Mathematical Modeling of BTX: Biotransformation and Transport in the Subsurface

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A two-dimensional compositional model is presented; this model describes the transport and biotransformation of organic contaminants in a variably saturated subsurface environment. Modeled processes include mass exchange between constituent phases (water, air, soil, and organisms), advective and dispersive fluxes in the water phase, diffusive flux in the air phase, and biotransformation and biomass production in the biophase. In this model, solute transfer across air/water and water/solid interfaces is modeled using equilibrium relationships. Rate-limited mass transfer between the water and biophases is described with a linear driving force expression. Microbial degradation and biomass net growth are modeled by Monod-type kinetics. Solute transport and microbial growth equations are solved using an iterative Galerkin finite element method with a variable time-weighting scheme. Coupled biophase mass balance equations for each component are solved with a Newton-Raphson iterative scheme. Model capabilities are illustrated with two-dimensional, cross-sectional simulations of natural bioattenuation. The influence of biotransformation processes on the transport and extent of a toluene plume is examined. — Environ Health Perspect 103(Suppl 5):85–88 (1995)

Key words: biodegradation, transport, modeling

Introduction

The presence of petroleum hydrocarbons in groundwater aquifers represents a serious public health threat, especially in regions where groundwater is the sole drinking water source. Among these organic, monoaromatic hydrocarbons such as benzene, toluene, and xylene isomers (BTX) have been of primary concern due to their ubiquity in many petroleum products and industrial solvents, their relatively high mobility in groundwater systems, and their potential threat to human health at relatively low concentrations. In the state of Michigan, recommended drinking water standards are 1 ppb for benzene, 1 ppm for toluene, and 10 ppm for xylene (DNR ACT 307 Clean-up Standards).

In order to clean up contaminated groundwater aquifers, many physical, chemical, and biological methods for groundwater remediation have been developed (1). In situ bioremediation, which involves the use of indigenous microbes for contaminant biodegradation within the aquifer, is a particularly promising approach (2, 3). In the development of this technology, there is a clear need for mathematical models that can serve as useful tools in our efforts to understand and quantify the complex interaction of physical, chemical, and biological processes influencing in situ bioremediation at the field scale. Such models can be especially helpful in assessing the processes limiting remediation performance, in comparing alternative remediation system designs, and in estimating the performance and duration of restoration operations.

An experimentally based mathematical model that describes the transport and biodegradation of BTX in the subsurface environment is currently under development. This model is formulated using a microcolony growth concept (4) and incorporates gas phase diffusional transport and liquid–gas mass exchange of model components. It differs from other biodegradation/transport models (4–6) in that it accounts for transport and degradation processes in the unsaturated soil zone: it models two substrates, two electron acceptors, one limiting nutrient, and two indigenous microbial populations. This work is also noteworthy in that model formulation and parameter estimation are based upon experimental observations of BTX degradation in natural sandy aquifer material. Additional laboratory experiments have been used to evaluate model applicability.

This report first outlines the processes incorporated in the conceptual BTX biodegradation/transport model. Following a brief description of the numerical simulator and comparisons between model simulations and laboratory measurements, a hypothetical two-dimensional simulation of natural attenuation of toluene in a sandy aquifer is presented to illustrate model capabilities.

Conceptual Model

The mathematical model describes biodegradation of the dissolved hydrocarbon plume. Because most petroleum hydrocarbons (e.g., BTX) are less dense than water and tend to be distributed in dissolved form near and above the water table and the capillary fringe zone, unsaturated zone processes such as vaporization of volatile components and oxygen diffusion from the atmosphere may play a significant role in controlling the biotransformation of the contaminants and should be incorporated in a general model. Thus, for an unsaturated/saturated soil system, three phases must be considered: water, gas, and soil.
Laboratory sediment–slurry experiments with natural aquifer materials from a contaminated site in Kalkaska, Michigan, revealed that benzene and toluene were degraded under aerobic conditions by a mixed population of indigenous microorganisms (7). Other laboratory evidence supports the existence of separate benzene and toluene degraders in this population (8). In addition, toluene was observed to degrade under denitrifying conditions in the laboratory. Based upon these experimental observations, a conceptual model of biotransformation was formulated. Model components include two independent primary substrates, benzene and toluene; two electron acceptors, oxygen for aerobic respiration and nitrate for anoxic respiration; one limiting nutrient; and two microbial populations.

Important processes incorporated in the model include: the transport of contaminants, electron acceptors, and the limiting nutrients in the porous medium by advection and dispersion; the partitioning of system components between constituent phases (the adsorption/desorption of organics between liquid/solid phases, the volatilization of organics and the diffusion of oxygen from the unsaturated zone, and mass transfer of all the nutrients from bulk fluid to biomass); microbial consumption of the nutrients; and microbial growth and decay.

Based upon mass conservation principles and the system components described above, a mathematical model was developed that consists of five nonlinear partial differential equations, two ordinary differential equations, and five nonlinear algebraic equations. The partial differential equations describe component transport in the bulk fluid phases, the nonlinear algebraic equations describe component utilization in the biophase, and the ordinary differential equations describe microbial growth and decay.

**Two-dimensional Simulator**

A two-dimensional simulator was developed to solve model-governing equations. Within the simulator, the advective and dispersive fluxes are explicitly evaluated from Darcy’s law using water pressures computed from an unsaturated–saturated flow package (SUTRA) (9). Transport and microbial growth equations are then solved using a Galerkin finite element technique with linear quadrilateral elements and a variable-weighted finite difference operator for discretization in time. Nonlinear algebraic equations for component utilization are solved using an iterative Newton-Raphson scheme. The simulator was initially verified through comparisons with analytical solutions for conservative solute transport. It was further tested by comparison to one-dimensional solutions obtained in other biotransformation modeling studies (4).

**Model Evaluation**

To evaluate model capability, the simulator was used to predict the performance of column experiments designed to investigate biodegradation in a continuous flow, water-saturated soil system (10). The columns were packed with aquifer material sampled aseptically from a site underlying the gas plant facility in Kalkaska, Michigan. To facilitate model experimental comparisons, efforts were made to measure or estimate the required model parameters independently. Most of these parameters were obtained through batch and sediment–slurry studies with the aquifer materials.

In the biodegradation experiments, columns were packed with the aquifer material, saturated, and then fed with a constant composition influent. Two types of influents were injected into different columns to create two different respiration conditions, aerobic and denitrifying, for the microorganisms. Effluent concentrations of benzene, toluene, and xyylene were measured as a function of time. Experimental procedures and results are described in more detail by Anid and Vogel (11).

The mathematical model was evaluated by employing the simulator to predict the effluent breakthrough curves that correspond to the above column experiments. Simulation results suggest that independently determined parameters (through laboratory batch experiments or aquifer slurry studies) can be used to obtain rea-

| Table 1. Parameters used in model simulations. |
|---------------------------------------------|
| **Parameter**                   | **Value**                      |
| ---------------------------------|--------------------------------|
| **Physicochemical parameters**    |                                |
| Homogeneous, medium to coarse sand |                                |
| Porosity                         | 0.30                           |
| Mean particle diameter           | 0.50 mm                        |
| Intrinsic permeability           | 1.755 x 10^{-11} m²            |
| Hydraulic gradient               | 5 m/1000 m                     |
| Pore velocity                    | 0.25 m/day                     |
| Soil bulk density                | 1.86 g/cm³                     |
| Longitudinal dispersivity        | 0.8 m                          |
| Vertical dispersivity            | 0.004 m                        |
| Capillary pressure-saturation    |                                |
| relationship (van Genuchten model)|                                |
| Molecular diffusivity in water   |                                |
| For toluene                      | 6.55 x 10^{-5} m²/day          |
| For oxygen                       | 1.86 x 10^{-4} m²/day          |
| Molecular diffusivity in air     |                                |
| For toluene                      | 0.694 m²/day                   |
| For oxygen                       | 1.63 m²/day                    |
| Sorption partitioning coefficient|                                |
| For toluene                      | 0.139 cm³/day                  |
| For oxygen                       | 0.0 cm³                        |
| Aqueous biodegradation mass transfer coefficient | | |
| For toluene                      | 1.31 x 10² m³/day              |
| For oxygen                       | 3.72 x 10² m³/day              |
| Henry’s law constant (on volume water/volume gas basis) | | |
| For toluene                      | 3.2 x 10⁻¹                    |
| For oxygen                       | 2.74 x 10⁻¹                    |
| **Microbial parameters**         |                                |
| Initial biomass                  | 0.5 mg/l                       |
| Colony population density        | 100 cells/colony               |
| Oxygen use coefficient for toluene| 2.19 mg O_2/mg T            |
| Maximum specific toluene utilization rate | 9.9 day⁻¹          |
| under aerobic conditions          |                                |
| Yield coefficient for toluene    | 0.5 g cell/g³                  |
| Colony mass                      | 10⁻⁸ g/colony                  |
| Contact area of one colony       | 1.19 x 10⁻³ m²/colony          |
| Half-saturation constant of toluene| 17.4 mg/l                     |
| Half-saturation constant of oxygen| 0.1 mg/l                      |
| Decay coefficient                 | 0.1 day⁻¹                      |
A Two-Dimensional Simulation of Natural Bioattenuation

The capabilities of the developed simulator can be illustrated through an application to a field contamination problem. This simulation example examines the fate of toluene in a variably saturated aquifer under natural conditions with and without biodegradation. The simulated aquifer was assumed to be composed of a medium to coarse sand, which is similar to that characterized at the Kalkaska site. The parameters used in the two-dimensional simulation are listed in Table 1. Microbial parameters are derived from the laboratory experiments. The average depth of the water table is approximately 1 m below the ground surface, with a local hydraulic gradient of 0.005. Hydrostatic water-phase pressures were prescribed on vertical boundaries to produce linear pore water velocities of approximately 0.25 m/day. Gas-phase pressures at the ground surface were prescribed as atmospheric. A zero dispersive flux condition was prescribed across the bottom and vertical boundaries. A point source of toluene in the vicinity of the water table was simulated by continuous injection of toluene solution at a constant rate of 60 mg/day in three grid elements. The concentration distribution of toluene in the water phase after 30 days with no biodegradation is shown in Figure 1A. Concentration contours of toluene and oxygen after 30 days of natural bioattenuation are shown in Figures 1B and 1C, respectively.

Figure 1A shows that after 30 days toluene has spread not only within the saturated zone but also in the unsaturated zone due to the gas/water exchange and volatilization processes. Some of the toluene vapor has reached the top of the vadose zone, diffusing into the atmosphere. Comparison of Figures 1A and 1B reveals a substantial impact of biodegradation. In the presence of microorganisms, the toluene plume (Figure 1B) shrinks in both the saturated and unsaturated zones. Under these conditions, the toluene plume in the vadose zone no longer reaches the ground surface. In the region in which the toluene concentration exceeds 1 ppm (Figure 1B), the oxygen is essentially depleted (lower than 0.1 ppm) (Figure 1C). As shown in Figure 1C, the oxygen concentrations decrease at the water table and large concentration gradients are observed in the vicinity of the contaminant plume. The higher concentration within the vadose zone is created by relatively rapid diffusion of oxygen from the atmosphere. The large concentration gradient around the contaminant plume is caused by the microbial consumption of oxygen within this region. Due to the continuous supply of dissolved oxygen from the area upstream of the plume, the concentration gradient in this upstream zone is reduced.

As these simulations illustrate, the two-dimensional model can serve as a tool to simulate field remediation or natural attenuation scenarios, to evaluate the influence of dimensionality on performance of bioremediation, and to explore the effects of vadose zone processes on in situ bioremediation.

REFERENCES

1. Environmental Engineering Research Council of ASCE. Ground-water protection and reclamation. J Environ Eng 116:654–662 (1990).
2. Lee MD, Thomas JM, Borden RC, Bedient PB, Ward CH, Wilson JT. Bioremediation of aquifers contaminated with organic compounds. CRC Crit Rev Environ Control 18:29–89 (1988).
3. Thomas JM, Lee MD, Bedient PB, Borden RC, Canter LW, Ward CH. Leaking underground storage tanks: remediation with emphasis on in situ bioremediation. EPA/600/S2-87/008, Washington: U.S. Environmental Protection Agency, 1987.
4. Molt FJ, Widdowson MA, Benefield LD. Simulation of microbial growth dynamics coupled to nutrient and oxygen transport in porous media. Water Resour Res 22:1207–1216 (1986).
5. Borden RC, Bedient PB. Transport of dissolved hydrocarbons...
influenced by oxygen-limited biodegradation: 1. Theoretical development. Water Resour Res 22:1973–1982 (1986).
6. Kinzelbach W, Schafer W, Herzer J. Numerical modeling of nitrate and enhanced denitrification processes in aquifers. Water Resour Res 27:1123–1135 (1991).
7. Alvarez PJJ, Vogel TM. Substrate interactions of benzene, toluene, and para-xylene during microbial degradation by pure cultures and mixed culture aquifer slurries. Appl Environ Microbiol 57:2981–2985 (1991).
8. Alvarez PJJ, Anid PJ, Vogel TM. Kinetics of biodegradation of benzene and toluene in sandy aquifer material. Biodegradation 2:43–51 (1991).
9. Voss CI. A finite-element simulation model for saturated-unsaturated, fluid density dependent groundwater flow with energy transport or chemically-reactive single species solute transport. U.S. Geological Survey Water Resources Investigations Rpt 84-4369. Washington: U.S. Geological Survey, 1984.
10. Chen Y-M, Abriola LM, Alvarez PJJ, Anid PJ, Vogel TM. Modeling transport and biodegradation of benzene and toluene in sandy aquifer material: comparisons with experimental measurements. Water Resour Res 28:1833–1847 (1992).
11. Anid PJ, Vogel TM. The potential of indigenous and added microorganisms for degrading benzene, toluene and xylene under different environmental conditions. In: Proceedings of the 1990 Specialty Conference of Environmental Engineering, ASCE, 8–11 July 1990, Arlington, VA (Charles R, O'Melia PE, eds). New York: American Society of Civil Engineers, 1990;382–389.