Simulation of Aerobic and Anaerobic Biodegradation Process for Contaminated Aquifers

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ABSTRACT: The high cost and poor performance of many groundwater remedial systems have led researchers to consider the natural aerobic and anaerobic biodegradation process as an alternative technique for effective groundwater remediation. In this study, bioremediation is simulated using U.S. Environmental Protection Agency (USEPA) developed software BIOPLUME III. The model simulates the biodegradation of organic contaminants for an aerobic and an anaerobic electron acceptor including oxygen and nitrate. The sensitivity of contaminant concentration due to various hydrogeological parameters such as hydraulic conductivity, longitudinal dispersivity, transverse dispersivity and retardation factor is investigated for a hypothetical aquifer system. The study suggests that hydraulic conductivity is the most significant parameter amongst the parameters considered and hence aquifers with higher permeabilities are more amenable to bioremediation. It is also observed that anaerobic biodegradation accounts for a major part of an overall contaminant reduction due to the biodegradation process.

INTRODUCTION

In many countries of the world including India, groundwater constitutes the main source of drinking water, the quality of which has deteriorated due to rapid industrialization and human mismanagement. The contamination of groundwater has thus been a major challenge faced by environmentalists in the recent past. Organic contaminants can enter into groundwater environment from a variety of sources that include toxic waste disposal sites, accidental chemical spills and improperly designed or maintained chemical transportation and storage facilities. Soil and groundwater contamination due to processing and storage of petroleum and its products and its widespread release to the environment has resulted into subsurface contamination by the toxic and water soluble compounds such as Benzene, Toluene, Ethyl benzene and Xylenes (BTEX). Groundwater contamination by this organic chemical is of immense concern because of their widespread use and harmful effects even when present at very low concentrations.

SIMULATION OF BIOREMEDIATION PROCESS

The spatial and temporal contaminant distribution in an aquifer system is simulated using *BIOPLUME III* (Rifai *et al.*, 1997) model. The *BIOPLUME III* model has been developed primarily to model the natural attenuation of organic contaminants in groundwater due to the process of advection, dispersion, sorption, and biodegradation. *BIOPLUME III* is an updated version of the earlier *BIOPLUME II* model of Rifai *et al.* (1988). The main difference in the models is the explicit incorporation of the anaerobic biodegradation process and the addition of multiple biodegradation kinetics in *BIOPLUME III*, which was not considered in *BIOPLUME II*. The model simulates biodegradation using any one of the three kinetic expressions (first-order, instantaneous, or Monod). The model simulates biodegradation using a number of aerobic and anaerobic electron acceptors like oxygen, nitrate, iron (III), sulfate and carbon dioxide. *BIOPLUME III* is based on the U.S. Geological Survey (USGS) Method of Characteristics model (Konikow and Bredehoeft 1989). The conceptual model used in *BIOPLUME III* to simulate aerobic and anaerobic biodegradation process tracks six different plumes simultaneously: hydrocarbon, oxygen, nitrate, ferric iron, sulfate and carbon dioxide. Biodegradation is assumed to occur sequentially in the following order (Rifai *et al.*, 2000) in the study.

Oxygen → Nitrate → Fe(III) → Sulfate → Carbon Dioxide

The transport equations for the contaminant, oxygen and nitrate can be expressed as (Rifai *et al.*, 1997),

$$\frac{\partial(bC_s)}{\partial t} = \frac{1}{R_s}\left[\frac{\partial}{\partial x_i}\left(bD_{ij}\frac{\partial C_s}{\partial x_j}\right) - \frac{\partial(bC_s v_i)}{\partial x_i}\right] - \frac{qC'_s}{\theta} \quad \dots (1)$$

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[1]Conference speaker

$$\frac{\partial(bC_o)}{\partial t} = \left[\frac{\partial}{\partial x_i} \left(bD_{ij} \frac{\partial C_o}{\partial x_j} \right) - \frac{\partial(bC_o v_i)}{\partial x_i} \right] - \frac{qC'_o}{\theta} \quad \ldots (2)$$

$$\frac{\partial(bC_n)}{\partial t} = \left[\frac{\partial}{\partial x_i} \left(bD_{ij} \frac{\partial C_n}{\partial x_j} \right) - \frac{\partial(bC_n v_i)}{\partial x_i} \right] - \frac{qC'_n}{\theta} \quad \ldots (3)$$

where C_s, C_o and C_n = concentration of contaminant (or substrate), oxygen and nitrate respectively (M/L^3); C'_s, C'_o and C'_n = concentration of contaminant, oxygen and nitrate respectively in a source or sink fluid (M/L^3); q = volume flux per unit area (L/T); b = saturated aquifer thickness (L); v_i = average linear velocity in direction i (L/T); θ = effective aquifer porosity (dimensionless); R_s = substrate retardation factor (dimensionless) which is defined in this study using linear adsorption isotherm and is determined (Bedient *et al.*, 1999) using the equation $R_s = (1 + \rho_b K_d / \theta)$, where ρ_b is the soil bulk density, K_d is the solute partition coefficient and θ is the porosity. Conceptually, the retardation factor is the ratio of the groundwater flow velocity to contaminant migration velocity (Bedient *et al.*, 1999). The retardation factor of oxygen and nitrate are taken to be 1 in Eqns. (2) and (3), indicating that oxygen and nitrate are moving with the same velocity as the groundwater flow velocity. D_{ij} = hydrodynamic dispersion tensor (L^2/T); i, j = 1, 2 (principal coordinate directions); and t = time. Furthermore, the biodegradation process is simulated by incorporating an instantaneous reaction model proposed by Borden and Bedient (1986). It is assumed that the utilization of oxygen and contaminants by microorganism in the subsurface zone can be simulated as an instantaneous reaction between the organic contaminant and electron receptors. The biodegradation of contaminants using aerobic and anaerobic electron acceptors is simulated using the principle of super-position such that Borden and Bedient (1986),

$$\Delta C_{so} = C_o / F_o; \ C_o = 0 \ \text{if} \ C_s > C_o / F_o \quad \ldots (4)$$

$$\Delta C_{os} = C_s F_o; \ C_s = 0 \ \text{if} \ C_o > C_s F_o \quad \ldots (5)$$

$$\Delta C_{sn} = C_n / F_n; \ C_n = 0 \ \text{if} \ C_s > C_n / F_n \quad \ldots (6)$$

$$\Delta C_{ns} = C_s F_n; \ C_s = 0 \ \text{if} \ C_n > C_s F_n \quad \ldots (7)$$

ΔC_{so} and ΔC_{sn} = loss in the contaminant concentration due to biodegradation using oxygen and nitrate respectively; ΔC_{os} and ΔC_{ns} = corresponding concentration loss in the electron acceptors; and F_o and F_n = stoichiometric ratio for oxygen and nitrate respectively.

Eqns. (1) to (7) are simulated by using *BIOPLUME~III* to obtain contaminant concentration and the maximum and minimum heads at the end of each pumping period.

APPLICATION OF THE DEVELOPED MODEL

Figure 1 depicts the layout and the initial concentration of the contaminated plume of Shieh and Peralta (2005) considered in this study. Table 1 presents the input parameters used in the *BIOPLUME III* model for the study area of 701.5 m × 518.5 m. The aquifer is assumed to be homogeneous with the west and the east sides of the domain of constant head boundaries of head values of 30.5 m and 27.7 m respectively where as the north and south sides are assumed to be impervious. Consequently, flow is assumed from west to east with an initial hydraulic gradient of 0.004. The groundwater flow simulation is assumed to be at steady state. The representative organic pollutant is BTEX.

Table 1: Input Parameters (Shieh and Peralta 2005) for *BIOPLUME III* Simulation Model

Input parameter	Value
Grid size	19 × 25
Cell size	30.5 × 30.5 m
Hydraulic conductivity	6×10^{-5} m/s
Aquifer thickness	15 m
Hydraulic gradient	0.004
Longitudinal dispersivity	10 m
Transverse dispersivity	2 m
Effective porosity	0.3
Retardation factor	1.0
Anisotropy factor	1.0
Background concentration of oxygen	5 ppm
Background concentration of nitrate	17 ppm
Remediation period	3 years

Figure 1 also shows the plume configuration after 5 years in the absence of any remediation. It can be seen from Figure 1 that the contaminated plume eventually reaches the monitoring wells after 5 years under the prevailing conditions. An in-situ bioremediation is therefore require to contain the plume and enhance the contaminant biodegradation process. It is also assumed that both, aerobic biodegradation (oxygen as an electron acceptor) and anaerobic biodegradation (nitrate as an electron acceptor) occur in the aquifer system. These two cases are simulated in the model by

using the instantaneous reaction model of *BIOPLUME III*. Furthermore, the maximum allowable concentration C_{max} is assumed to be 5 ppm for the entire study area. The upper and lower bounds on hydraulic heads are also taken as 31.4 m and 27.7 m (the constant head boundary values at the west and east sides of the aquifer) respectively.
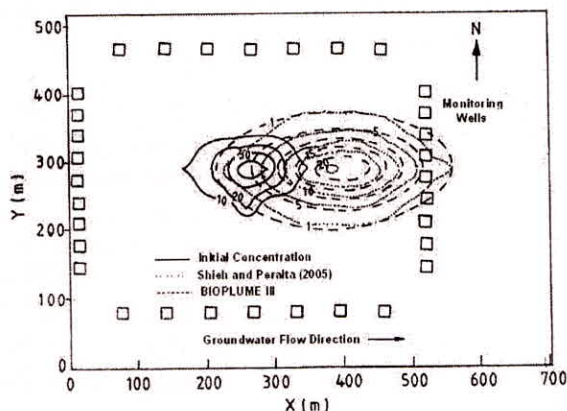

**Fig. 1:** Comparison of unmanaged contaminated plume concentrations (mg/L) after 5 years

RESULTS AND DISCUSSIONS

The results obtained using *BIOPLUME III* taking data of Table 1 is validated by comparing the results of Shieh and Peralta (2005) and from Figure 1 one can observe that a good match for spatial variation of plume concentration after 5 years is obtained.

A Sensitivity analysis is conducted to identify key parameters that have the most significant effect on contaminant concentration and on mass loss due to biodegradation besides investigating the sensitivity of the predicted outcome of the bioremediation model due to variability in aquifer parameters. The parameters analyzed include: hydraulic conductivity (K), longitudinal (α_L) and transverse (α_T) dispersivity and retardation factor (R). The parameter values given in Table 1 serves as a base case for sensitivity analysis and the parameter under consideration is perturbated keeping all other parameters constant. Thus Eqn. (1) to Eqn. (7) are simulated first using the base values of aquifer parameters as given in Table 1 using *BIOPLUME III* to obtain contaminant concentration and oxygen concentration. Subsequently the perturbated values of model parameters are used in different model runs of *BIOPLUME III* again to obtain contaminant and oxygen concentration. Keeping in view the symmetry of the problem, only one section along the centerline of the aquifer system from west to east is taken for sensitivity analysis for each parameter.
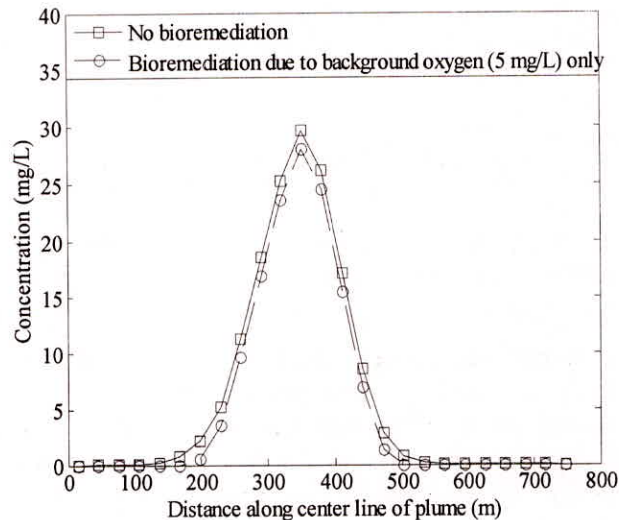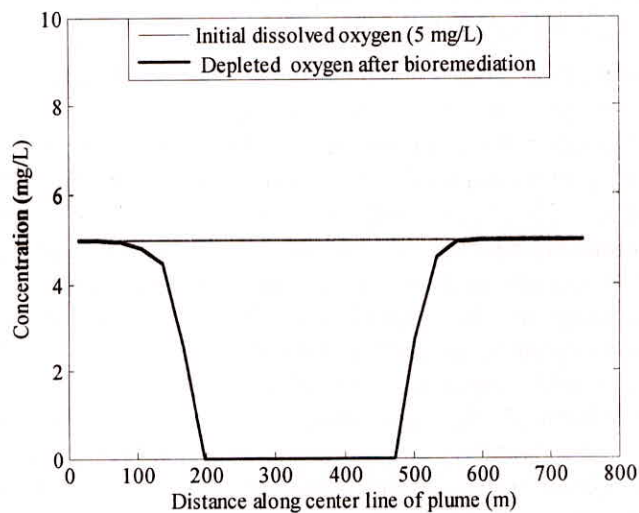
Fig. 2: Effect of bioremediation on (a) contaminant concentration distribution and (b) oxygen concentration along centerline of plume after 3 years

Figure 2 shows oxygen is absent wherever the contaminant is present in a relatively high concentration. The oxygen plume forms an envelope for the contaminant plume with oxygen concentrations gradually increasing to initial background levels as one moves away from the centerline of the contaminant plume. The % mass lost by biodegradation due to background oxygen of 5 mg/L is found to be approximately 18%.

Figure 3 shows the variation in contaminant and oxygen concentration along the centerline of the plume for three values of K ranging from 0.86 m/day to 9.5 m/day. It is observed that the shape and the peak concentration of the contaminant plume vary significantly with the hydraulic conductivity. The oxygen plume also exhibits a similar variation.

Similarly, Figure 4 shows the variation of the contaminant and oxygen concentration along the centerline of the plume for three different values of α_L ranging from 5 m to 15 m. The variation in contaminant concentration decreases as the value of α_L increases compared to the case of hydraulic conductivity. However, the peak contaminant concentration value is found to vary significantly as the value of retardation factor R increases as shown in Figure 5. As the value of R increases the peak concentration decreases indicating slow migration of contaminant implying more contaminants getting absorbed in the soil matrix.

The output of *BIOPLUME III* is further studied for mass balance in the aquifer system. The output presents the initial mass of the contaminant, contaminant mass at the end of simulation period and the mass loss due to biodegradation because of the presence of various electron acceptors. The results of the mass loss due to biodegradation is further verified by the simple empirical equation proposed by Rifai *et al.*

(1988) which calculates the Dissolved Mass (DM) at time t using an average plume concentration (C_{avg}), thus $DM_t = C_{avg,t} \times b \times \theta \times L \times W$; where b = aquifer thickness; θ = porosity; L = plume length; W = plume width.

The % mass biodegraded is found to increase with the hydraulic conductivity and the longitudinal dispersivity as shown in Figure 6. However, the % biodegraded mass increases significantly as hydraulic conductivity increases whereas longitudinal dispersivity is found to have a small effect on the % mass biodegraded. Similarly, the % biodegraded mass changes very little due to the variation in transverse dispersivity and retardation factor are shown in Figure 7. From Figures 6 and 7 it is clear that as the hydraulic conductivity, longitudinal and transverse dispersivity increases the % mass degraded also increases, however, the % degraded mass decreases as the retardation factor increases.
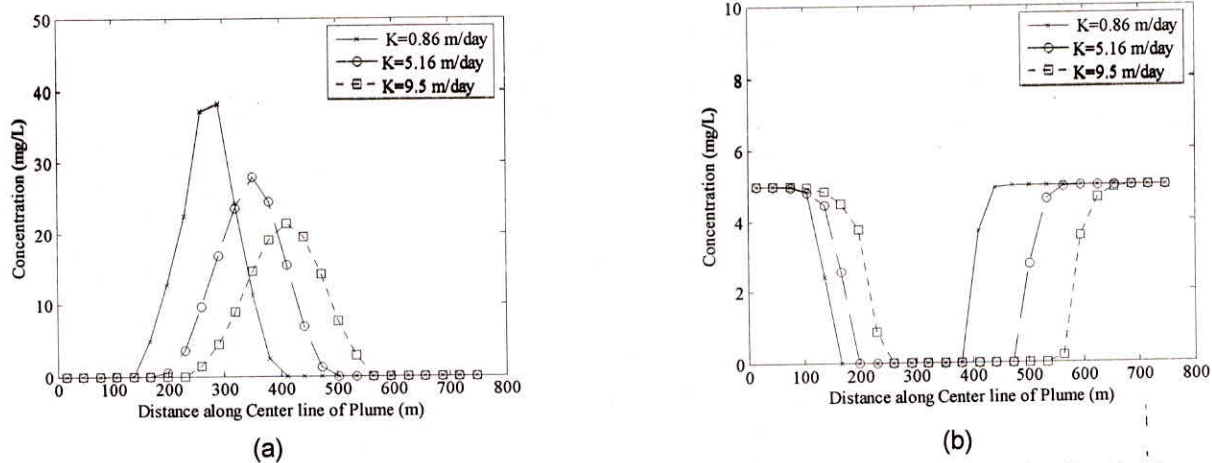

Fig. 3: Variation of contaminant and oxygen concentration with hydraulic conductivity: (a) contaminant; (b) oxygen
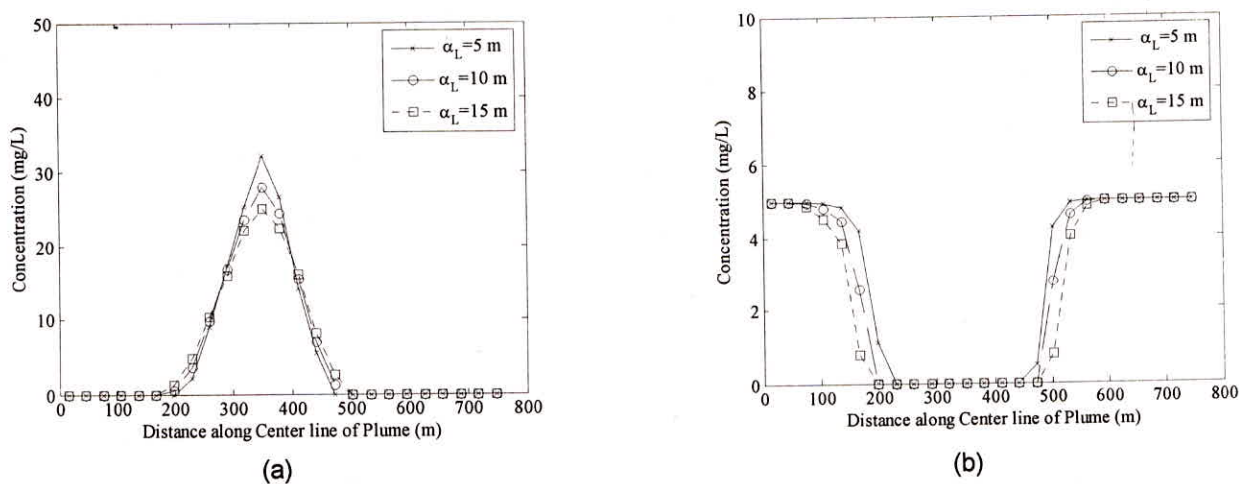

Fig. 4: Variation of contaminant and oxygen concentration with longitudinal dispersivity: (a) contaminant; (b) oxygen

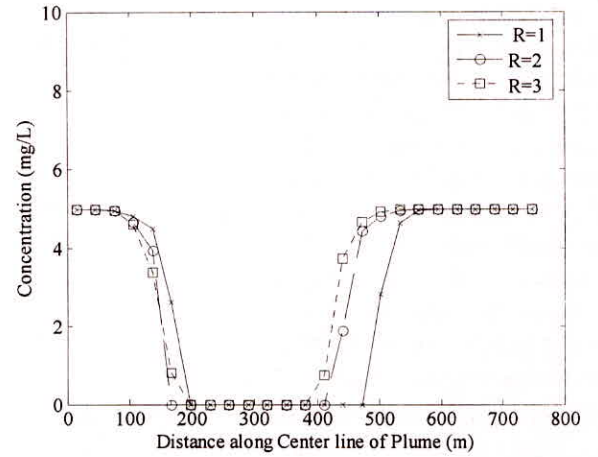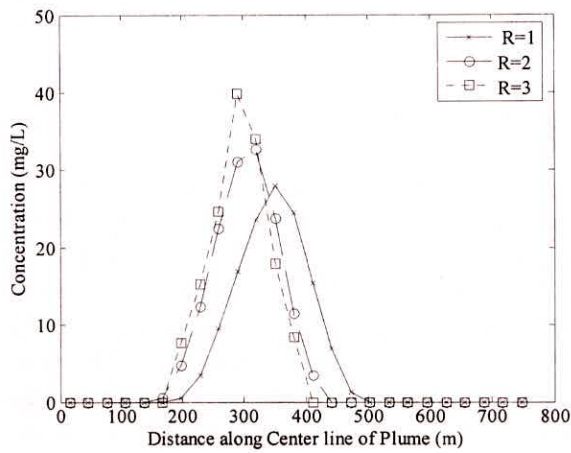(a)   (b)

Fig. 5: Variation of contaminant and oxygen concentration with Retardation: (a) contaminant; (b) oxygen

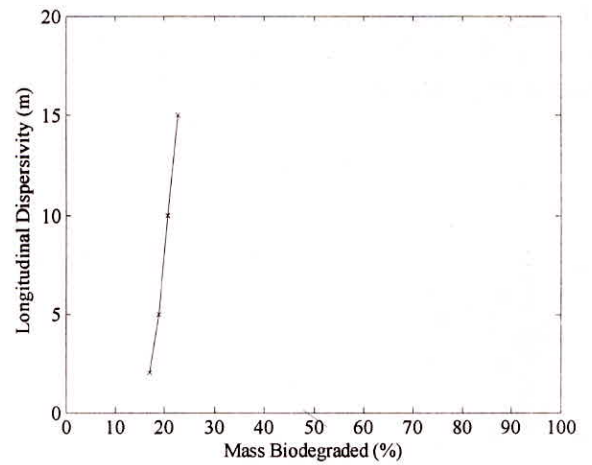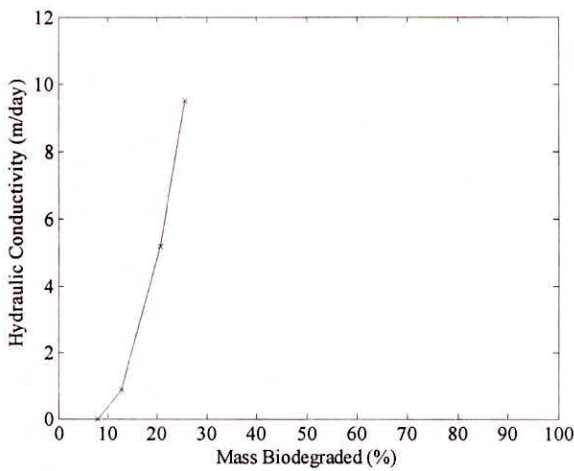(a)   (b)

Fig. 6: Variation of mass loss due to biodegradation with hydraulic conductivity and longitudinal dispersivity:
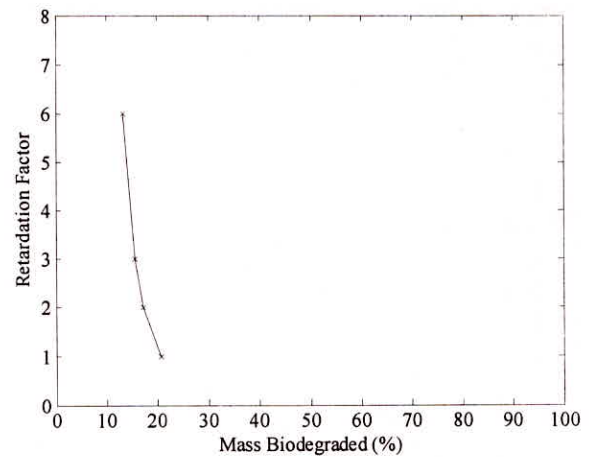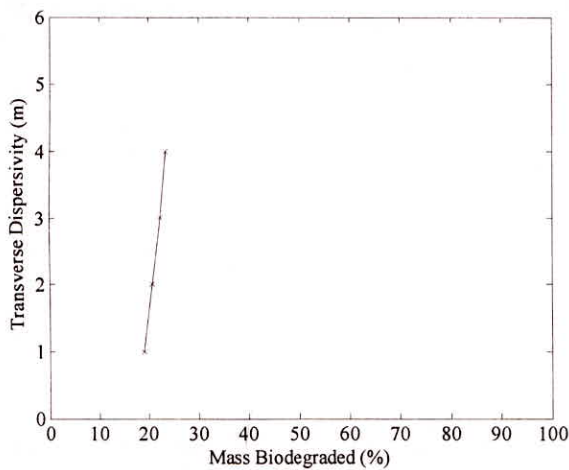(a) hydraulic conductivity (b) longitudinal

(a)   (b)

Fig. 7: Variation of mass loss due to biodegradation with transverse dispersivity and retardation factor
(a) transverse dispersivity (b) retardation factor

Figures 8(a) shows the spatial variation of contaminant concentration for various background oxygen concentration whereas Figures 8(b) highlights the spatial variations of contaminant concentration with the combined availability of both oxygen and nitrate as background concentrations. It is observed that as the available oxygen concentration increases the biodegradation increases. However, even if the background oxygen concentration increases to 20 mg/L, the contaminant concentration does not decrease to the desired level say 5 mg/L. This is because oxygen is not transported to the contamination area where it can be most useful. An oxygen concentration of 20 mg/L can be achieved by providing hydrogen peroxide, which is very costly preposition. Instead addition of other anaerobic electron acceptors such as nitrate could be a better alternative. It is further observed that the effect

of adding 17 mg/L of nitrate and 5 mg/L of oxygen is almost equivalent to adding 20 mg/L of oxygen for contaminant degradation. Thus addition of both an aerobic (oxygen) and anaerobic (nitrate) electron acceptor can substantially reduce the contaminant concentration in an aquifer system.

CONCLUSIONS

The study shows that hydraulic conductivity is the most significant parameter amongst the various parameters considered and aquifers with higher permeability are more amenable to in-situ bioremediation. The aerobic biodegradation is found to be limited by the rate of transport of oxygen into the contaminated plume. The rate of biodegradation of the contaminant can be enhanced considerably by injecting electron acceptors in the depleted oxygen region and also by providing an extraction well downgradient of the contaminated plume. Furthermore, biodegradation seems to increase when both an aerobic and an anaerobic electron acceptor is added in comparison to the case when only an aerobic electron acceptor is added.

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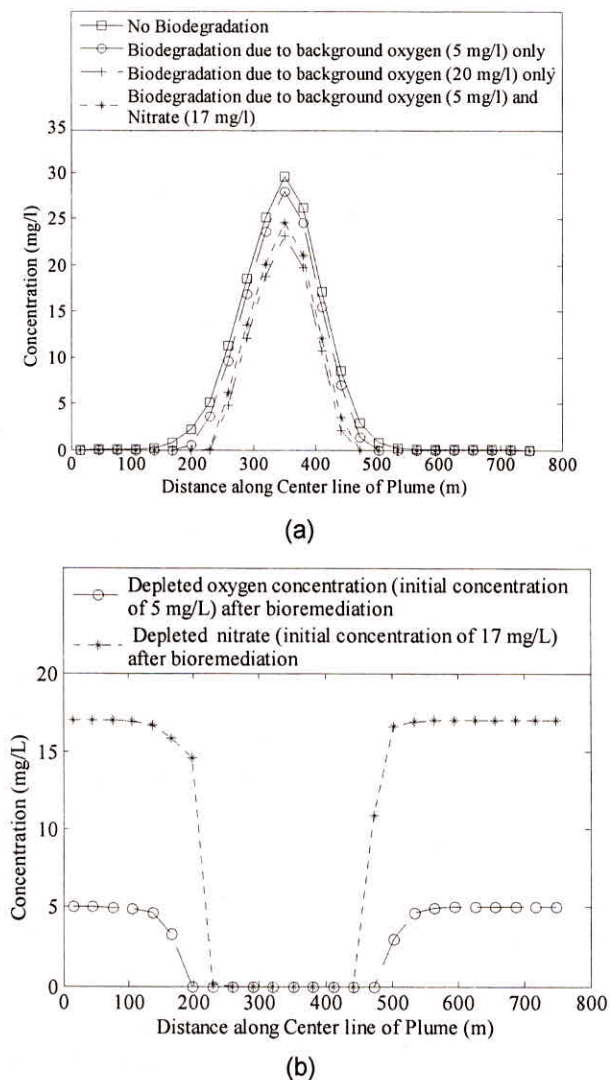

(a)

(b)

Fig. 8: Effect of aerobic and anaerobic bioremediation on (a) contaminant concentration distribution and (b) oxygen concentration along centerline of plume after 3 years