United States
Environmental Protection
Agency

Robert S. Kerr Environmental
Research Laboratory
Ada, OK 74820

Research and Development
EPA/600/M-89/019 August 1989

EPA

ENVIRONMENTAL RESEARCH BRIEF

BIOPLUME Model for Contaminant Transport Affected by Oxygen Limited Biodegradation

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Introduction

Many of the organic pollutants entering ground water are potentially biodegradable in the subsurface. This potential has been demonstrated in aquifers contaminated by wood-creosoting process wastes (Borden et al., 1986) and gasoline (McKee et al., 1972, Wilson et al., 1986). The persistence of many of these organic compounds in the subsurface indicated that some factors must be limiting biodegradation.

Current research at Rice University through the National Center for Ground Water Research and the R.S. Kerr Environmental Research Laboratory (RSKERL) of the U.S. EPA has been aimed at identifying the major processes that limit biodegradation in aquifers and developing a mathematical model (BIOPLUME) for simulating these processes.

Recent studies have shown the presence of quite active, diverse microbial populations in the subsurface (Britton and Gerba, 1984; Ghiorse and Balkwill, 1985). These organisms have the ability to degrade a wide variety of organic contaminants (Wilson et al., 1983; Lee and Ward, 1985; Kuhn et al., 1985; Gibson and Suflita, 1986; and Barker et al., 1987). Key factors which seem to limit biodegradation is the lack of an essential nutrient, typically nitrogen or phosphorous, or an electron acceptor such as oxygen. Addition of the necessary electron acceptor(s) stimulates the microorganisms and enhances the restorative capacity of the contaminated aquifer.

In order to identify the rate limiting processes for biodegradation, the equations describing microbial growth and decay and transport of oxygen and contaminants were developed and solved in one and two dimensions. The main purpose of this research was to develop the mathematical tools necessary to describe and simulate the process of oxygen limited biodegradation of organics in ground water.

The United Creosoting Company, Inc. (UCC) site in Conroe, Texas was evaluated in testing of the simulation models. Field work at the site suggested that lack of oxygen was limiting the microbial degradation of dissolved aromatic hydrocarbons present in the shallow aquifer (Borden et al., 1986).

A numerical model, BIOPLUME, was developed to simulate oxygen-limited biodegradation. BIOPLUME simulates advection, dispersion and retardation processes as well as the reaction between oxygen and the contaminants under steady, uniform flow. The model allows the computation of two plumes sequentially, one for the contaminants and one for oxygen. At every time step, the two plumes are combined using superposition to simulate the reaction between oxygen and the contaminants. Other processes such as anaerobic degradation and diffusion of oxygen from the unsaturated zone (reaeration) are simulated as a first order decay in contaminant concentrations.

BIOPLUME was also applied to an aviation gasoline spill site at Traverse City, Michigan (TCM). The model was used to simulate the behavior of the degrading plume over a two year period. Model predictions for the rates of mass loss closely matched calculated rates from the field data.

Objectives

The overall objectives were:

1. Develop and test the equations for describing oxygen transport, contaminant transport and microbial growth and decay.

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2. Develop BIOPLUME based on an existing solute transport model to include the major processes which limit biodegradation.

3. Evaluate BIOPLUME against selected analytical solutions and against the UCC site data and the TCM site data.

4. Develop a PC version of the model (BIOPLUME II) and a user's guide for the model.

Methods

Growth of microorganisms and removal of organics and oxygen were simulated using a modification of the Monod function (Borden and Bedient, 1986). These functions were combined with the classic form of the advection-dispersion equation for a solute undergoing linear instantaneous adsorption to obtain Eqns. 1, 2, and 3 in Table 1.

Table 1. Two Dimensional Transport Equations with Reaction Terms

$$\frac{\partial H}{\partial t} = \frac{\nabla(D\nabla H - vH)}{R_h} - \frac{M_t k}{R_h} \bullet \frac{H}{k_h + H} \bullet \frac{O}{k_o + O} \qquad (1)$$

$$\frac{\partial O}{\partial t} = \nabla(D\nabla O - vO) - M_t \bullet k \bullet F \bullet \frac{H}{k_h + H} \bullet \frac{O}{k_o + O} \qquad (2)$$

$$\frac{\partial M_s}{\partial t} = \frac{\nabla(D\nabla M_s - vM_s)}{R_m} + M_s \bullet k \bullet Y \bullet \frac{H}{k_h + H} \bullet \frac{O}{K_o + O} + \frac{k_c \bullet Y \bullet OC}{R_m} - bM_s \qquad (3)$$

Where,

D = dispersion tensor
v = ground water velocity vector
O = concentration of dissolved oxygen
H = concentration of contaminant
R_h = retardation factor for contaminant
M_s = concentration of microbes in solution
R_m = microbial retardation factor
M_t = $R_m \bullet M_s$
k_h = contaminant half saturation constant
k_o = oxygen half saturation constant
k_c = first order decay of natural carbon
OC = natural organic carbon concentration
b = microbial decay rate
F = ratio of oxygen to contaminant consumed
Y = microbial yield coefficient (g cells /g contaminant)
k = maximum contaminant utilization rate per unit mass microorganisms

Instantaneous Reaction Assumption

$$H(t+1) = H(t) - O(t)/F;\ O(t+1) = O \text{ where } H(t) > O(t)/F \qquad (4)$$

$$O(t+1) = O(t) - H(t)\cdot F;\ H(t+1) = O \text{ where } O(t) > H(t)\cdot F \qquad (5)$$

where H(t), H(t+1), O(t) and O(t+1) are the concentrations of contaminant and oxygen at time t and t+1 respectively.

One- and two-dimensional models were developed to study the behavior of Eqns. 1, 2, and 3. One-dimensional simulations indicated that in the region closest to the contaminant source, biodegradation rates will be very high and result in nearly complete removal of oxygen. In the body of the organic plume, biodegradation will be limited by the rate of mass transfer of oxygen into the plume. In the third region downstream of the bulk organic plume, oxygen will be present in excess of the oxygen demand and contaminants will be absent.

Sensitivity analyses performed with the 1-D model indicated that microbial kinetics had little or no effect on the contaminant distribution. This suggested that the consumption of organics and oxygen by the microorganisms could be approximated as an instantaneous reaction (Eqns. 4 and 5, Table 1).

The two-dimensional simulations indicated that biodegrading plumes are narrower than non-biodegrading plumes. This characteristic has been confirmed at Traverse City, Michigan (Twenter et al., 1985). The simulations also suggested that reaeration could be a significant source of oxygen into a plume (Wilson et al., 1986).

Model Development - BIOPLUME

BIOPLUME solves the governing equations (Eqns. 1 and 2, Table 1) under the assumption of instantaneous reaction between oxygen and the contaminants. The USGS solute transport model (Konikow and Bredehoeft, 1978) was modified to allow parallel computation of an organic plume and an oxygen plume. The two plumes are combined at every timestep using superposition.

The model is very versatile in that it allows the simulation of retarded plumes. More important, however, is the capability of simulating in situ restoration schemes such as injecting oxygenated water into the aquifer. Sensitivity analyses on the different model parameters indicated that the amount of mass biodegraded is most sensitive to the hydraulic conductivity, the coefficient of anaerobic decay and the coefficient of reaeration (Rifai et al., 1988). The model had a weak sensitivity to dispersion and the retardation factor. For contaminant plumes which are naturally biodegrading, increasing the retardation factor decreases the amount of mass biodegraded.

A PC version of the model (BIOPLUME II) has been developed and is supported with a preprocessor to aid in defining the input data. A postprocessor supports the preparation of output files which can be used by most any plotting package for obtaining graphical output. A user's guide (Rifai et al., 1987) which outlines the modeling concepts and the use of the model as well as illustrative sample problems is available.

Application of BIOPLUME

United Creosoting Site, Conroe, Texas

Organic contaminants present at the Conroe, Texas field site are predominantly polycyclic aromatic hydrocarbons from the wood creosoting process (Borden et al., 1986). A chloride plume is also present in the shallow aquifer and is moving at 15 ft./yr. A detailed description of the site's geology, hydrology and subsurface microbiology can be found in Bedient et al., 1984, Lee et al., 1984, and Wilson et al., 1985.

A three well injection-production test was performed at the site to estimate the effective retardation factors and to evaluate the biotransformation of the hydrocarbons present in the aquifer (Borden and Bedient, 1987). Results indicate that degradation is the major process limiting contaminant transport at the site. A significant loss of contaminant mass was observed at the two production wells.

BIOPLUME was calibrated to the observed chloride distribution and was used to simulate hydrocarbon and oxygen transport. Figure 1 shows contours of equal hydrocarbon concentration for three cases. Case 1 is the best estimate of conditions at the site. Case 2 assumes no reaeration and Case 3 assumes no biodegradation. It is clear that reaeration appears to be the major source of oxygen to the plume at the site and that the observed distribution could not be simulated with a transport code that ignores biodegradation.

Traverse City Field Site, Michigan

The basic contaminant at the Traverse City Field site is aviation gasoline. The water-table aquifer is about 50 ft. deep and overlies 100 ft. of impermeable glacial clay. The water table varies from 12 to 18 ft. below land surface, with ground water velocities approximately 5 ft./day (Twenter et al., 1985.) The plume is about 200-400 ft. wide (Figure 2). A pumping field was installed in April, 1985 to halt the migration of BTX contaminants (Benzene, Toluene, and Xylene) across the property boundary.

The research effort at the site included field sampling and modeling of the contaminant plume with BIOPLUME. Data collected by Rice University and RSKERL indicated that strong anaerobic biological activity was occurring in the immediate spill area (dissolved oxygen was absent). Four distinct regions of contamination were identified: 1) The body of the plume: high concentrations of BTX and trace concentrations of oxygen; 2) Zone of anaerobic treatment: low to moderate concentrations of BTX, significant concentrations of methane at depths of 17 to 35 ft., and trace concentrations of oxygen; 3) Zone of aerobic treatment: low to moderate concentrations of oxygen (0.5-3 mg); and 4) Pristine zone: high concentrations of oxygen (8 mg/l) and trace concentrations of BTX.

In addition, data was collected on a regular basis from a number of wells at the site. The total BTX from about 25 wells were averaged over three month intervals beginning with the second quarter of 1985. The data were also averaged vertically.

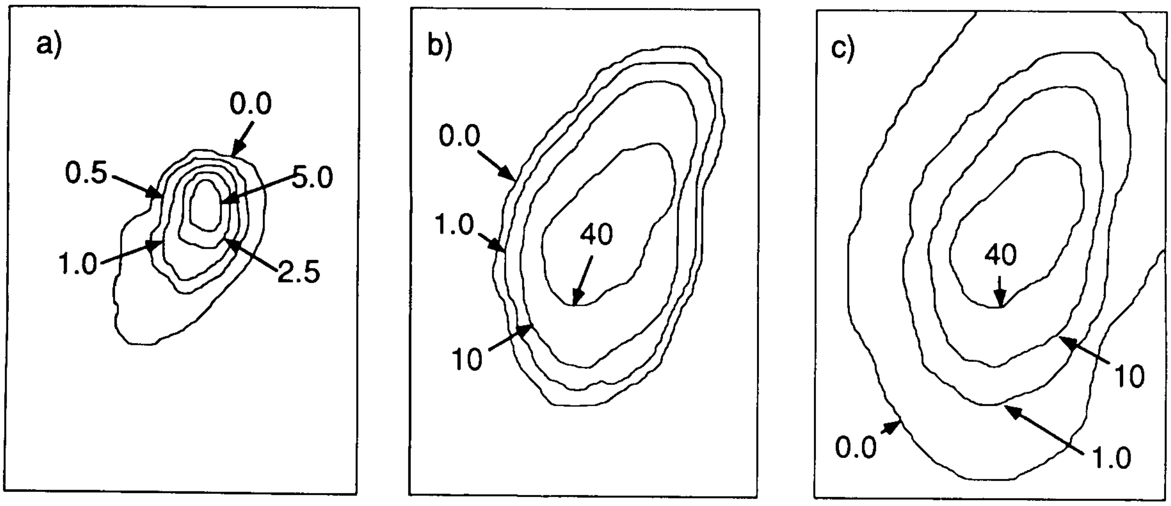

Figure 1. Simulated hydrocarbon plumes for three cases: (a) case 1, best estimate simulation of the plume including biodegradation due to horizontal mixing and vertical exchange with unsaturated zone; (b) case 2, simulated plume assuming no reaeration; and (c) case 3, simulated plume with no biodegradation. Contours are lines of equal hydrocarbon concentration in mg/L.

Concentration contours were developed from the averaged data and are shown in Figures 2, 3 and 4. As can be seen, the plume is changing in time and exhibiting a significant loss of mass.

The contour figures were used to calculate the mass of BTX remaining in the system at the end of each quarter (Figure 5). The mass captured by the pumping field is also shown on Figure 5, and it is obvious that degradation accounts for most of the mass loss at the site. Dispersion and volatilization would not account for the total mass loss observed. The rate of mass loss calculated from Figure 5 is about 1.25 percent per day.

BIOPLUME was calibrated to the observed data prior to the installation of the pumping field. The data in Figure 6 show the results of the simulation along the centerline of the plume. The model predictions matched the observed concentrations except in the vicinity of well M31. This is to be expected since anaerobic degradation was identified in that zone of the site, but was not included in the model.

The calibrated model was then used to simulate the field data from April 1985 to the end of 1986. The predicted rate of degradation was about 1.0 percent per day in comparison to the observed rate of 1.25 percent per day.

The BIOPLUME II model is presently being used to design and operate an on-going biorestoration experiment at the Traverse City field site. A nutrient mix containing phosphate, nitrogen and an oxygen source are injected into a portion of the contaminated aquifer next to the Hangar building (Figure 2). The objective is to stimulate the microorganisms and enhance the bioremediation activity occurring at the site. The BIOPLUME II model was used to determine the required number of injection wells, the injection flow rates and the required time for cleanup under different scenarios of oxygen delivery. Preliminary data indicate that oxygen and inorganic nutrients are being consumed and overall contaminant concentrations are decreasing.

The results of the restoration experiment will be published when the test is concluded.

Conclusions

The following conclusions can be made from the previous analysis:

1. Biodegradation processes have significant effects on contaminant plumes. Naturally occurring biodegradation causes a narrow plume and loss of mass in the body of the plume.

2. BIOPLUME simulates oxygen limited biodegradation and incorporated reaeration and anaerobic processes as a first order decay process.

3. BIOPLUME was calculated at the Conroe, Texas and Traverse City, Michigan sites where biodegradation was observed.

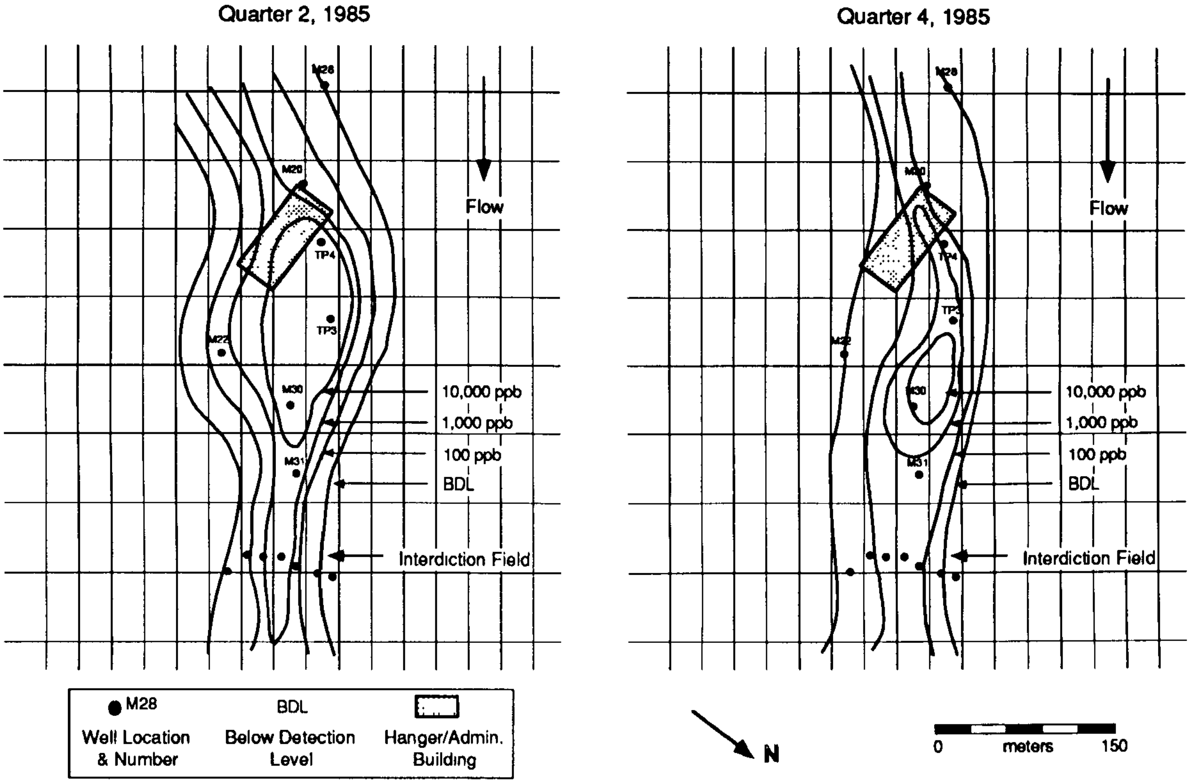

Figure 2. Contaminant plume at Traverse City, quarters 2 & 4, 1985.

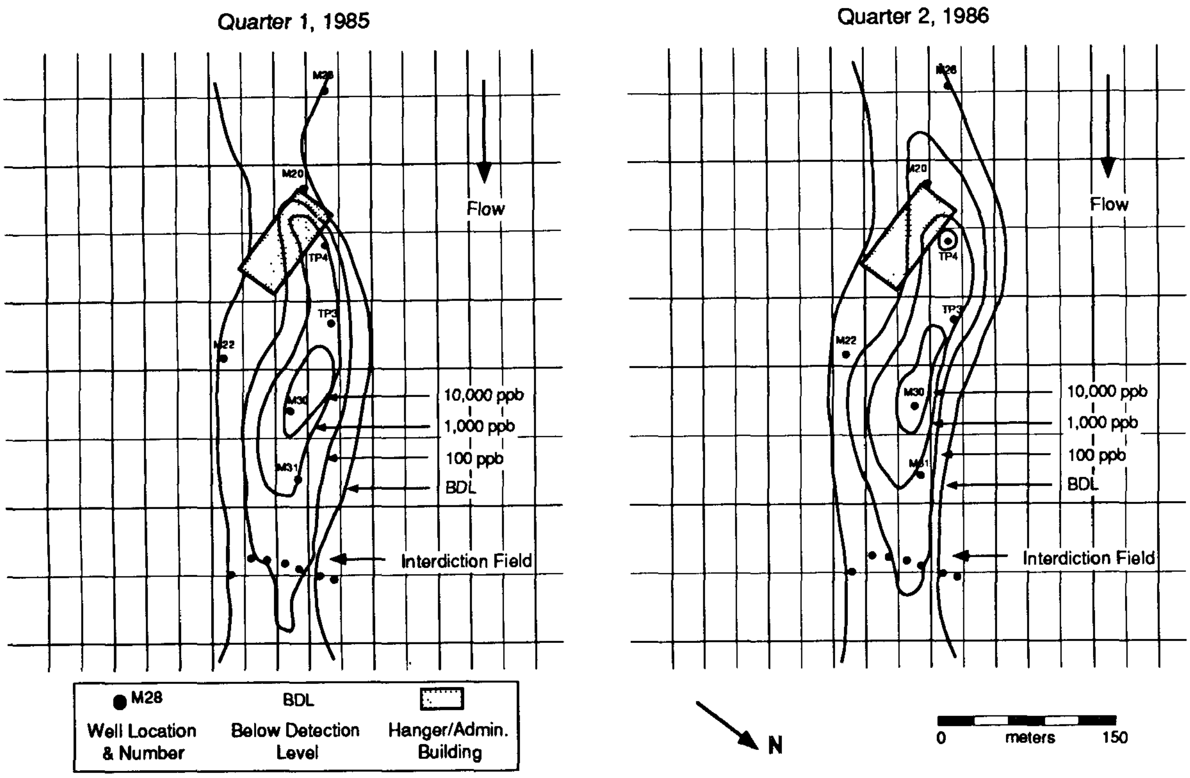

Figure 3. Contaminant plume at Traverse City, quarters 1 & 2, 1986.

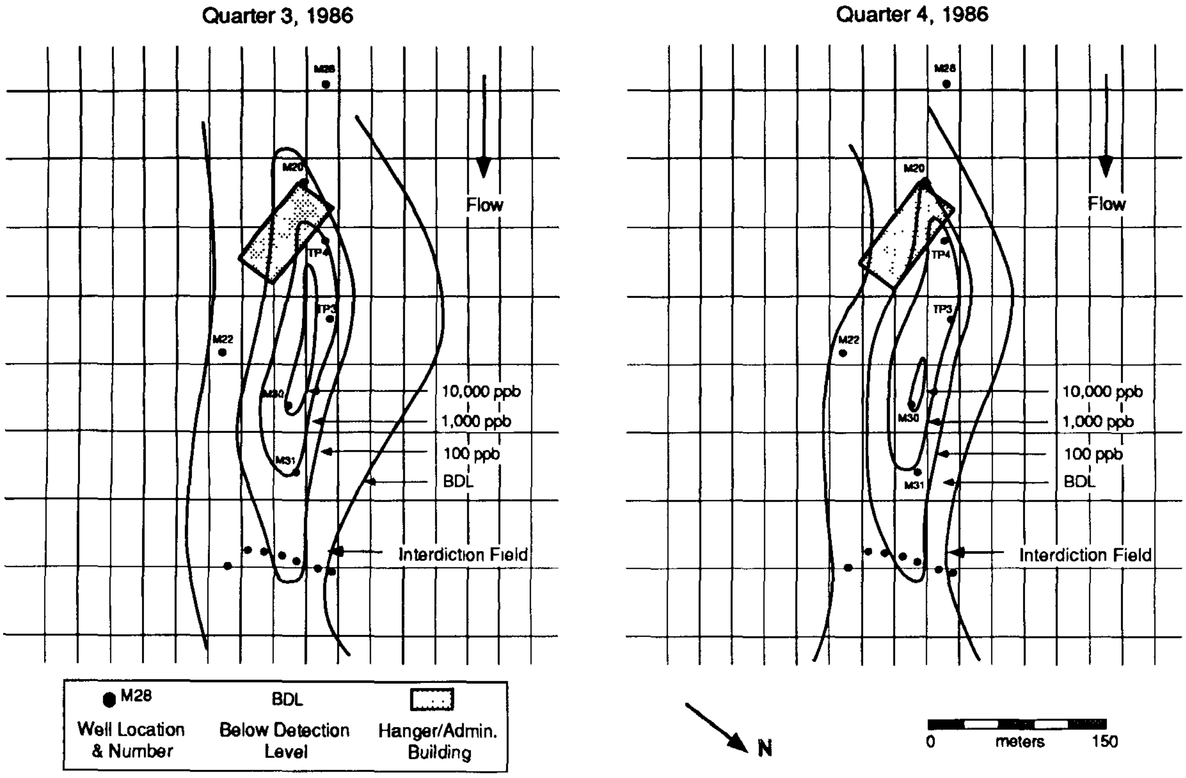

Figure 4. Contaminant plume at Traverse City, quarters 3 & 4, 1986.

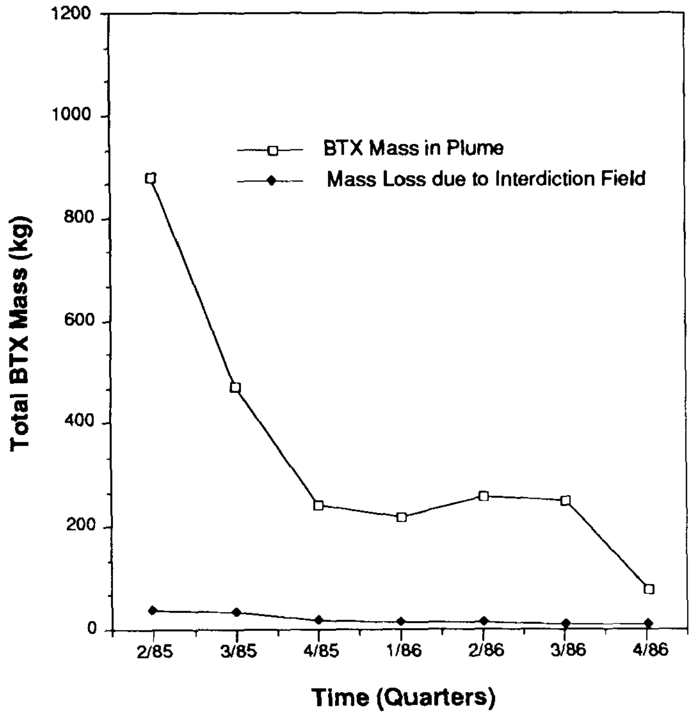

Figure 5. Contaminant mass loss at Traverse City.

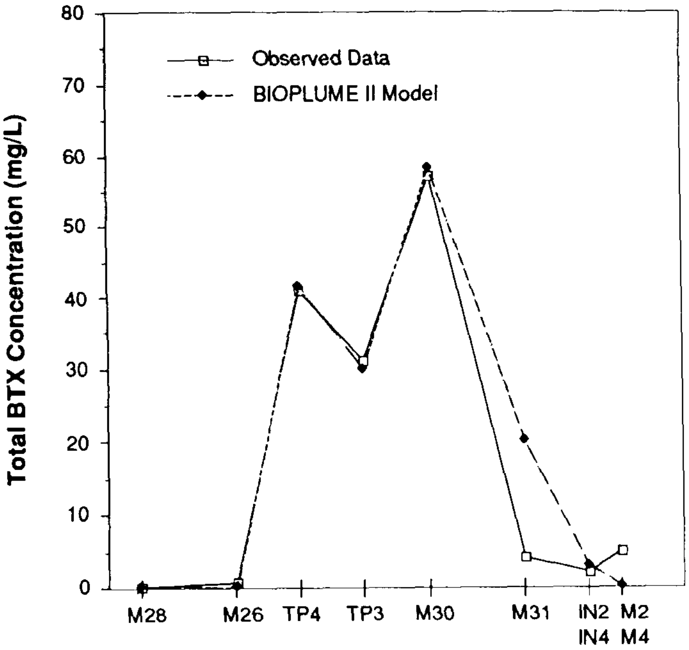

Figure 6. Calibration results at Traverse City. Contaminant concentrations along plume centerline.

The model provided a better match than a standard transport code.

4. Retardation can be handled in the new version, BIOPLUME II, so that biodegradation effects on retarded plumes can be simulated and analyzed.

5. BIOPLUME has the capability of simulating in situ restoration by modeling the injection of oxygenated water, which appears to be a viable alternative to the classic pump/treat schemes.

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