Ground water contaminant modeling for bioremediation: A review*

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Abstract

This paper presents an overview of biodegradation as a remediation technology for contaminated ground water. A discussion of design issues for the remediation process and a review of models applied to biodegradation in groundwater are included. Following a description of BIO-PLUME II numerical degradation model, the authors discuss its application to field studies of an aviation fuel spill in Traverse City, Michigan.

Introduction

One of the remediation methods that has been gaining more widespread attention recently is bioremediation, the treatment of subsurface pollutants by stimulating the native microbial population. The technology is not novel, the biodegradation potential of organic contaminants has been recognized and utilized in the wastewater treatment process for years. The biodegradation process is simply a biochemical reaction which is mediated by microorganisms where an organic compound is oxidized (loses hydrogen electrons) by an electron acceptor which itself is reduced (gains hydrogen electrons). Several electron acceptors have been identified to date: oxygen, nitrate, sulfate, or carbon dioxide. The utilization of oxygen as an electron acceptor is termed aerobic biodegradation and that of nitrate is called anaerobic biodegradation. An example of the simple aerobic biodegradation reaction for benzene is given by:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$
 (1)

The ultimate goal of the biodegradation process is to convert organic wastes into biomass and CO₂, CH₄, and inorganic salts. Two essential criteria must

^{*}Paper presented at the GCHSRC Fourth Annual Symposium on Ground Water—The Problem and Some Solutions, Lamar University, Beaumont, TX, U.S.A., April 2-3, 1992. Correspondence to: Dr. P.B. Bedient, Department of Environmental Science and Engineering, Rice University, P.O. Box 1892, Houston, TX 77251 (USA).

be in place before biodegradation or biorestoration can occur. First, the subsurface geology must have a relatively large hydraulic conductivity to allow the transport of oxygen and nutrients through the aquifer. Secondly, microorganisms must be present in sufficient numbers and types to degrade the contaminants of interest. Because of the heterogeneous nature of the subsurface, hydraulic conductivity should be evaluated at multiple locations on a site. Formations with K-values greater than 10^{-4} cm/s or greater are most amenable to in situ biorestoration.

Laboratory and field pilot studies of biodegradation are needed to ensure the successful implementation of the bioremediation technology at the field scale. There are several questions that need to be answered in these experiments: is a given organic compound biodegradable and under what conditions? What numbers and types of microorganisms are required for degradation? Would the microorganisms respond to stimulation if growth-limiting nutrients are added? and at what rates would a given organic chemical degrade under natural or enhanced conditions?

In ground water, the problem of determining whether a compound is degradable or not and under what conditions is complicated by several factors. The combination of soil and water imposes a mixed-media analysis approach and the complexity of the physical and chemical processes which control the transport and fate of the organic contaminants provide a challenge for designing indicator parameters for biodegradation in the subsurface. The current state-of-the-art does not offer a concise and uniform methodology for laboratory and fleld quantitative estimation of biodegradation.

To date, the most aerobically biodegradable compounds in the subsurface have been light petroleum hydrocarbons such as gasoline, crude oil, heating oil, fuel oil, lube oil waste, and mineral oil [1]. Other compounds such as alcohols (isopropanol, methanol, ethanol), ketones (acetone, methyl ethyl ketone) and glycols (ethylene glycol) are also aerobically biodegradable.

Design issues for the bioremediation process

The basic steps involved in an in situ biorestoration program [1] are: (1) site investigation, (2) free product recovery, (3) microbial degradation enhancement study, (4) system design, (5) injection and pumping operation, and (6) system maintenance. It is important to define the hydrogeology and the extent of contamination at the site prior to the initiation of any in situ effort. The parameters of interest at a field site include the direction and rate of ground water flow, the depths to the water table and to the contaminated zone, the specific yield of the aquifer, and the heterogeneity of the soil. In addition, other parameters such as hydraulic connections between aquifers, potential recharge and discharge zones, and seasonal fluctuations of the water table should be considered. A number of monitoring wells should be installed

and slug tests and pump tests should be performed for determining the hydraulic conductivity. Water levels should be measured in the wells to determine a potentiometric map of the site. Secondly monitoring wells should be sampled for presence of hydrocarbon contamination and a plume should be mapped for the site. The pumping rate that can be sustained in the aquifer is an important consideration because it limits the amount of water that can be circulated in the system during the bioremediation process.

After defining the hydrogeology, recovery of free product, if any, at the site should be completed. The pure product can be removed using physical recovery techniques such as a single pump system that produces water and hydrocarbon or a two-pump, two-well system that steepens the hydraulic gradient and recovers the accumulating hydrocarbon. Physical recovery often accounts for 30 to 60% of the hydrocarbon before yields decline [2].

Prior to the initiation of a bioremediation activity, it is important to conduct a feasibility study for the biodegradation of the contaminants present at the site. First, contaminant-degrading microorganisms must be present, and second the response of these native microorganisms to the proposed treatment method must be evaluated. In addition, the feasibility study is conducted to determine the nutrient requirements of the microorganisms. These laboratory studies provide a reliable basis for performance at the field level only if they are performed under conditions that simulate the field.

The chemistry of a field site will affect the types and amounts of nutrients that are required. Limestone and high mineral content soils, for example, will affect nutrient availability by reacting with phosphorous. Silts and clays at sites may induce nutrient sorption on the soil matrix, and hence decrease the amount of nutrients available for growth. In general, a chemical analysis of the ground water provides little information about the nutrient requirements at a field site, it is mostly the soil composition that is of significance.

In situ biorestoration usually requires the addition of an electron receptor such as oxygen. The rate of aerobic biodegradation is usually limited by the amount of oxygen that can be transported to the organisms in the zone of contamination. A number of methods are available to supply oxygen to ground water including the addition of air, pure oxygen, or hydrogen peroxide, with increasing concentrations, respectively. Addition of hydrogen peroxide must be carefully monitored to avoid being toxic to microorganisms at elevated concentrations [3]. Aquifer plugging due to precipitation of inorganic nutrients is a possible side effect.

A system for injection of nutrients into the formation and circulation through the contaminated portion of the aquifer must be designed and constructed [4]. The system usually includes injection and production wells and equipment for the addition and mixing of the nutrient solution [5]. A typical system is shown in Fig. 1. Placement of injection and production wells may be restricted by the presence of physical structures. Wells should be screened to accommodate sea-

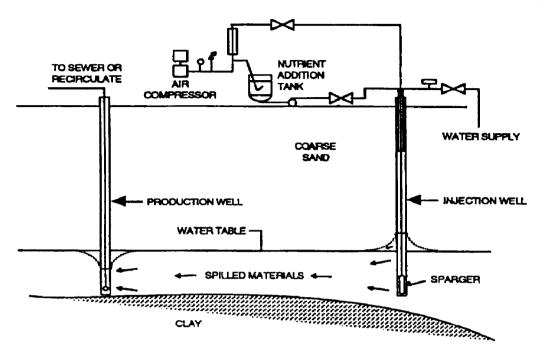


Fig. 1. Typical system.

sonal fluctuations in the level of the water table. Wells are often installed within the contaminant plume to monitor concentrations of hydrocarbon, nutrients, microbes, and other parameters. Monitoring of the process is critical for evaluating its success or failure. Microbial cell counts and contaminant breakthrough curves are indicators of how well the process is performing.

Well installation should be performed under the direction of a hydrogeologist to ensure adequate circulation of the ground water. Produced water can be recycled to recirculate unused nutrients, avoid disposal of potentially contaminated ground water, and avoid the need for make-up water. Inorganic nutrients can be added to the subsurface once the system is constructed. Continuous injection of the nutrient solution is labor intensive but provides a more constant nutrient supply than a discontinuous process. Continuous addition of oxygen is recommended because the oxygen is likely to be a limiting factor in hydrocarbon degradation.

Bioremediation is not without its problems, however. The most important being the lack of well documented field demonstrations that show the effectiveness of the technology and what if any are the long term effects of this treatment on ground water systems. The lack of documented field studies may be attributed in part to the significant commercial potential of the technology which basically means that the information is proprietary. Other problems include the possibility for generating undesirable intermediate compounds during the biodegradation process which are more persistent in the environment than the parent compound.

Enhanced aerobic bioremediation for a petroleum spill is essentially an engineered delivery of nutrients and oxygen to the contaminated zone in an aquifer. Oxygen sources include air, pure oxygen (gaseous and liquid forms), and hydrogen peroxide. Sparging the ground water with air and pure oxygen can supply only 8 to 40 mg/L of oxygen depending on the temperature of the injection fluid [2].

Hydrogen peroxide, which dissociates to form water and half a molecule of oxygen, is infinitely soluble in water [6]; however, hydrogen peroxide can be toxic to microorganisms at concentrations as low as 100 ppm [3]. A stepping-up procedure is usually utilized to allow the microorganisms to adapt to the higher concentrations of the oxidant. Other problems have to do with the stability of hydrogen peroxide. The key to success in using hydrogen peroxide as an oxygen source is to add a relatively large quantity to water and have oxygen released in a controlled manner as it advances through the aquifer. If hydrogen peroxide is destabilized, oxygen will come out of solution as a gas, and the process becomes less efficient [7]. Proprietary techniques have been developed to stabilize hydrogen peroxide.

Review of models applied to biodegradation in ground water

The problem of quantifying biodegradation in the subsurface can be addressed by using models which combine physical, chemical and biological processes. Developing such models is not simple, however, due to the complex nature of microbial kinetics and degradation pathways, the limitations of well monitored sites, the general lack of field data on biodegradation, and the lack of robust numerical schemes that can simulate the physical, chemical, and biological processes simultaneously. Several researchers have developed ground water biodegradation models. The main approaches utilized for modeling biodegradation kinetics have included:

- (1) First-Order Decay
- (2) Biofilm Models (including kinetic expressions)
- (3) Instantaneous Reaction Model
- (4) Dual-Substrate Monod Model

McCarty et al. [8] modeled the biodegradation process using biofilm kinetics. They assumed that substrate concentration within the biofilm changes only in the direction which is normal to the surface of the biofilm and that all the required nutrients are in excess except the rate-limiting substrate. The model employs three basic processes: mass transport from the bulk liquid, biodecomposition within the biofilm, and biofilm growth and decay. The authors evaluated the applicability of the biofilm model to aerobic subsurface biodegradation using a laboratory column filled with glass beads. The experimental data and the model predictions were relatively consistent.

Kissel et al. [9] developed differential equations describing mass balances

on solutes and mass fractions in a mixed-culture biological film within a completely mixed reactor. The model incorporates external mass transport effects, Monod kinetics with internal determination of limiting electron donor or acceptor, competitive and sequential reactions, and multiple active and inert biological fractions which vary spatially. Results of hypothetical simulations involving competition between heterotrophs deriving energy from an organic solute and autotrophs deriving energy from ammonia and nitrite were presented.

Molz et al. [10] and Widdowson et al. [11] presented one-dimensional and two-dimensional models for aerobic biodegradation of organic contaminants in ground water coupled with advective and dispersive transport. A microcolony approach was utilized in the modeling effort, microcolonies of bacteria are represented as disks of uniform radius and thickness attached to aquifer sediments. A boundary layer of a given thickness was associated with each colony across which substrate and oxygen are transported by diffusion to the colonies. Their results indicated that biodegradation would be expected to have a major effect on contaminant transport when proper conditions for growth exist. Simulations of two-dimensional transport suggested that under aerobic conditions microbial degradation reduces the substrate concentration profile along longitudinal sections of the plume and retards the lateral spread of the plume. Anaerobic conditions developed in the plume center due to microbial consumption and limited oxygen diffusion into the plume interior.

Widdowson et al. [12] also extended their previous work to simulate oxygen and/or nitrate based respiration. Basic assumptions incorporated into the model include a simulated particle-bound microbial population comprised of heterotrophic, facultative bacteria in which metabolism is controlled by lack of either an organic carbon-electron donor source (substrate), electron acceptor (oxygen and or nitrate), or mineral nutrient, or all three simultaneously.

Borden and Bedient [13] developed the first version of the BIOPLUME model. They developed a system of equations to simulate the simultaneous growth, decay, and transport of micro-organisms combined with the transport and removal of hydrocarbons and oxygen. Simulation results indicated that any available oxygen in the region near the hydrocarbon source will be rapidly consumed. In the body of the hydrocarbon plume, oxygen transport will be rate limiting and the consumption of oxygen and hydrocarbon can be approximated as an instantaneous reaction. The major sources of oxygen, the researchers concluded, are transverse mixing, advective fluxes and vertical exchange with the unsaturated zone.

Borden et al. [14] applied the first version of the BIOPLUME model to simulate biodegradation at the Conroe Superfund site in Texas. Oxygen exchange with the unsaturated zone was simulated as a first-order decay in hydrocarbon concentration. The loss of hydrocarbon due to horizontal mixing with oxygen-

ated ground water and resulting biodegradation was simulated by generating oxygen and hydrocarbon distributions independently and then combining by superposition. Simulated oxygen and hydrocarbon concentrations closely matched the observed values.

Srinivasan and Mercer [15] presented a one-dimensional, finite difference model for simulating biodegradation and sorption processes in saturated porous media. The model formulation allows for accommodating a variety of boundary conditions and process theories. Aerobic biodegradation was modeled using a modified Monod function; anaerobic biodegradation is modeled using Michaelis-Menten kinetics. In addition, first-order degradation was allowed for both substances. Sorption was incorporated using linear, Freundlich, or Langmuir equilibrium isotherms for either substance.

MacQuarrie et al. [16] utilized a similar approach to Borden et al. [14] and Rifai et al. [17,18] to develop a biodegradation model. The advection-dispersion equation was coupled with a dual-Monod relationship. The system of equations was solved using an iterative principal direction finite element technique. Comparisons of numerical results with the results of a laboratory column experiment showed that the model equations adequately describe the behavior of toluene, dissolved oxygen, and the microbial population, without considering solute diffusion through stagnant fluid layers or biofilms. The authors conclude that in a two-dimensional shallow aquifer setting, an organic plume experiences mass loss, spreading controlled by the availability of dissolved oxygen, and skewing in the direction of ground water flow.

MacQuarrie and Sudicky [19] utilized the model developed by MacQuarrie et al. [16] to examine plume behavior in uniform and random flow fields. In uniform ground water flow, a plume originating from a high-concentration source will experience more spreading and slower normalized mass loss than a plume from a lower initial concentration source because dissolved oxygen is more quickly depleted. Large ground water velocities produced increases in the rate of organic solute mass loss because of increased mechanical mixing of the organic plume with oxygenated ground water.

Recently, Odencrantz et al. [20] presented a contaminant transport model which allows for different biodegradation kinetics. Monod kinetics and biofilm kinetics are compared in a two-dimensional transport model, where the differential equations are solved using a nonlinear operator splitting. Results indicated that the two models could differ for a large enough biofilm thickness.

Celia et al. [21] presented two papers on developing a numerical biodegradation model designed to handle co-metabolism, multiple substrates, and aerobic and anaerobic metabolism. The model is currently one-dimensional and therefore has limited applications to field sites.

Description of the BIOPLUME II model

Rifai et al. [17,18,22] developed one of the first numerical biodegradation models (BIOPLUME II) by modifying the USGS two-dimensional solute trans-

port model [23]. The basic concept applied in developing BIOPLUME II includes the use of a dual-particle mover procedure to simulate the transport of oxygen and contaminants in the subsurface.

Biodegradation of the contaminants is approximated by the instantaneous reaction model proposed by Borden and Bedient [13]. The ratio of oxygen to contaminants consumed by the reaction is determined from an appropriate stoichiometric model (assuming complete mineralization). In general, the transport equation is solved twice at every time step to calculate the oxygen and contaminant distributions:

$$\frac{\partial (Cb)}{\partial t} = \frac{1}{R_o} \left[\frac{\partial}{\partial x_i} \left(bD_{ij} \frac{\partial C}{\partial x_i} \right) - \frac{\partial}{\partial x_i} (bCV_i) \right] - \frac{C'W}{n}$$
 (2)

$$\frac{\partial (Ob)}{\partial t} = \left[\frac{\partial}{\partial x_i} \left(b D_{ij} \frac{\partial O}{\partial x_i} \right) - \frac{\partial}{\partial x_i} (b O V_i) \right] - \frac{O'W}{n}$$
(3)

where C and O are the concentration of contaminant and oxygen respectively, C' and O' the concentration of contaminant and oxygen in a source or sink fluid, n is the effective porosity, b the saturated thickness, t the time, x_i and x_j the cartesian coordinates, W the volume flux per unit area, V_i the seepage

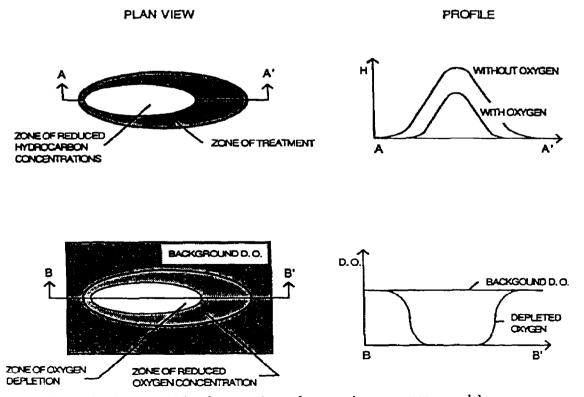


Fig. 2. Principle of superposition for organics and oxygen in BIOPLUME II model.

velocity in the direction of x_i , R_c =retardation factor for contaminant, and D_{ij} the coefficient of hydrodynamic dispersion. It is emphasized that the BIO-PLUME II model simulates dissolved contaminant concentrations which are vertically averaged over the thickness of the aquifer.

The two plumes are combined using the principle of superposition (Fig. 2) to simulate the instantaneous reaction between oxygen and the contaminants, and the decrease in contaminant and oxygen concentrations is calculated from:

$$DC_{RC} = O/F;$$
 $O = 0$ where $C > O/F$ (4)
 $DC_{RO} = C \times F;$ $C = 0$ where $O > C \times F$

where DC_{RC} , DC_{RO} are the calculated changes in concentrations of contaminant and oxygen, respectively, due to biodegradation.

The only model input parameters to BIOPLUME II which are required to simulate biodegradation include the amount of dissolved oxygen in the aquifer prior to contamination, and the oxygen demand of the contaminant determined from a stoichiometric relationship.

Examples of recent field studies

In a controlled field experiment at the Canada Forces Base Borden site, two plumes of gasoline contaminated ground water were introduced into the aquifer. Immediately upgradient of one plume, ground water spiked with nitrate was added so that a nitrate plume would overtake the organic plume [24]. The success of the field experiment was limited [25]. The dissolved organic contaminant mass (BTEX) decreased rapidly due to residual oxygen concentrations in the aquifer prior to the nitrate overlap. Organic mass left in the aquifer was not adequate to evaluate anaerobic biotransformation.

Semprini et al. [26] presented the results from a field evaluation of in situ biodegradation of trichloroethylene (TCE) and related compounds. The method that was used in the field demonstration relied on the ability of methane-oxidizing bacteria to degrade these contaminants to stable, non-toxic, end products. The field site is located at the Moffett Naval Air Station in Mountain View, California and the test zone is a shallow confined aquifer composed of coarse grained alluvial sediments. Results from the biotransformation experiments at the site indicates that biodegradation of TCE was on the order of 30% of the mass injected.

Semprini and McCarty [27] presented two papers on modeling the in-situ biodegradation of chlorinated aliphatics. Their model solves ordinary differential equations by standard numerical integration, and the model was applied to two sets of field data at the above site.

Major et al. [28] investigated the biodegradation of benzene, toluene and the isomers of xylene (BTX) in anaerobic batch microcosms containing shal-

low aquifer material. BTX loss occurred with the addition of either nitrate or oxygen. Denitrification was confirmed by nitrous oxide accumulation. When a limiting amount of nitrate was added, there was a corresponding limit to the loss of BTX and a limited amount of nitrous oxide production.

Borden and Bedient [29] conducted a three-well injection-production test at the United Creosoting Company (UCC) site in Conroe, Texas, to evaluate the significance of biotransformation in limiting the transport of polycyclic aromatics present in the shallow aquifer. During the test, chloride, a non-reactive tracer and two organic compounds, naphthalene and paradichlorobenzene (pDCB), were injected into a center well for 24 hours followed by clean ground water for six days. Ground water was continuously produced from two adjoining wells and monitored to observe the breakthrough of these compounds. A significant loss of naphthalene and pDCB attributed to biotransformation processes was observed during the test.

Rifai et al. [22] studied the naturally occurring biodegradation at an aviation fuel spill in Traverse City, Michigan. Contamination data from approximately 25 wells at the site were utilized to define the dissolved benzene, toluene and xylene plume over a two year period. Rifai et al. [22] calculated a biodegradation rate of 1.0% a day at the Traverse City site (Fig. 3) and indicated that the pump and treat system at the site was removing a very small percentage of the total dissolved mass present at the site. A modeling effort was completed using the BIOPLUME II model. The modeling results along the centerline of the contaminant plume are shown in Fig. 4. In general, the BIOPLUME II model results match the field results except in the area between monitoring

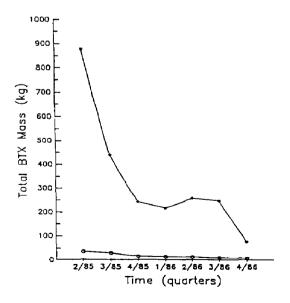


Fig. 3. Variation in total BTX with time at Traverse City.

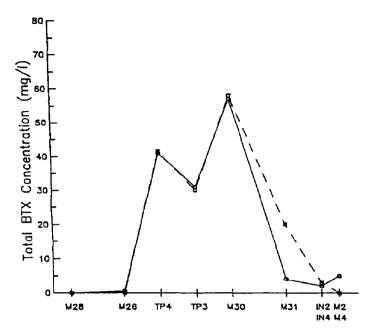


Fig. 4. Calibrated (-) versus observed (-) BTX concentrations at Traverse City.

wells M30 and the pumping wells. The researchers discuss the possibility of anaerobic biodegradation taking place in that zone.

Chiang et al. [30] characterized soluble hydrocarbon and dissolved oxygen in a shallow aquifer beneath a field site by sampling ground water at 42 monitoring wells. Results from 10 sampling periods over three years showed a significant reduction in total benzene mass with time in ground water. The natural attenuation rate was calculated to be 0.95% per day. Spatial relationships between DO and total benzene, toluene, and xylene (BTX) were shown to be strongly correlated by statistical analyses and solute transport modeling.

Modeling natural biodegradation with BIOPLUME II

Modeling studies using the extensive data from field programs at Traverse City, Michigan (TCM) were run to understand and aid in the evaluation of natural biodegradation at the site. Modeling studies at the TCM site were performed to: (1) help understand rates of natural biodegradation, (2) model sensitivity of certain key parameters, (3) determine conditions favorable to use of natural biodegradation as a remedial scheme, and (4) aid in the calibration, formulation and understanding of modeling overall bioremediation at the site.

The Coast Guard Air Station is the site of an aviation fuel spill which occurred somewhere near the Hangar Administration Building in 1969, pictured in Fig. 5. A plume of contamination migrated in the shallow drinking water

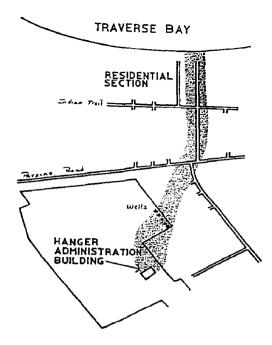


Fig. 5. Traverse City site map.

aquifer from the spill toward the bay and underneath a residential area. Investigation into the spill revealed that 10,000 to 20,000 gallons of aviation fuel had been released into the ground when a flange failed on one of the tanks. Alkylbenzenes (BTEX) from the fuel were found in the ground water in concentrations ranging from 30 μ g/L to 30,000 μ g/L near the source area [31].

Extensive studies have been carried out at the site since the mid 1980's by the U.S. Coast Guard Station, U.S. Environmental Protection Agency Robert S. Kerr Environmental Research Laboratory, the Traverse Group, Inc., and Rice University. Clean-up of the Air Station is underway using purge wells (pump and treat). An interdiction well field (Fig. 5) was installed in April of 1985 to limit the contamination to the site and to pump and treat contaminants intersected by the wells. These wells have been very effective in stopping contaminant migration downgradient of the interdiction field (Fig. 6). Within about 24 months of the pumping system installation, the rapid dissipation of the downgradient BTEX plume underlying the residential area was observed at a number of wells located north of the site and is the subject of this modeling study. In situ bioremediation and soil venting pilot studies have been underway at the base since 1988 [22,31]. Preliminary results of the current effort were presented at a meeting in San Diego in 1990 [32].

Site characterization at TCM

The study area is underlain by lacustrine glacial deposits consisting of an upper sand and gravel layer and underlying clay layer. The upper 15 to 20 feet

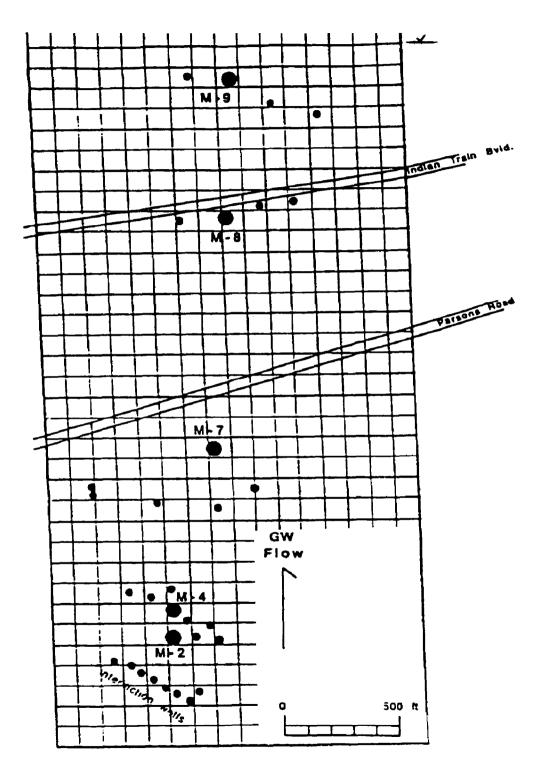


Fig. 6. Model and grid wells.

of this unit, the zone in which the water table occurs, is generally fine to medium grained sand. Below this, gravel and coarse to very coarse sand are more abundant. Based on wells in the area the thickness of the upper sand and gravel unit ranges from 29 to 118 feet. The underlying clay unit is relatively impermeable and its thickness in the study area is not known as no wells have pene-

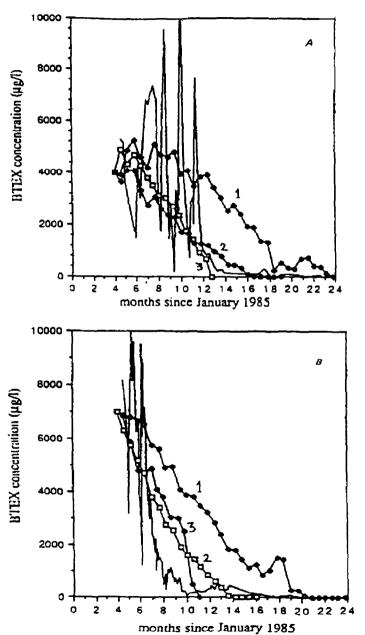
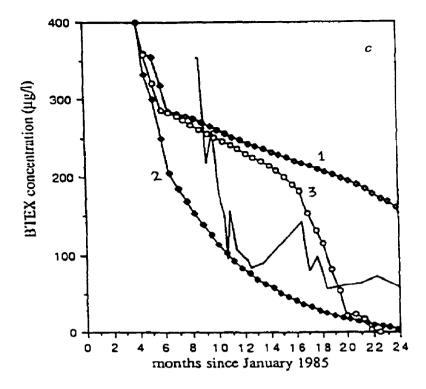


Fig. 7. Results for (a) M-4, (b) M-2, and (c) M-9. (—) Observed, (1) 95 ft/day, (2) 95 ft/day at $r=0.01 \,\mathrm{d}^{-1}$ and (3) 150 ft/day.



trated it fully [33]. Cone penetrometer data [34] show a distinct change in the density of the sand unit at approximately 20–25 feet, which corresponds to the change in sediment type reported by Twenter at 15–20 feet.

Hydraulic conductivity ranges from 100 ft/day to 150 ft/day based on pump test data acquired several years ago in the initial site investigation [33]. Slug tests performed in 1988 by Smythe confirm these results for the upper sands. However, the lower dense sands have a hydraulic conductivity of about 20 ft/day according to permeameter tests performed under *in situ* conditions [34]. The hydraulic gradient averages 0.005 and effective porosity is in the range of 0.30.

Model application and parameter selection

The model study represents a unique application of the BIOPLUME II model to contaminant migration and biodegradation. Previous uses of the model have dealt mostly with modeling plumes with a variable source component. The lack of definition of source terms has always presented a serious problem in predicting the fate and transport of plumes, since it creates poorly defined mass rates of contaminant feeding a plume and therefore does not allow for biodegradation to be evaluated accurately. This application, given that the interdiction field has effectively cut off the source and created a well-defined flush out of the aquifer, offers a real advantage in modeling the biodegradation process at a real field site.

The modeling approach taken here starts with a well-defined initial source concentration in the aquifer below the pump and treat wells and attempts to match observed dissipation results from a number of well-monitored points downstream. Both hydraulic conductivity and degree of biodegradation, using both an instantaneous reaction method and a reaeration coefficient, were used to fit to the observed dissipation in the aquifer over a two year period.

Modeling of the plume downgradient of the interdiction field (Fig. 5) was performed using BIOPLUME II [17,18]. This study was performed under steady state conditions using an effective porosity of 30%, a longitudinal dispersivity of 5 feet, a ratio of transverse to longitudinal dispersivity of 0.3, and a 16 by 58 grid (Fig. 6). Saturated thickness ranges from 30 to 100 feet and the hydraulic gradient averages 0.005. These parameters are in line with previous geologic and model studies of the site (Smythe et al., 1989).

Initial model runs were made without biodegradation to evaluate the sensitivity of the model to observed total BTEX concentrations, based solely on the hydraulic flushout of the system over about a 24 month period. An initial contaminant plume configuration at the time of the interdiction field start-up of April of 1985 was used for input. This plume was defined based on measurements made by the Traverse City Group Inc. (TGI) and EPA RSKERL in 1985. Three monitoring wells were selected to allow for the comparison of calculated to observed total BTEX concentrations. These wells are M-2, M-4, and M-9 (Fig. 6). Also the seven interdiction wells that were pumping as of April of 1985 are included in the model and are modeled with an average pumping rate of 20 gpm per well as reported for the period of the simulations.

A large number of model runs were made to evaluate the effect of biodegradation as simulated using an instantaneous reaction assumption and a reaeration coefficient. Initial background dissolved oxygen values were input as a grid over the site. A number of results have been reported elsewhere (Bedient et al., 1992) and only are summarized here.

Results of natural biodegradation modeling

Model results for wells M-2, M-4, and M-9 are shown in Figure 7a, 7b, and 7c. These plots indicate that the most reasonable match is found using a hydraulic conductivity of 150 ft/day (with biodegradation) or by using a hydraulic conductivity of 95 ft/day coupled with a reaeration coefficient of 0.01 day⁻¹. Comparisons with lower hydraulic conductivities (48 or 72 ft/day) produced much poorer results since the rate of flushout was reduced. With these higher hydraulic conductivities values, the observed increases attributed to reaeration were expected due to the results seen in the sensitivity analysis study. However in well M-9, Figure 7c, the match was more difficult due to the fact that the well M-9 is not on the centerline of the plume and is in a zone where the plume has narrowed. It would have been useful to have another well between M-2 and M-9, but no other data was available.

Biodegradation modeling at the Traverse City aviation spill site for the portion of the plume downgradient of the interdiction well system indicated some interesting results. The modeling of the dissipation of BTEX concentrations was greatly simplified by the cutoff of the variable source 1500 ft upgradient. This allowed the remaining plume to flush out naturally and biodegrade according to natural kinetic rates for the site. The success of the modeling effort was largely a function of the accuracy of the initial downgradient plume and the hydraulics of the system. The modeling results show a distinct and reasonable comparison to observed dissipation in 3 wells downgradient of the interdiction well field. Measured hydraulic conductivities (K) ranged from 48 to 150 ft/day, and a range of values were used to help fit the observed declines at the wells. The higher the K value used, the faster the flush out and decline, and the lower the K value used, the more biodegradation was required to match the decline. It was found that using a hydraulic conductivity of 150 ft/day coupled with biodegradation simulated with both an instantaneous reaction and a reaeration coefficient gave a good match to observed contaminant declines. A similar match to observed contaminant declines was obtained by using a hydraulic conductivity of 95 ft/day coupled with both an instantaneous reaction and a reaeration coefficient of $0.01 \, \text{day}^{-1}$.

Conclusions

Biodegradation modeling has progressed significantly since the mid 1980s with more than a dozen papers and modeling studies reported in the general literature since 1985. However, the need still exists for well-documented field sites where biodegradation is being measured as part of a cleanup operation. There has always been a real problem in extrapolating from degradation rates measured in the laboratory to the field for certain classes of compounds. Only through more detailed monitoring and modeling efforts at real field sites can we ever hope to gain a better understanding of natural or enhanced biodegradation processes.

References

- M.D. Lee, V.W. Jamison, R.L. Raymond, Applicability of in situ Bioreclamation as a Remedial Action Alternative, Proc. of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, Houston, Texas, National Water Well Association, Dublin, OH, 1987, pp. 167-185.
- 2 M.D. Lee, J.M. Thomas, R.C. Borden, P.B. Bedient, C.H. Ward and J.T. Wilson, Biorestoration of aquifers contaminated with organic compounds, Natl. Counsil Ground Water Res., R.S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, Ada, OK, 18 (1) (1988) 29-89.
- 3 S. Fiorenza, Use of Hydrogen Peroxide for Subsurface Remediation: Microbial Responses and Their Implications, Thesis, Rice University, Houston, TX, September 1991.

- 4 M.D. Lee and C.H. Ward, Biological methods for the restoration of contaminated aquifers, J. Environ. Toxicol. Chem., 4 (1985) 743.
- 5 R.L. Raymond, Environmental bioreclamation, 1978 Mid-Continent Conf. and Exhibition on Control of Chemicals and Oil Spills, Detroit, MI, September 1978.
- 6 J.M. Thomas and C.H. Ward, in situ biorestoration of organic contaminants in the subsurface, Environ. Sci. Technol., 23 (7) (1989) 760-766.
- 7 R.E. Hinchee, D.C. Downey and E.J. Coleman, Enhanced bioremediation, soil venting, and ground-water extraction; a cost-effectiveness and feasibility comparison, Proc. Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Natl. Water Well Assoc., Dublin, OH, 1987, pp. 147-164.
- 8 P.L. McCarty, M. Reinhard and B.E. Rittmann, Trace organics in groundwater, Environ. Sci. Technol., 15 (1) (1981) 40-51.
- 9 J.C. Kissel, P.L. McCarty and R.L. Street, Numerical simulation of mixed culture biofilm, J. Environ. Eng. Div. Am. Soc. Civ. Eng., 110 (1984) 393.
- F.J. Molz, M.A. Widdowson and L.D. Benefield, Simulation of microbial growth dynamics coupled to nutrient and oxygen transport in porous media, Water Resour. Res., 22 (1986) 107.
- M.A. Widdowson, F.J. Molz, L.D. Benefield, Development and application of a model for simulating microbial growth dynamics coupled to nutrient and oxygen transport in porous media, Proc. AGWSE/IGWMCH Conf. on Solving Ground Water Problems with Models, Denver, CO, Natl. Water Well Assoc., Dublin, OH, 1987, pp. 28-51.
- 12 M.A. Widdowson, F.J. Molz, L.D. Benefield, A numerical transport model for oxygen- and nitrate-based respiration linked to substrate and nutrient availability in porous media (Paper 7W5057), Water Resour. Res., 24 (9) (1988) 1553-1565.
- 13 R.C.Borden and P.B. Bedient, Transport of dissolved hydrocarbons influenced by reaeration and oxygen limited biodegradation: 1. Theoretical development, Water Resour. Res., 22 (1986) 1973–1982.
- 14 R.C. Borden, P.B. Bedient, M.D. Lee, C.H. Ward and J.T. Wilson, Transport of dissolved hydrocarbons influenced by oxygen limited biodegradation: 2. Field application, Water Resour. Res., 22 (1986) 1983-1990.
- 15 P. Srinivasan and J.W. Mercer, Simulation of biodegradation and sorption processes in ground water, Ground Water, 26 (4) (1988) 475-487.
- 16 K.T.B. MacQuarrie, E.A. Sudicky and E.O. Frind, Simulation of biodegradable organic contaminants in groundwater, (1), numerical formulation in principal directions, Water Resour. Res., 26 (2) (1990) 207—222.
- 17 H.S. Rifai and P.B. Bedient, "BIOPLUME II"—Two dimensional modeling for hydrocarbon biodegradation and *in situ* restoration, Proc. Natl. Water Well Assoc. Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, TX, 1987, pp. 431-450.
- 18 H.S. Rifai, P.B. Bedient, R.C. Borden and J.F. Haasbeek, "BIOPLUME II" Computer Model of Two-Dimensional Contaminant Transport Under the Influence of Oxygen Limited Biodegradation in Ground Water User's Manual Version 1.0, National Center for Ground Water Research, Rice University, Houston, TX, October, 1987.
- 19 K.T.B. MacQuarrie and E.A. Sudicky, Simulation of biodegradable organic contaminants in groundwater, (2), plume behavior in uniform and random flow fields, Water Resour. Res., 26 (2) (1990) 223-239.
- 20 J.E. Odencrantz, A.J. Valocchi and B.E. Rittman, Modeling two dimensional solute transport with different biodegradation kinetics, Proc. Petroleum Hydrocarbons and Organic Chemicals in Ground Water Prevention, Detection, and Restoration, Houston, TX, October 31-November 2, 1990, pp. 355-368.

- 21 M.A. Celia, J.S. Kindred and I. Herrera, Contaminant transport and biodegradation, 1. A numerical model for reactive transport in porous media, Water Resour. Res., 25 (6) (1989) 1141-1148.
- 22 H.S. Rifai, P.B. Bedient, J.T. Wilson, K.M. Miller and J.M. Armstrong, Biodegradation modeling at a jet fuel spill site, ASCE J. Environ. Eng., 114 (1988) 1007-1019.
- 23 L.F. Konikow and J.D. Bredeheoft, Computer Model of Two-Dimensional Solute Transport and Dispersion in Ground Water, Automated Data Processing and Computations, Techniques of Water Resources Investigations of the U.S. Geological Survey, Washington, DC, 1978.
- 24 K. Berry-Spark, J.F. Barker, D. Major and C.I. Mayfield, Remediation of gasoline-contaminated ground-waters: a controlled field experiment, Proc. Petroleum Hydrocarbons and Organic Chemicals in Ground Water, NWWA, pp. 613-623, 1986.
- 25 K. Berry-Spark and J.F. Barker, Nitrate remediation of gasoline contaminated ground waters: results of a controlled field experiment, Proc. Petroleum Hydrocarbons and Organic Chemicals in Ground Water, NWWA/API, pp. 3—10, 1987.
- 26 L. Semprini et al., A field evaluation of in situ biodegradation for aquifer restoration, U.S. Environmental Protection Agency, U.S. Government Printing Office, Ada, OK, EPA/600/S2/87/096, 1988.
- 27 L. Semprini and P.L. McCarty, Comparison between model simulations and field results for in situ biorestoration of chlorinated aliphatics: Part 1. Biostimulation of methanotrophic bacteria, Groundwater, 29 (3) (1991) 1991.
- 28 D.W. Major, C.I. Mayfield and J.F. Barker, Biotransformation of benzene by denitrification in aquifer sand, Ground Water, 26 (1988) 8-14.
- 29 R.C. Borden and P.B. Bedient, in situ measurement of adsorption and biotransformation at a hazardous waste site, Water Resour. Bull., 23 (1987) 629-636.
- 30 C.Y. Chiang, J.P. Salanitro, E.Y. Chai, J.D. Colthart and C.L. Klein, Aerobic biodegradation of benzene, xylene in a sandy aquifer—Data analysis and computer modeling, Ground Water, 27 (6) (1989) 823-834.
- 31 B.H. Wilson, B.E. Bledsoe, D.H. Kampbell, J.T. Wilson, J.M. Armstrong and J.H. Sammons, Proc. Natl. Water Well Assoc./Am. Pet. Inst. Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, Houston, TX, 1986, pp. 78–89.
- 32 H.S. Rifai, G.P. Long and P.B. Bedient, Modeling bioremediation: Theory and field application, In: R.E. Hinchee and R.F. Olfenbuttel (Eds.), *In situ* Bioreclamation, Applications and Investigations for Hydrocarbon and Contaminated Site Remediation, Battelle Memorial Institute, Butterworth-Heinemann, Boston, MA, 1991, pp. 535-541.
- 33 F.R. Twenter, T.R. Cummings and N.G. Grannemann, Groundwater Contamination in East Bay Township, Michigan, U.S. Geologic Survey, Water Resources Investigation Report 85-4064, 1985.
- 34 J.M. Smythe, P.B. Bedient and R.A. Klopp, Cone penetrometer technology for hazardous waste site investigations, Proc. 2nd Natl. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, Assoc. of Ground Water Sci. and Eng., Las Vegas, NV, 1989, pp. 71—94.
- P.B. Bedient, G.P. Long and H.S. Rifai, Modeling natural biodegradation with BIOPLUME, Proc. 5th Int. Conf. Solving Ground Water Problems with Models, IGWMC and AGWSE, Dallas, TX, February 11-13, 1992, pp. 699-714.