

**BIOMOC is a two-dimensional numerical solute-transport model that simulates the transport and biotransformation of multiple reacting solutes. BIOMOC simulates:**

- **Advection, hydrodynamic dispersion, fluid sources, retardation, decay, and biodegradation.**
- **Multiple solute species and immobile phase concentrations.**
- **One-dimensional and two-dimensional areal or cross-sectional problems.**
- **Multiple degradation processes and microbial populations, including sequential biodegradation.**
- **Biological transformation rates including single, multiple, and minimum Monod kinetics; and competitive, noncompetitive, and Haldane inhibition.**
- **Zero-order or first-order approximations of biodegradation rates.**
- **Microbial growth and decay either disabled, limited by biomass inhibition, or limited by nutrient availability.**

**This publication describes the major features of BIOMOC, provides an example application of this model for the Bemidji, Minnesota crude-oil spill site, and gives information on obtaining BIOMOC and other USGS modeling programs and documentation.**

## Introduction

Bioremediation, a method that relies on natural and enhanced biodegradation processes can be an effective remedial action at many contaminated sites. The challenge in assessing the feasibility of bioremediation is to demonstrate that contaminant concentration attenuation is linked to biodegradation processes and degradation products.

Numerical models that simulate transport and biodegradation processes are useful for integrating information collected in the field, developing an overall contaminant mass balance, and studying the relative importance of simultaneously occurring processes. If sufficient data are available, a numerical model can be used to test conceptual hypotheses, estimate biodegradation rates, predict plume evolution, and evaluate factors limiting biodegradation.

BIOMOC (Essaid and Bekins, 1997) is a two-dimensional multispecies solute-transport model that includes reactions resulting from biodegradation processes. It is designed to be flexible and can allow any number and combination of simultaneous or sequential biodegradation processes mediated by one or more microbial populations. Simulations, among others, can be designed to represent aerobic and anaerobic degradation of hydrocarbons and chlorinated solvents.

## Biodegradation Terms

In BIOMOC, macroscopic concentrations of fluid substrates, electron acceptors, and cellular nutrients are used to calculate uptake and growth. Monod kinetics is used to represent biodegradation uptake that depends on a single solute concentration. For biodegradation processes that involve several solutes, two alternate modified Monod formulations are included in BIOMOC. The multiple Monod formulation assumes that the biodegradation reaction is limited by the concentration of each solute involved in the reaction, whereas the alternative minimum Monod formulation assumes that a single solute is limiting the process. In addition, the Monod parameters can be specified to approximate zero-order or first-order biodegradation rates.

All kinetics formulations include competitive, noncompetitive, Haldane, and biomass inhibition. The noncompetitive inhibition formulation is useful for modeling the transition between redox zones within contaminant plumes. An example 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 a primary substrate is still present. Haldane inhibition is used to model toxicity effects.

The metabolism of substrate will result in biomass growth if sufficient cellular nutrients are available. The growth and decay of multiple microbial populations can be simulated in BIOMOC. Microbial growth can be disabled, limited by biomass inhibition, or limited by the availability of a cellular nutrient. Biomass inhibition is an empirical means for limiting biomass growth.

BIOMOC does not include pore-scale processes and does not account for the effect of diffusion into and out of the biophase. It also has been assumed in BIOMOC that the biomass remains attached to the sediments. Pore clogging by biomass growth is not accounted for.

## Numerical Approach

BIOMOC is an extension of the U. S. Geological Survey's Method of Characteristics (MOC) flow and transport model (Konikow and Bredehoeft, 1978; Goode and Konikow, 1989). The two-dimensional transport equation solved in BIOMOC for each solute species is:

$$R_i \frac{\partial C_i}{\partial t} = \frac{1}{b} \frac{\partial}{\partial x_j} \left( b D_{jk} \frac{\partial C_i}{\partial x_k} \right) - V_j \frac{\partial}{\partial x_j} C_i + \frac{W(C_i - C'_i)}{(\epsilon b)} - R_i \lambda_i C_i - B_i,$$

where  $j, k=1,2$ ,  $C_i$  is the concentration of the  $i$ th solute ( $\text{ML}^{-3}$ ),  $R_i$  is the retardation factor for the  $i$ th solute,  $D_{jk}$  is the dispersion tensor ( $\text{L}^2\text{T}^{-1}$ ),  $C'_i$  is the concentration of the  $i$ th solute in the source fluid ( $\text{ML}^{-3}$ ),  $b$  is the aquifer thickness (L),  $W$  is the source fluid flux ( $\text{LT}^{-1}$ ),  $V_j$  is the average linear flow velocity in the  $x_j$  direction ( $\text{LT}^{-1}$ ),  $\epsilon$  is the effective porosity,  $\lambda_i$  is the first-order decay rate constant ( $\text{T}^{-1}$ ) for the  $i$ th solute (half life  $t_{1/2} = (\ln 2)/\lambda$ ), and  $B_i$  is the biodegradation reaction rate term ( $\text{ML}^{-3}\text{T}^{-1}$ ) representing the total uptake of the  $i$ th solute due to all simultaneously occurring biodegradation processes.

The flow and transport equations are discretized using a rectangular, uniformly spaced, block-centered, finite-difference grid. Implicit finite-difference equations are used to solve the flow equation. The average linear flow velocities are then calculated and used to solve the transport equation by the method of characteristics and a particle tracking procedure that represents advective transport.

Multiple particle sets can be tracked in BIOMOC. Solutes with the same retardation factor can be associated with a single particle set. Immobile particles may also be specified to facilitate the representation of a solid phase such as iron coatings on sediment grains. Particles of each set are initially distributed uniformly throughout the finite-difference grid. During each time step, mobile particles are moved based on the average linear velocity adjusted for retardation. After all the particles have been moved, the average concentration of the particles located within a block is calculated. This new concentration,  $C_i^*$ , is the result of advective transport only. Explicit finite-difference approximations then are used to solve for the change in concentration due to hydrodynamic dispersion, fluid sources, changes in fluid storage, and biodegradation reactions using the average of the concentration from the previous time step and the advected concentration,  $C_i^*$ . After the biodegradation uptake terms have been calculated for the time step, the amount of biomass growth is determined.

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 steady-state transport with first- and zero-order decay, or Monod degradation. BIOMOC results have also compared favorably to results from two other numerical codes.

## Application of BIOMOC

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.

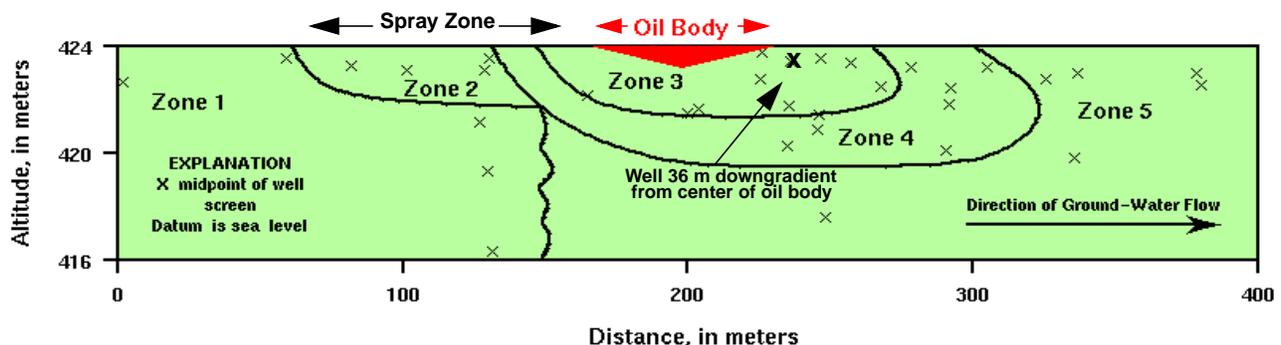
Following conceptual model development, estimates of flow, transport, and biodegradation parameters must be made. These may be based on a combination of field measurements and observations, laboratory values, and (or) literature values. The uncertainty involved in estimating parameters should be taken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

BIOMOC simulations can be used to test alternate biodegradation conceptual models, develop mass balances for contaminants, assess the potential for bioremediation at a site, examine the relative contributions of competing biodegradation processes to contaminant attenuation, and to compare remediation schemes.

## The Bemidji, Minn., Spill Site:

Application of BIOMOC is illustrated with a two-dimensional, transient simulation of the Bemidji, Minnesota, crude-oil spill site. The evolution of redox zones and microbial populations in the ground-water plume were simulated. In this example, BIOMOC was used to evaluate the relative contribution of aerobic and anaerobic biodegradation processes to natural attenuation of the petroleum hydrocarbon plume. The following sections summarize the BIOMOC application to the Bemidji, Minn., ground-water plume published by Essaid and others (1995).

A buried oil pipeline located in a glacial outwash plain near Bemidji, Minnesota, ruptured in 1979, spilling about  $1.7 \times 10^6$  liters (11,000 barrels) of crude oil. An estimated  $1.2 \times 10^6$  liters (7,800 barrels) of the spilled oil were recovered. The remaining oil infiltrated into the subsurface and provides a long-term, continuous source of hydrocarbons that dissolve in, and are transported with ground water. The spill site became a USGS Toxic Substances Hydrology Program research site in 1983. Evidence for microbial degradation of the petroleum hydrocarbons has been documented in several studies (Bennett and others, 1993; Eganhouse and others, 1993; Baedecker and others, 1993). Five geochemical zones (fig. 1) have been identified in the ground water along a cross-section through the northern oil body.



- Zone 1 - oxygenated uncontaminated native ground water.**
- Zone 2 - reduced oxygen concentrations with refractory high molecular-weight hydrocarbons.**
- Zone 3 - anoxic and with high concentrations of hydrocarbons, dissolved manganese, iron, and methane.**
- Zone 4 - transitional from anoxic conditions to fully oxygenated conditions.**
- Zone 5 - oxygenated water with slightly elevated dissolved inorganic and organic constituents.**

Figure 1. The simulated two-dimensional cross section at the Bemidji, Minnesota, site, showing the geochemical zones of the ground-water plume [Modified from Baedecker and others (1993)].

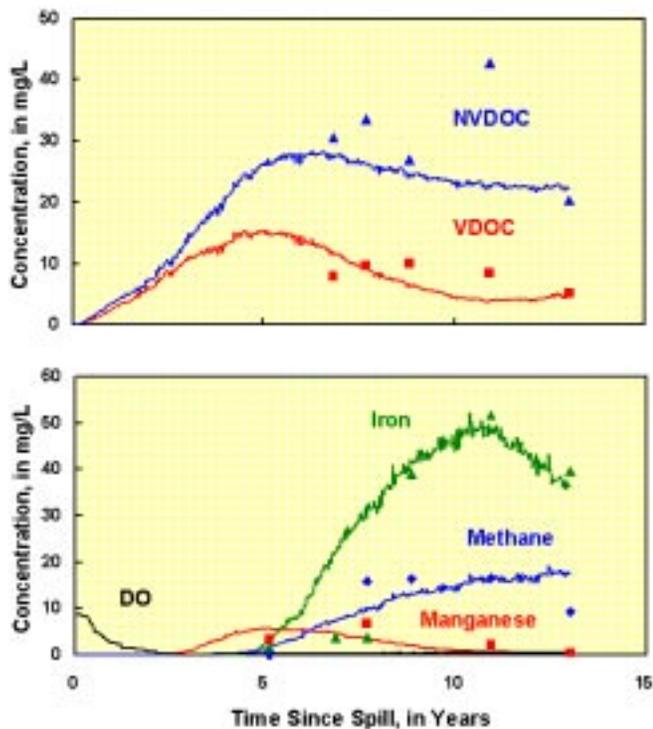


Figure 2. Changes in simulated (lines) and observed (symbols) concentrations since 1979 at a location 36 m downgradient from the center of the oil body (VDOC - volatile dissolved organic carbon, NVDOC - nonvolatile dissolved organic carbon, DO - dissolved oxygen, Manganese - dissolved  $Mn^{2+}$ , Iron - dissolved  $Fe^{2+}$ ).

Ground-water samples from numerous wells along this section have been analyzed beginning in 1985. Total dissolved organic carbon (TDOC) was split into two operationally defined fractions: volatile dissolved organic carbon (VDOC) and nonvolatile dissolved organic carbon (NVDOC). VDOC includes benzene and alkylbenzenes, and NVDOC includes polysaccharides, organic acids, and polyaromatic hydrocarbons. The temporal evolution of concentrations observed since 1979 at a well located 36 m downgradient from the center of the oil body (fig. 1) is shown in figure 2. VDOC and NVDOC concentrations initially increased and then achieved steady concentrations approximately 10 years after the spill. Dissolved manganese ( $Mn^{2+}$ ) increased, peaking after eight years, and then decreased suggesting that the solid phase manganese [ $Mn(IV)$ ] available for reduction was being depleted. Dissolved iron ( $Fe^{2+}$ ) concentrations began to increase after the drop in  $Mn^{2+}$ , and peaked at 11 years, suggesting solid phase iron [ $Fe(III)$ ] reduction. Likewise methane concentration abruptly increased after eight years and then leveled off, suggesting the onset of methanogenesis.

### Simulation of the Bemidji, Minn., Spill Site:

A simplified conceptual model was developed to make the Bemidji plume simulations computationally practical. Seven mobile solutes (VDOC, NVDOC, DO, Nitrogen,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $CH_4$ ), two solid-phase concentrations [ $Mn(IV)$  and  $Fe(III)$ ], and three microbial populations (aerobes, Mn/Fe reducers, and methanogens) were modeled. The eight biodegradation processes simulated using BIOMOC and the solutes involved in each process are summarized in table 1. Volatile and nonvolatile dissolved organic carbon both undergo aerobic degradation, Mn reduction, Fe reduction, and methanogenesis. It is assumed that VDOC is degraded more rapidly than NVDOC and that some VDOC is partially degraded to NVDOC (Cozzarelli and others,

1994). 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 [ $Mn(IV)$ ]; dissolved iron ( $Fe^{2+}$ ) produced by reduction of solid phase iron [ $Fe(III)$ ]; 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.

A vertical cross-section parallel to the direction of ground-water flow along the sampling transect (fig. 1) was simulated from the time of the spill in 1979 until September 1992. Steady-state flow was assumed. Literature values, theoretical estimates, and field biomass measurements were used to obtain reasonable estimates of the transport and biodegradation parameters used in the simulation. Comparisons to the observed spatial and temporal variations in solute concentrations were used to calibrate the model

The simulated concentrations at a well that is 36 m downgradient from the center of the oil body are presented in figure 2. The simulated VDOC and NVDOC concentrations reproduce the observed trends. Observed  $Mn^{2+}$  and  $Fe^{2+}$  concentrations are reproduced in the simulations; however, the simulated increase in concentrations occurs earlier than observed. This may be because the model does not include a lag period for adjustment of the microbes, or because DO is being depleted too quickly in the simulation. The observed methane concentrations could only be matched when there was no  $Fe^{3+}$  inhibition. This suggests the presence of microenvironments due to the heterogeneous nature of the pore space and aquifer material, with some zones undergoing iron reduction and other zones undergoing methanogenesis.

The two-dimensional character of the simulated solute plumes are shown in figure 3. In general the ground-water plume begins in the spray zone, where it is relatively thin. It thickens below the low conductivity oil zone because ground-water flow is diverted beneath the oil body. Downgradient from the oil zone, the plume is pushed down into the aquifer by recharging ground water. The VDOC plume is localized because most of the VDOC is being degraded. The less degradable NVDOC has migrated farther downgradient than the VDOC plume. Plumes of dissolved  $Mn^{2+}$ , dissolved  $Fe^{2+}$ , and methane have developed. The  $Mn^{2+}$  plume has migrated farther than the  $Fe^{2+}$  plume, which has migrated farther than the methane plume. This is a reflection of the sequence of  $Mn(IV)$  reduction,  $Fe(III)$  reduction, and methanogenesis.

Table 1. Biodegradation processes, the solutes involved in each process, and the microbial population responsible for each process in the Bemidji simulation (VDOC = volatile dissolved organic carbon, NVDOC = nonvolatile dissolved organic carbon, DO = dissolved oxygen, N = nitrogen, Aerobic = aerobic biodegradation, Mn red. = Mn reduction, Fe red. = Fe reduction, Meth. = methanogenesis, X = consumed, ++ = produced,  $I_{nc}$  = inhibits noncompetitively, 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

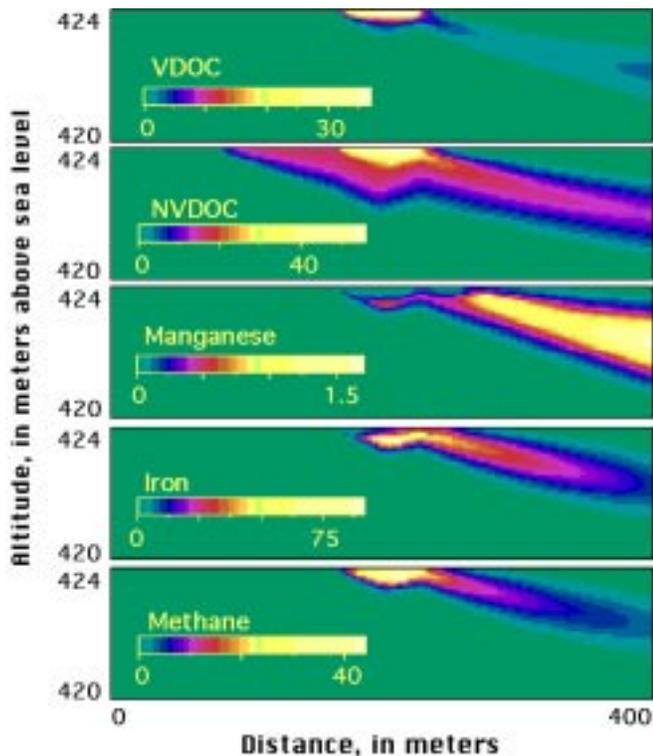


Figure 3. Simulated plumes of volatile (VDOC) and nonvolatile (NVDOC) dissolved organic carbon, dissolved  $Mn^{2+}$  (Manganese), dissolved  $Fe^{2+}$  (Iron), and methane. The simulated cross-section showing aquifer features is presented in figure 1.

The simulation predicts that 46 percent of the TDOC, 66 percent of the VDOC, and 39 percent of the NVDOC introduced into the aquifer is degraded. Aerobic degradation accounts for 40 percent of the TDOC degraded. Anaerobic processes account for the remaining 60 percent of degradation of TDOC: 5 percent by Mn reduction, 19 percent by Fe reduction and 36 percent by methanogenesis. Thus, the simulation suggests that anaerobic processes account for over half of the removal of DOC at this site

## Conclusions

BIOMOC is a flexible model that can be adapted to many biodegradation settings. The user specifies the solutes and microbial populations involved in each biodegradation process, and multiple biodegradation processes that occur simultaneously or sequentially can be simulated. Simulations can be designed to represent aerobic and anaerobic degradation of individual hydrocarbons as well as chlorinated solvents. Simulations of this type are useful in assessing the potential for natural or enhanced bioremediation.

## References Cited

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## Additional Information Can be Obtained From:

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U.S. Geological Survey  
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The Toxic Substances Hydrology Program “Home Page” on the World Wide Web:

<http://toxics.usgs.gov/toxics/>

BIOMOC and other USGS model programs are available at no cost from the Water Resources Applications Software “Home Page” on the World Wide Web:

<http://water.usgs.gov/software/>

Reports documenting BIOMOC and other USGS model programs can be purchased from:

U.S. Geological Survey  
Branch of Information Services  
Box 25286  
Denver, CO 80225-0286