+00
   CHEM.TIME(SECONDS) =   .00000E+00
   CHEM.TIME(DAYS)    =   .00000E+00
        TIME(YEARS)   =   .00000E+00
   CHEM.TIME(YEARS)   =   .00000E+00
  NO. MOVES COMPLETED =     0

 BETA= 1.00
  10 ITERATION  PARAMETERS:
     .000000E+00    .479590E+00    .729173E+00    .859059E+00    .926653E+00    .000000E+00
     .479590E+00    .729173E+00    .859059E+00    .926653E+00
0

   N =    1
 NUMBER OF ITERATIONS=   2
 MAXIMUM HEAD CHANGE FOR EACH ITERATION:
       .79895      .00000
1HEAD DISTRIBUTION - ROW
 NUMBER OF TIME STEPS =     1
        TIME(SECONDS) =   .57119E+06
        TIME(DAYS)    =   .66110E+01
        TIME(YEARS)   =   .18100E-01

     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000   1.7989495   1.7844495   1.7699495   1.7554495   1.7409495   1.7264495   1.7119495   1.6974495   1.6829495
    1.6684495   1.6539495   1.6394495   1.6249495   1.6104495   1.5959495   1.5814496   1.5669496   1.5524496   1.5379496
    1.5234496   1.5089496   1.4944496   1.4799496   1.4654496   1.4509496   1.4364496   1.4219496   1.4074496   1.3929496
    1.3784496   1.3639497   1.3494497   1.3349497   1.3204497   1.3059497   1.2914497   1.2769497   1.2624497   1.2479497
    1.2334498   1.2189498   1.2044498   1.1899498   1.1754498   1.1609498   1.1464498   1.1319499   1.1174499   1.1029499
    1.0884499   1.0739499   1.0594499   1.0449499   1.0304500   1.0159500   1.0014500    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
     .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000    .0000000
1HEAD DISTRIBUTION - ROW
 NUMBER OF TIME STEPS =     1
        TIME(SECONDS) =   .57119E+06
        TIME(DAYS)    =   .66110E+01
        TIME(YEARS)   =   .18100E-01

1DRAWDOWN
0  CUMULATIVE MASS BALANCE -- (IN L**3)


    RECHARGE AND INJECTION     =  -.82823E+02
    PUMPAGE AND E-T WITHDRAWAL =   .00000E+00
    CUMULATIVE  NET  PUMPAGE   =  -.82823E+02
    WATER RELEASE FROM STORAGE =   .00000E+00
    LEAKAGE INTO AQUIFER       =   .00000E+00
    LEAKAGE OUT OF AQUIFER     =  -.82823E+02
    CUMULATIVE  NET  LEAKAGE   =  -.82823E+02
0       MASS BALANCE RESIDUAL  =   .10182E-03
        ERROR  (AS PERCENT)    =   .12293E-03

0  RATE MASS BALANCE -- (IN C.F.S.)


    LEAKAGE INTO AQUIFER       =   .00000E+00
    LEAKAGE OUT OF AQUIFER     =  -.14500E-03
    NET LEAKAGE    (QNET)      =  -.14500E-03
    RECHARGE AND INJECTION     =  -.14500E-03
    PUMPAGE AND E-T WITHDRAWAL =   .00000E+00
    NET WITHDRAWAL   (TPUM)    =  -.14500E-03
1X VELOCITIES
                           AT NODES

     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00   1.908E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04
    3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04
    3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04
    3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04
    3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04
    3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   3.816E-04   1.908E-04    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
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     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
1Y VELOCITIES
                          AT NODES

     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
     .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00    .000E+00
1          STABILITY CRITERIA --- M.O.C.


0     MAXIMUM FLUID VELOCITIES:  X-VEL =  3.82E-04     Y-VEL =  1.00E-10
0 TMV (MAX. INJ.) =   2620.7
  TIMV (CELDIS)   =   262.07
0 TIMV =  2.62E+02     NTIMV =  2179     NMOV =  2180

   TIM (N)  =   .57119E+06
   TIMEVELO =   262.01
   TIMEDISP =   .58498E+03
0 TIMV =  2.62E+02     NTIMD =   976     NMOV =  2180
0          THE LIMITING STABILITY CRITERION IS CELDIS
     MAX. X-VEL. IS CONSTRAINT AND OCCURS BETWEEN NODES (   2,   2) AND (   3,   2)
0          NO. OF PARTICLE MOVES REQUIRED TO COMPLETE THIS TIME STEP  = 2180


0  NP     =            224        IMOV     =          1  Particle Set   1
0  NP     =            224        IMOV     =          1  Particle Set   2
0  NP     =            224        IMOV     =          1  Particle Set   3
0  NP     =            224        IMOV     =          2  Particle Set   1
0  NP     =            224        IMOV     =          2  Particle Set   2
0  NP     =            224        IMOV     =          2  Particle Set   3
0  NP     =            224        IMOV     =          3  Particle Set   1
0  NP     =            224        IMOV     =          3  Particle Set   2
0  NP     =            224        IMOV     =          3  Particle Set   3
.
.
.
.
.
0  NP     =            480        IMOV     =       2179  Particle Set   1
0  NP     =            572        IMOV     =       2179  Particle Set   2
0  NP     =            462        IMOV     =       2179  Particle Set   3
0  NP     =            480        IMOV     =       2180  Particle Set   1
0  NP     =            572        IMOV     =       2180  Particle Set   2
0  NP     =            462        IMOV     =       2180  Particle Set   3
1CONCENTRATION

 NUMBER OF TIME STEPS =     1
        DELTA T       =   .57119E+06
        TIME(SECONDS) =   .57119E+06
   CHEM.TIME(SECONDS) =   .57118E+06
   CHEM.TIME(DAYS)    =   .66108E+01
        TIME(YEARS)   =   .18100E-01
   CHEM.TIME(YEARS)   =   .18099E-01
  NO. MOVES COMPLETED =  2180

 Solute   1

 CHEMICAL MASS BALANCE

        MASS IN BOUNDARIES     =   .00000E+00
        MASS OUT BOUNDARIES    =  -.64337E+02
        MASS PUMPED IN         =   .16565E+04
        MASS PUMPED OUT        =   .00000E+00
        MASS LOST BY DECAY     =   .00000E+00
        MASS ADSORBED ON SOLIDS=   .95598E+00
        INITIAL MASS ADSORBED  =   .00000E+00
        INFLOW MINUS OUTFLOW   =   .15922E+04
        INITIAL MASS DISSOLVED =   .00000E+00
        PRESENT MASS DISSOLVED =   .15936E+01
        CHANGE MASS DISSOLVED  =   .15936E+01
        CHANGE TOTL.MASS STORED=   .25496E+01
        mass lost by degradation= -.15895E+04
        mass gain by production=   .00000E+00
      COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION:
        MASS BALANCE RESIDUAL  =   .10938E+00
        ERROR  (AS PERCENT)    =   .66028E-02
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Solute   2

CHEMICAL MASS BALANCE

       MASS IN BOUNDARIES     =   .00000E+00
       MASS OUT BOUNDARIES    =  -.15532E+03
       MASS PUMPED IN         =   .16565E+04
       MASS PUMPED OUT        =   .00000E+00
       MASS LOST BY DECAY     =   .00000E+00
       MASS ADSORBED ON SOLIDS=   .54583E+00
       INITIAL MASS ADSORBED  =   .00000E+00
       INFLOW MINUS OUTFLOW   =   .15012E+04
       INITIAL MASS DISSOLVED =   .00000E+00
       PRESENT MASS DISSOLVED =   .13599E+01
       CHANGE MASS DISSOLVED  =   .13599E+01
       CHANGE TOTL.MASS STORED=   .19058E+01
       mass lost by degradation= -.14980E+04
       mass gain by production=   .00000E+00
     COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION:
       MASS BALANCE RESIDUAL  =   .12701E+01
       ERROR  (AS PERCENT)    =   .76677E-01
Solute   3

CHEMICAL MASS BALANCE

       MASS IN BOUNDARIES     =   .00000E+00
       MASS OUT BOUNDARIES    =  -.34872E+04
       MASS PUMPED IN         =   .10991E+05
       MASS PUMPED OUT        =   .00000E+00
       MASS LOST BY DECAY     =   .00000E+00
       MASS ADSORBED ON SOLIDS=   .00000E+00
       INITIAL MASS ADSORBED  =   .00000E+00
       INFLOW MINUS OUTFLOW   =   .75035E+04
       INITIAL MASS DISSOLVED =   .18088E+03
       PRESENT MASS DISSOLVED =   .98249E+03
       CHANGE MASS DISSOLVED  =   .80161E+03
       CHANGE TOTL.MASS STORED=   .80161E+03
       mass lost by degradation= -.67016E+04
       mass gain by production=   .00000E+00
     COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION:
       MASS BALANCE RESIDUAL  =   .34863E+00
       ERROR  (AS PERCENT)    =   .31721E-02
```