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A simple method to study the effectiveness of bioremediation aided, pump-and-treat technology for aquifers contaminated by non-aqueous phase liquids. I. Single component systems

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Abstract

Various physical processes occurring during the dissolution and biodegradation of non-aqueous phase liquids (NAPLs) have been quantified based on the local-equilibrium assumption involving liquid–liquid equilibrium, sorption equilibrium and biochemical reaction equilibrium. The mass fraction of contaminant remaining in the aquifer and the aqueous concentration of the contaminant have been obtained as functions of the number of flushings (volume of the flushing solution/aqueous phase void volume). The present simplistic approach illustrates that bioremediation can significantly reduce the remediation period for sites contaminated by the NAPLs. Bioremediation is recommended as a 'polishing step' to remove the trace contaminants not readily removed by the flushing process. The proposed model should provide a useful bound regarding the efficiency of bioremediation aided, pump-and-treat technology. The actual number of flushings may exceed the values reported here.

1. Introduction

Spills or leaks of organic chemicals into the subsurface result in the contamination of groundwater. Many of the pollutants are essentially immiscible with water and thus exist as non-aqueous phase liquids (NAPLs). These NAPLs persist in the subsurface for a long time, during which they migrate through a complex process.

Following a spill, a NAPL migrates downwards through the vadose zone. If the spill volume is sufficiently large, the NAPL eventually reaches the groundwater. A LNAPL, less dense than water, spreads laterally in the capillary fringe zone whereas a DNAPL continues to migrate downwards because its density is greater than water.

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This migration continues until the NAPL encounters a low permeability stratum or until all NAPL 'blobs' are immobilized or trapped. The movement, entrapment and displacement of NAPLs have been the focus of attention for more than a decade [1–3]. In recent years, the emphasis has shifted towards examining the dissolution of NAPLs because of their impact on groundwater quality. Remedial measures for reducing contaminants in the pore spaces of the saturated zone often include pump-and-treat processes which seek to dissolve and move the contaminants to an extraction point where they are captured and treated. Pump-and-treat techniques when adopted in conjunction with other transformation techniques such as biodegradation often result in successful remediation of aquifers [4, 5].

In situ bioremediation is a highly attractive technology for remediation because contaminants are transformed or mineralized, not simply moved to another location or immobilized, thus decreasing the cost, risk, and time, while increasing the efficacy and public and regulatory acceptability [6] . In situ bioremediation involves stimulating the growth and metabolic activity of soil microbes that degrade contaminants in the subsurface environment to carbon dioxide and water. It also yields microbial biomass and humic materials associated with incomplete mineralization and dead cells. For aerobic degradation, the common methods to stimulate bacteria include the addition of oxygen as the electron acceptor and nutrients for microbial growth. These nutrients include water soluble nitrogen or phosphorus compounds.

The conventional view is that chlorinated solvents, e.g., TCE, are degraded by reductive dehalogenation under anaerobic conditions. Unfortunately, in subsurface materials these transformations are often incomplete and occasionally result in the accumulation of more potent carcinogens such as vinyl chloride. Various recent studies have shown that methanotrophic bacteria can degrade chlorinated solvents under aerobic conditions [7–10]. In methanotrophs, methane monooxygenase, the enzyme that catalyzes the oxidation of methane to methanol, frequently is nonspecific and fortuitously catalyzes the oxidation of TCE. This degradation of TCE is typical of cometabolism. In situ biodegradation of TCE is possible by adding sufficient methane (a major component of natural gas) and oxygen to the soil to stimulate the growth of indigenous microbes. Injection of oxygen into the subsurface is achieved by a variety of ways, the most common of which are flushing the aquifer with water, injecting air or pure oxygen, and adding hydrogen peroxide. Addition of hydrogen peroxide of a desired concentration is capable of delivering 500 mg/l of oxygen. Nevertheless, rapid decomposition, poor oxygen distribution, and microbial toxicity at high concentrations have been observed in some applications [11–13].

2. Model description

The model proposed here addresses the applicability of biodegradation aided, pump-and-treat technology in treating the saturated zone contaminated by a NAPL. It incorporates the following phases: the aqueous phase, the NAPL, and the soil solids. This model is derived from an equilibrium approach and assumes that the

residence time of the soil water in each flushing is large enough so that all processes attain equilibrium. This includes sorption to solid surfaces, dissolution of the NAPL, and biochemical oxidation. Complete mineralization of organic compounds has been assumed in this model.

2.1. Sorption/desorption

For uncharged organic solutes, it is recognized that adsorption is controlled to a large extent by the natural organic content of the porous media [14, 15]. The sorption characteristics are constant at typical field moisture conditions and are assumed not to depend on water content. The distribution of the contaminant between the liquid phase and the organic carbon in and on the solid phase is described by the partition coefficient, K_D. The value of K_D is evaluated by multiplying the normalized partition coefficient, K_{OC}, by the fraction of organic carbon, f_{OC}, in the aquifer, i.e.,

$$K_D = K_{OC} f_{OC}. \tag{1}$$

2.2. NAPL dissolution

Since equilibrium conditions are assumed to exist, the concentration of the contaminant in the aqueous phase equals its solubility as long as a NAPL is present. After the NAPL disappears, the aqueous phase concentration is governed by the amount of biodegradation and adsorption of the contaminant onto the soil. The assumption of interphase equilibrium simplifies calculations in the model. This assumption is valid under some circumstances. Results from experimental studies on the dissolution of the NAPL blobs by various workers have indicated that the NAPL and aqueous phase were at equilibrium [16–18]. Dimensionless analysis by Seagren et al. [19] has indicated that local equilibrium conditions are valid for a certain set of values for the Peclet and Damkohler numbers. Physical conditions creating the local equilibrium conditions are large mass-transfer coefficients, large specific NAPL-aqueous phase interfacial surface areas, i.e., small blobs, large domains of the NAPL and small pore water velocities.

2.3. In situ biodegradation

The residence time of water in the saturated zone is assumed to be sufficiently long such that the amount of oxygen injected into the aquifer in one flushing can be completely consumed by microorganisms in degrading the contaminant. The proposed model assumes complete mineralization of the contaminant into carbon dioxide and water, which is true for most hydrocarbons. Other times, however, the hydrocarbons do not reach a mineralized end point but rather result in relatively stable aliphatic and aromatic compounds. These compounds may become an integral part of the soil humus [20] or may be flushed out of the immediate vicinity in the form of soluble organic compounds. The amount of contaminant biodegraded can be

calculated from the stoichiometric relationship proposed by Rifai and Bedient [21]

$$\Delta C = -O/Y, \tag{2}$$

where ΔC is the change in the contaminant concentration due to biodegradation, O is the dissolved oxygen concentration, and Y is the stoichiometric coefficient giving the ratio of the oxygen consumed to the contaminant degraded for complete mineralization. For example, the following reaction can be considered for complete mineralization of benzene.

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O,$$

which yields the stoichiometric coefficient, $Y = 240/78 = 3.076$. This procedure for calculating the amount of biodegradation implies that the substrate is freely available whereas oxygen transport is the limiting process in bioremediation.

The following variables partition the contaminant into three compartments, i.e., solid, aqueous and NAPL phases: C_W is the concentration of the contaminant in the aqueous phase (gm/cm^3); C_S is the concentration of the contaminant sorbed to the solid phase (gm/gm); ρ_B is the bulk density of the soil (gm/cm^3); ρ_N is the density of the pure contaminant (gm/cm^3); ε_W is the soil water porosity, i.e., aqueous phase void volume/total soil volume (cm^3/cm^3); ε_N is the soil NAPL porosity, i.e., NAPL volume/total soil volume (cm^3/cm^3); and ε_T is the total soil porosity, i.e., total void volume/total soil volume (cm^3/cm^3).

The total concentration of the contaminant in the saturated water, soil, and NAPL is

$$C_T = C_W\varepsilon_{W,1} + C_S\rho_B + \rho_N\varepsilon_{N,1}. \tag{3}$$

C_T is an indicator of the average value that might be obtained when various core samples, saturated with the NAPL–water mixture, are extracted and analyzed for the total contaminant concentration. The subscript for the porosity indicates the number of flushing cycles. The number of flushings are an indicator of the amount of the water pumped out of the aquifer calculated in multiples of the aqueous phase void volume in the saturated zone. The porosity values for the first flushing are the initial values. The concentration of the sorbed contaminant is governed by a linear isotherm which is a special case of Freundlich equation, i.e.,

$$C_S = K_D C_W, \tag{4}$$

where K_D is the partition coefficient (cm^3/gm). As long as the NAPL is present, the concentration of the contaminant in the aqueous phase, C_W, equals its solubility in water, S_{HC}.

The first flushing operation simply involves pumping out the saturated aqueous phase through extraction wells. The mass fraction of the contaminant removed through this operation, $MF_{O,1}$, can be calculated as follows:

$$MF_{O,1} = \frac{C_W\varepsilon_{W,1}}{C_W\varepsilon_{W,1} + C_S\rho_B + \rho_N\varepsilon_{N,1}} \tag{5}$$

The above equation assumes that the dissolved contaminant moves at the same rate as the pore water. The mass fraction remaining in the aquifer, $MF_{R,1}$, is

$$MF_{R,1} = 1 - MF_{O,1}. \tag{6}$$

From the second cycle onwards, water is injected into the aquifer. Introduction of fresh water stimulates dissolution of the NAPL. Due to the availability of oxygen, microbes act on the contaminant and accomplish biodegradation. It is assumed that all the required nutrients are present adequately in the aquifer. The decrease in the aqueous concentration of the contaminant due to biodegradation causes further dissolution of the NAPL. This process continues until all the oxygen is consumed. The saturated aqueous phase is then pulled out of the aquifer through extraction wells. The stoichiometric expression for mineralization, Eq. (2), gives the decrease in contaminant owing to biodegradation. The NAPL blobs shrink due to the transfer of contaminant into the aqueous phase. The new porosity can be calculated by applying a mass balance on the contaminant,

$$\rho_N \varepsilon_{N,1} = \rho_N \varepsilon_{N,2} + C_W \varepsilon_{W,2} + (S_O/Y)\varepsilon_{W,1}, \tag{7}$$

where S_O is the entering concentration of oxygen in the aqueous phase. This equation is solved for $\varepsilon_{W,2}$ by resorting to the relation

$$\varepsilon_T = \varepsilon_{N,2} + \varepsilon_{W,2}. \tag{8}$$

On dividing Eq. (7) throughout by ρ_N and substituting the value of $\varepsilon_{N,2}$ from Eq. (8) into Eq. (7), we obtain

$$\varepsilon_{W,2} = \varepsilon_{W,1} \frac{[1 + (S_O/Y\rho_N)]}{[1 - (C_W/\rho_N)]}, \tag{9}$$

where $\varepsilon_{W,2}$ is the resulting aqueous phase porosity at the end of the second flushing. The void fraction occupied by the NAPL at the end of the second flushing can be calculated using Eq. (8). The mass fraction of the contaminant removed in the second flushing is

$$MF_{O,2} = \frac{C_W \varepsilon_{W,2} + (S_O/Y)\varepsilon_{W,1}}{C_S \rho_B + \rho_N \varepsilon_{N,1}}. \tag{10}$$

The corresponding mass fraction remaining in the aquifer after the second flushing is

$$MF_{R,2} = (1 - MF_{O,2})MF_{R,1}. \tag{11}$$

The above analysis remains unchanged in further flushings of the saturated zone until NAPL disappears in the Qth flushing, i.e., $\varepsilon_{N,Q} = 0$ and $\varepsilon_{W,Q} = \varepsilon_T$. For an arbitrary Pth flushing ($P < Q$), the following equations are applicable:

$$\varepsilon_{W,P} = \varepsilon_{W,P-1} \frac{[1 + (S_O/(Y\rho_N))]}{[1 - (C_W/\rho_N)]}, \tag{12}$$

$$\varepsilon_{N,P} = \varepsilon_T - \varepsilon_{W,P}, \tag{13}$$

$$MF_{O,P} = \frac{C_W \varepsilon_{W,P} + (S_O/Y)\varepsilon_{W,P-1}}{C_S \rho_B + \rho_N \varepsilon_{N,P-1}}, \tag{14}$$

$$MF_{R,P} = (1 - MF_{O,P})MF_{R,P-1}. \tag{15}$$

2.4. Disappearance of NAPL

Due to recursive biodegradation and flushing, the volume of the NAPL shrinks continuously and finally disappears in the Qth flushing. At this moment, the aqueous phase concentration of the contaminant begins to decrease. C_W is governed by the extent of biodegradation and that of sorption; it can be evaluated by applying a mass balance on the contaminant as follows:

(Mass present at the beginning of the Qth flushing) = (Mass present at the end of the Qth flushing) + (Mass biodegraded during the Qth flushing) + (Mass flushed-out at the end of the Qth flushing),

i.e.,

$$C_{S,Q-1}\rho_B + \rho_N \varepsilon_{N,Q-1} = C_{S,Q}\rho_B + (S_O/Y)\varepsilon_{W,Q-1} + C_{W,Q}\varepsilon_T. \tag{16}$$

Notice the introduction of a subscript for the concentration terms because contaminant concentration no longer remains constant but instead decreases steadily from the Qth flushing onwards. Eq. (16) can be solved for $C_{W,Q}$ by resorting to the following relationship:

$$C_{S,Q} = K_D C_{W,Q}. \tag{17}$$

On substituting Eq. (17) into Eq. (16) and solving for $C_{W,Q}$, we obtain

$$C_{W,Q} = \frac{C_{S,Q-1}\rho_B + \rho_N \varepsilon_{N,Q-1} - (S_O/Y)\varepsilon_{W,Q-1}}{K_D \rho_B + \varepsilon_T}. \tag{18}$$

An equation similar to Eq. (14) can be used to calculate the mass fraction removed from the aquifer during the Qth flushing with appropriate values of $C_{W,Q}$ and $C_{S,Q-1}$, i.e.,

$$MF_{O,Q} = \frac{C_{W,Q}\varepsilon_T + (S_O/Y)\varepsilon_{W,Q-1}}{C_{S,Q-1}\rho_B + \rho_N \varepsilon_{N,Q-1}}, \tag{19}$$

where $C_{S,Q-1} = C_S$. The mass fraction of the contaminant remaining in the aquifer after the Qth flushing is computed from Eq. (15).

For any Zth flushing ($Z > Q$), the following equations can be used until the aqueous concentration of the contaminant vanishes or decreases to a safe concentration.

$$C_{W,Z} = \frac{C_{S,Z-1}\rho_B - (S_O/Y)\varepsilon_T}{K_D \rho_B + \varepsilon_T}, \tag{20}$$

$$MF_{O,Z} = \frac{C_{W,Z}\varepsilon_T + (S_O/Y)\varepsilon_T}{C_{S,Z-1}\rho_B}, \tag{21}$$

$$MF_{R,Z} = (1 - MF_{O,Z})MF_{R,Z-1}. \tag{22}$$

3. Model simulation

Table 1 lists the parameter values specified for the simulation. Table 2 lists the organic compounds serving as contaminants for the simulation and their representative properties. The organic compounds chosen were benzene, toluene, ethylbenzene, xylene, phenanthrene and trichloroethylene (TCE). All these compounds have been known to aerobically biodegrade. The values of Y have been calculated by assuming complete mineralization of the contaminant. All the compounds except TCE mineralize in the same manner as benzene. For complete mineralization of TCE, the following reaction can be hypothesized:

$$2C_2HCl_3 + 5O_2 + CH_4 \rightarrow 6HCl + 5CO_2 \cdot \quad (23)$$

For this reaction, $Y = 160/263 = 0.608$. In the proposed model, 100 mg/l is the upper limit of oxygen supplied to the saturated zone. According to Eq. (23), this value corresponds to the methane concentration of 10 mg/l, which is plausible since the aqueous solubility of methane is 24.4 mg/l [24]. Hence, it has been assumed that the supply of methane is not limiting for the biodegradation of TCE. It has been observed that competition between methane and chlorinated aliphatics has an inhibitory effect on methane monooxygenase [10]. Such an inhibitory effect has been neglected in our model. The modeling of the competitive inhibition phenomenon can be found in the work by Broholm et al. [25].

Table 1
Values of model parameters

Parameter	Value
Total soil porosity, ε_T	0.50
Soil bulk density, ρ_B	1.4 gm/cm^3
Fraction of organic carbon, f_{OC}	0.03

Table 2
Values of density, normalized partition coefficient, solubility in water, and yield coefficient for each contaminant[a]

Contaminant	ρ_N (gm/cm^3)	K_{OC} (l/kg)	S_{HC} (mg/l)	Y
Benzene	0.895	85	1780	3.076
Toluene	0.875	151	537	3.13
Ethylbenzene	0.874	158	152	3.47
Xylene	0.870	210	162	3.47
Phenanthrene	1.179	22908	1	2.96
TCE	1.466	107	1100	0.608

[a] Values taken from Knox et al. [22] , Lyman et al. [23] and US EPA [4].

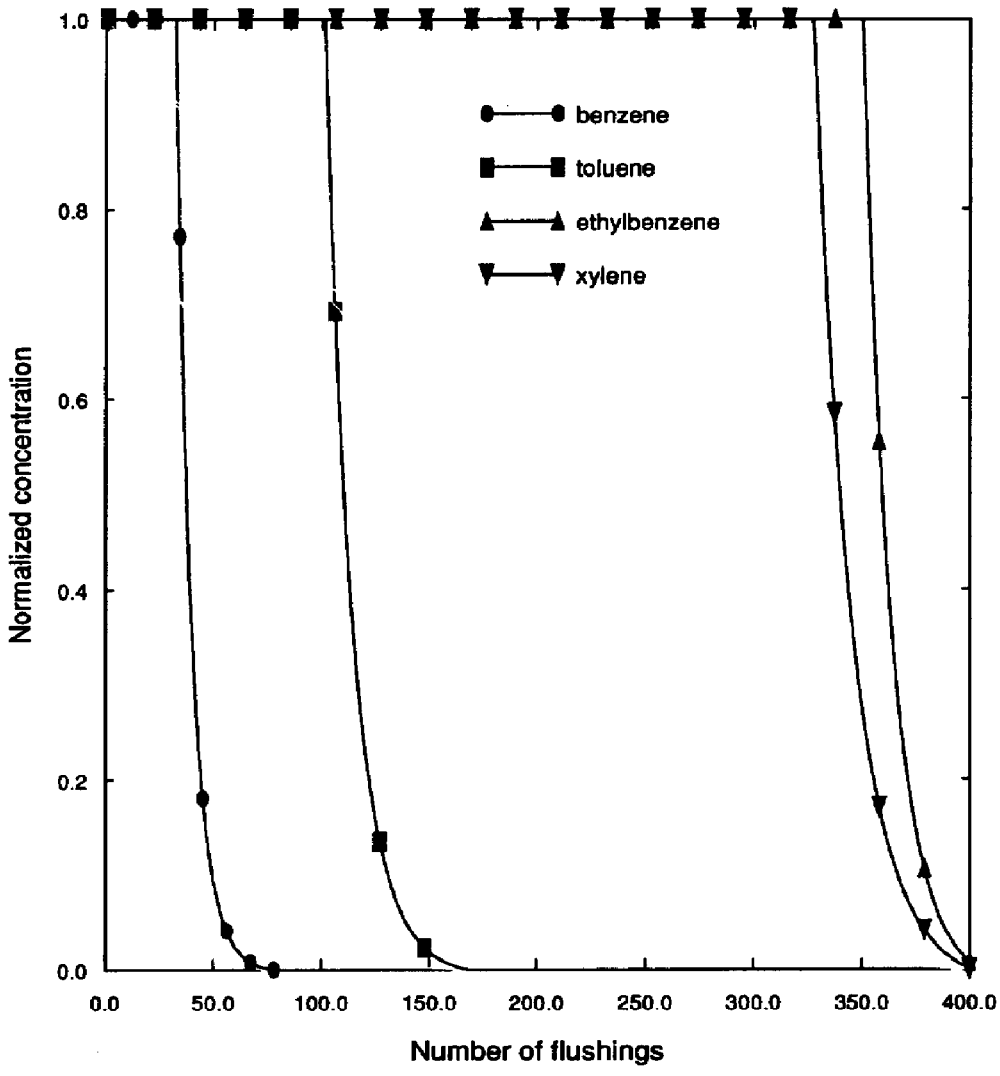

Fig. 1. Aqueous concentration of the contaminant in the aquifer as a function of the number of flushings under conditions of equilibrium dissolution and biodegradation of the NAPL initially occupying 6% of the void volume in the saturated zone when the inlet oxygen concentration is 10 mg/l.

4. Results and discussion

Computer simulation was carried out and the resulting values were plotted. The points are simulated values after the indicated number of flushings. Fig. 1 plots the normalized concentrations of benzene, toluene, ethylbenzene and xylene in the aqueous phase against the number of flushings. Equilibrium dissolution and biodegradation are considered to occur with the inlet oxygen concentration of 10 mg/l. The normalized concentration is calculated by dividing the aqueous phase concentration of the solute by its solubility. The fraction of the total soil volume occupied by the NAPL is assumed to be 0.03, which corresponds to 6% saturation since the total soil

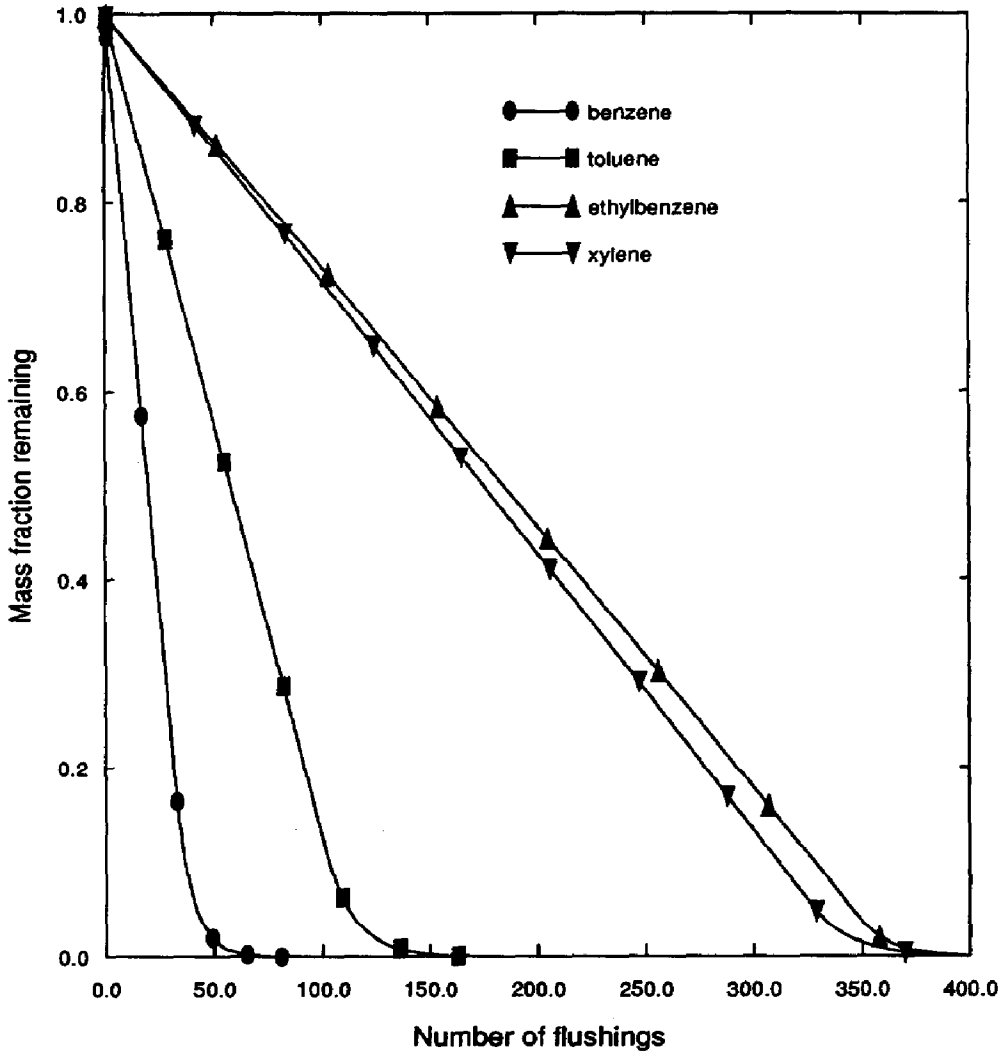

Fig. 2. Mass fraction of the contaminant remaining in the aquifer as a function of the number of flushings under the conditions of equilibrium dissolution and biodegradation of the NAPL initially occupying 6% of the void volume in the saturated zone when the inlet oxygen concentration is 10 mg/l.

porosity is 0.5. This is quite typical of the NAPL volume fraction in field conditions when the NAPL is present at residual saturation [26]. Fig. 1 illustrates the fact that the aqueous phase concentration of the solute remains constant at its solubility as long as the NAPL persists in the aquifer. Once the NAPL disappears, the aqueous phase concentration decreases steadily. The tailing behavior for different solutes is governed by their adsorption affinity towards the soil.

The mass fraction of the solutes remaining in the aquifer is plotted in Fig. 2 as a function of the number of flushings. The decrease in the mass fraction of the solutes is essentially linear when the NAPL is present in the aquifer. Once all the NAPL disappears, the tailing behavior is manifested. Depending on the value of the

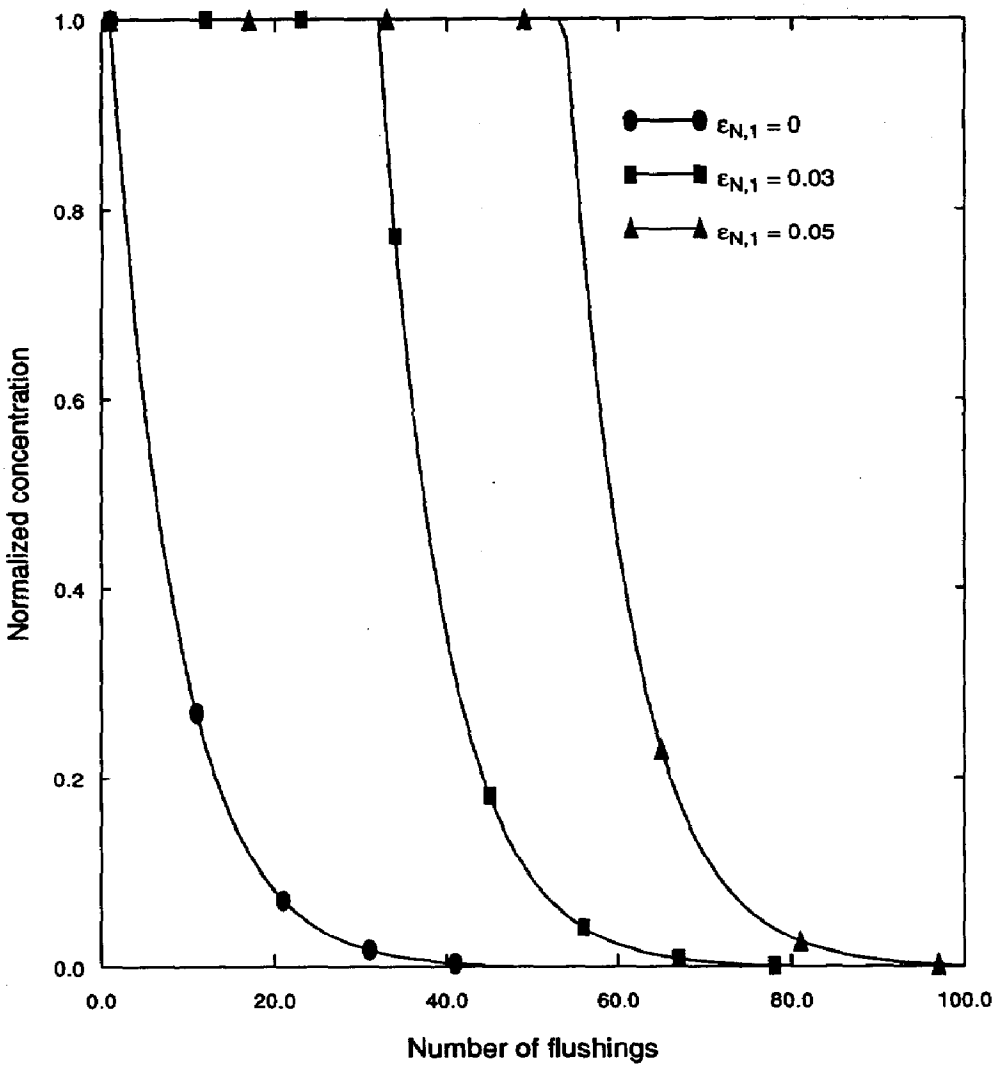

Fig. 3. Influence of the initial NAPL volume fraction on the persistence of benzene in the aquifer under the conditions of equilibrium dissolution and biodegradation for an inlet oxygen concentration of 10 mg/l.

partitioning coefficient, K_D, it may require up to 100 flushings to remove the sorbed contaminant.

The effects of the initial NAPL volume fraction on the persistence of the contaminant in the aquifer are demonstrated in Fig. 3. When no NAPL exists in the aquifer ($\varepsilon_{N,1} = 0$), it takes approximately 50 flushings to remove benzene from the aquifer. Nevertheless, if the initial residual saturation of benzene is 10%, i.e., $\varepsilon_{N,1} = 0.05$, the number of flushings required nearly doubles to 100.

Fig. 4 illustrates the effectiveness of biodegradation in remediating a site contaminated with benzene when the NAPL is initially present at 6% by volume in the pore spaces of the saturated zone. Two cases with the inlet oxygen concentration, S_O, of 40 and 100 mg/l have been considered. The inlet oxygen concentration of 40 mg/l

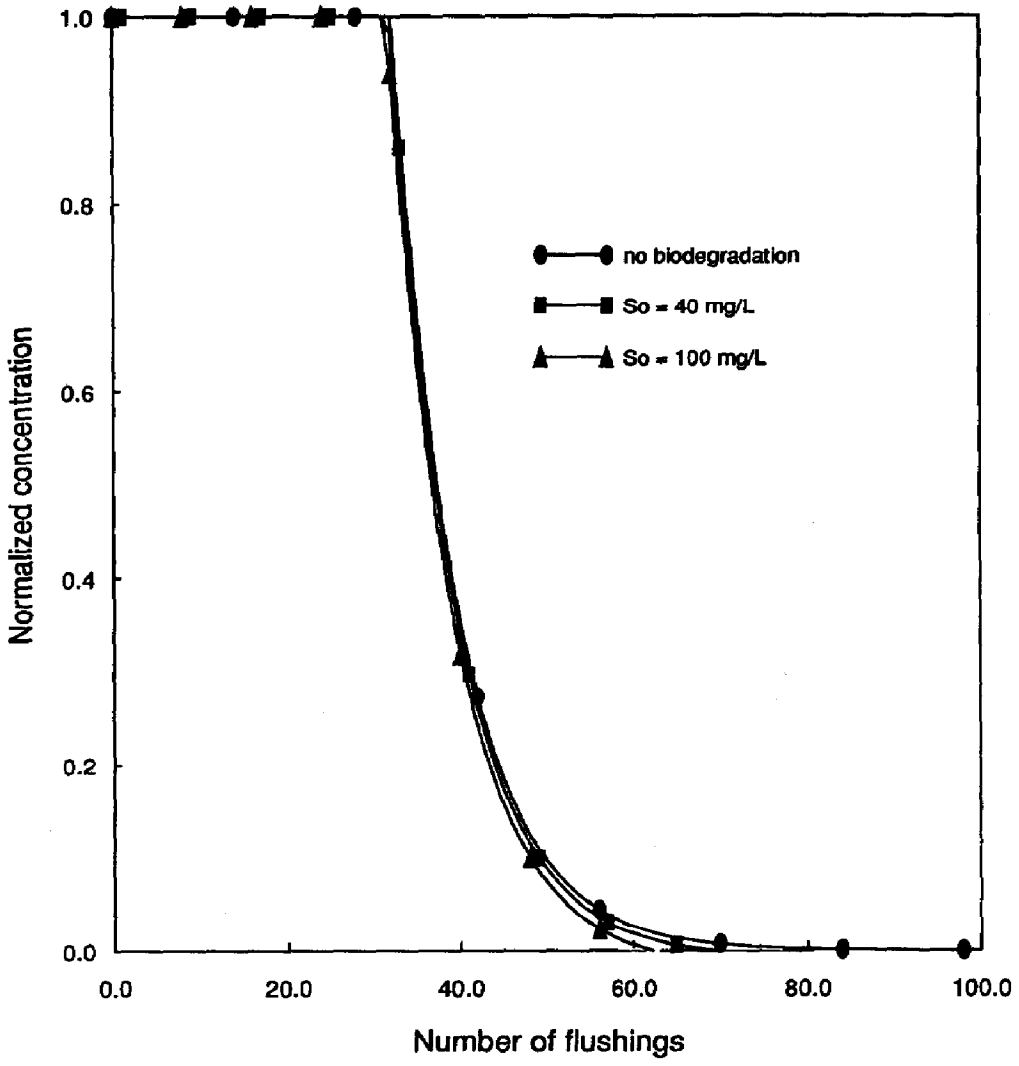

Fig. 4. Effectiveness of biodegradation in remediating a site contaminated with benzene for different inlet oxygen concentrations; the NAPL initially occupies 6% of the pore volume in the saturated zone.

can be supplied by adding water saturated with pure oxygen while that of 100 mg/l can be provided by adding hydrogen peroxide into the saturated zone. The case with 100 mg/l represents an upper limit at which oxygen can be supplied effectively. Some authors suggest that H_2O_2 may not be fully utilized [11, 12] while others have reported microbial toxicity at 100 mg/l [13]. Bioremediation is not significant in the initial phase of the clean up since benzene is mainly removed from the aquifer by the pump-and-treat scheme owing to its relatively high solubility in the aqueous phase (1780 mg/l). Bioremediation, however, plays an important role for the complete site remediation because it extirpates the trace contaminants exhibiting tailing when removed only by flushing. This can be readily discerned in Fig. 5, which is a magnification of the results given in Fig. 4 in the range between 50 and 110 flushings. The

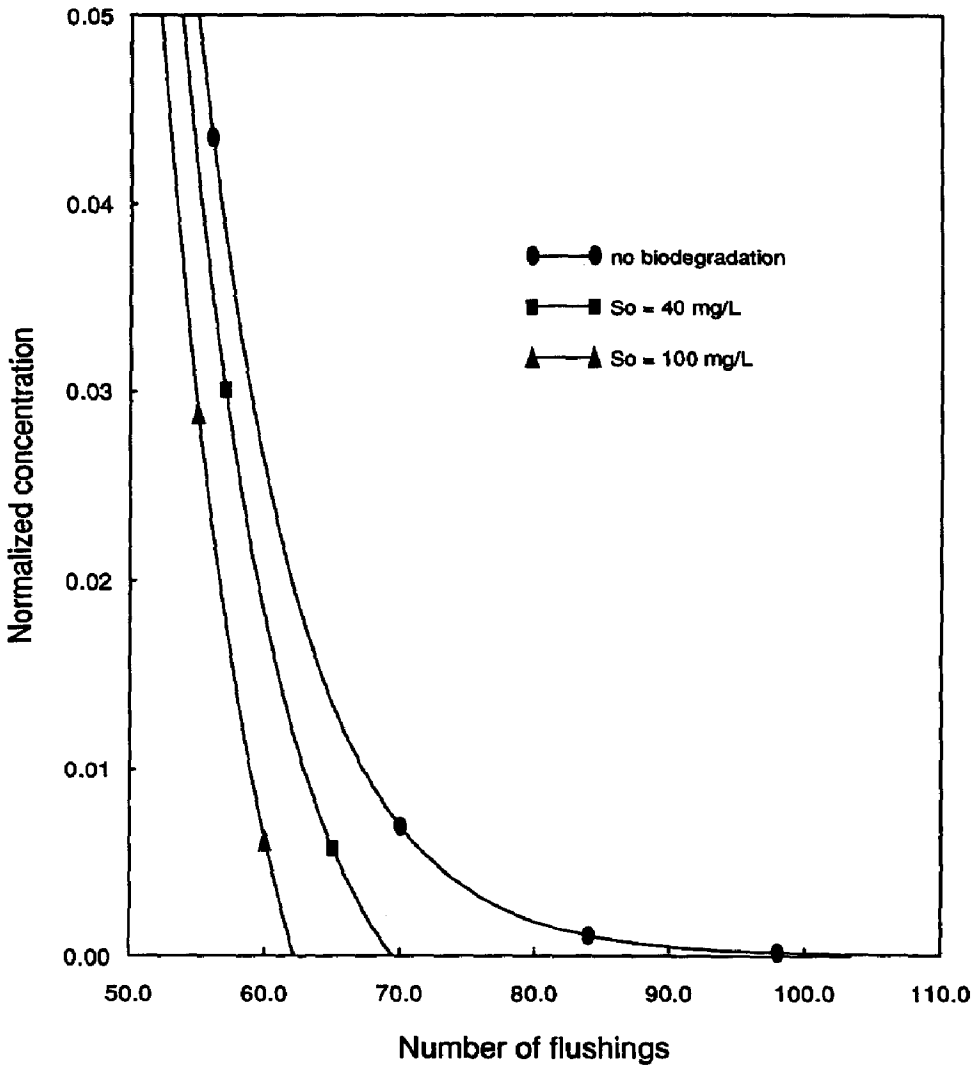

Fig. 5. Effectiveness of biodegradation in remediating a site contaminated with benzene in the range of 50–110 flushings; the NAPL initially occupies 6% of the pore volume in the saturated zone.

usefulness of bioremediation for the final 'polishing' of the contaminant is noticeable in Fig. 5. This fact is corroborated by the results of the simulations for the two inlet oxygen concentrations of 8 and 40 mg/l, and three initial NAPL saturations of 2, 5 and 10%; see Table 3.

Fig. 6 illustrates the effectiveness of biodegradation in remediating a site contaminated with the NAPL of xylene initially occupying 6% of the pore volume in the saturated zone with an inlet oxygen concentration of 100 mg/l. In this scenario, biodegradation does accelerate the process of removal of the contaminant out of the aquifer. It appears that almost complete remediation is achieved in the aquifer in approximately 320 flushings by the biodegradation aided, pump-and-treat scheme as opposed to approximately 500 flushings when only the conventional pump-and-treat

Table 3
Number of flushings required for remediating the sites contaminated by selected organic compounds for three values of the NAPL saturation and three values of the inlet oxygen concentration

Initial NAPL saturation		2%			5%			10%		
Inlet oxygen level (mg/l)		0[a]	8	40	0	8	40	0	8	40
Solute	Final conc. (ppb)	Number of flushings								
Benzene	1	121	61	49	137	77	65	164	104	92
	10	104	61	49	120	77	65	147	104	92
	100	86	61	49	102	77	65	129	104	92
Toluene	1	208	105	83	259	155	133	347	243	219
	10	178	105	83	229	155	133	317	243	219
	100	143	105	83	198	155	133	286	243	219
Xylene	1	328	186	152	494	350	308	785	636	579
	10	286	186	152	453	350	308	743	636	579
	100	244	186	152	411	350	308	701	636	579
Ethylbenzene	1	282	174	146	461	350	312	772	656	601
	10	250	174	146	429	350	312	740	656	601
	100	219	174	146	397	350	312	708	656	601
TCE	1	160	70	54	202	111	93	274	182	161
	10	138	70	54	180	111	93	252	182	161
	100	117	70	54	158	111	93	230	182	161

[a] An inlet oxygen concentration of zero corresponds to the case without biodegradation.

methodology is applied. Fig. 7 is similar to Figs. 4 and 6, with the contaminant modeled being trichloroethylene. Again, it indicates that bioremediation facilitates the attenuation of the tailing period and removal of the contaminant.

Fig. 8 depicts the effectiveness of biodegradation in remediating a site contaminated with phenanthrene. Phenanthrene, a component in a multicomponent NAPL such as creosote, is one of the most persistent organic compounds in the subsurface because of its extremely low solubility (1 mg/l). Owing to its extremely high melting point (approximately 100 °C), phenanthrene is a solid at room temperature. Strictly speaking, therefore, it cannot be categorized as a NAPL. It is, however, worthwhile to examine its dissolution and subsequent biodegradation because these processes are similar to those of the NAPLs. The initial NAPL saturation of phenanthrene has been taken to be 1% such that the role of bioremediation can be illustrated in a reasonable number of flushings. Without biodegradation, almost 97% of phenanthrene remains in the aquifer even after 400 flushings. With the stimulation of the microbes by injecting oxygen dissolved in water (10 mg/l), the mass fraction of phenanthrene remaining in the aquifer decreases to 87%. If the inlet oxygen level is maintained by hydrogen peroxide at 100 mg/l, all the phenanthrene disappears in 400

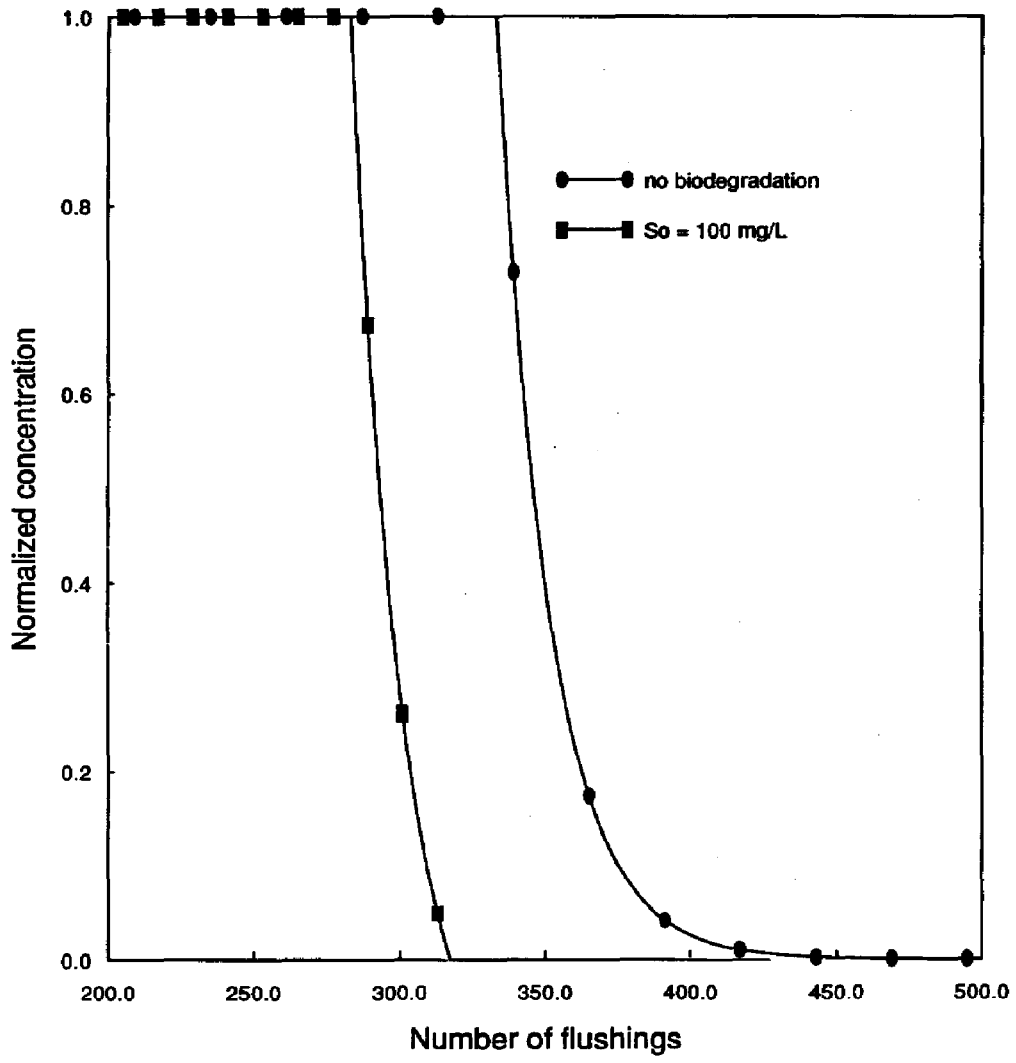

Fig. 6. Effectiveness of biodegradation in remediating a site contaminated with xylene in the range of 200–500 flushings; the NAPL initially occupies 6% of the pore volume in the saturated zone.

flushings. Since the amount of phenanthrene oxidized is directly proportional to the oxygen supplied, no tail appears in Fig. 8.

If the desired goal is to reduce the aqueous phase concentration of the contaminant to below drinking water standards, then bioremediation can play an effective role in decreasing the remediation time. Table 3 summarizes the calculated results for benzene, toluene, ethylbenzene, xylene, and trichloroethylene. Three final concentrations, namely 1, 10 and 100 ppb, and three initial NAPL saturations of 2%, 5% and 10% have been considered. In addition, the simulation has been performed for three inlet oxygen concentrations of 0, 8 and 40 mg/l. Table 3 shows that bioremediation does indeed decrease the required number of flushings considerably, as compared to the pump-and-treat mechanism alone, for achieving drinking water standards. Since

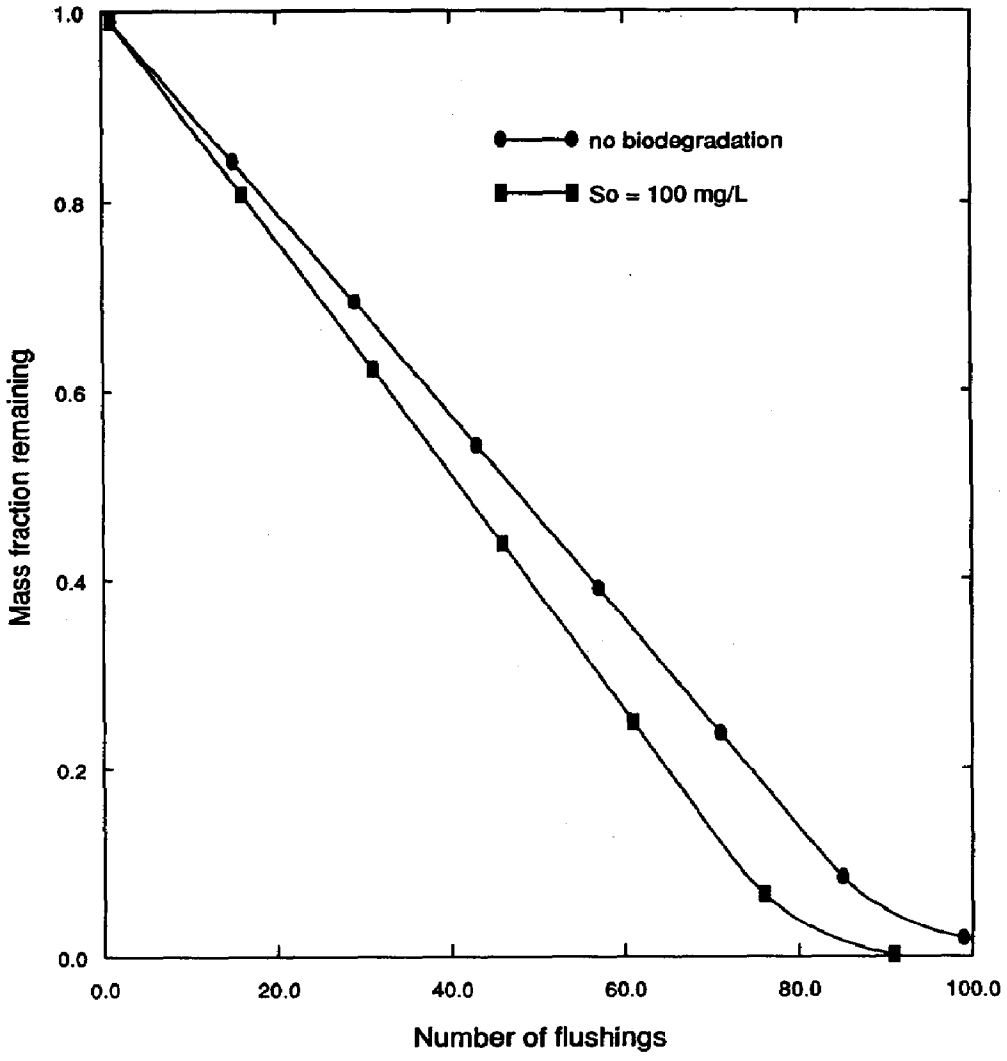

Fig. 7. Effectiveness of biodegradation in remediating a site contaminated with TCE; the NAPL initially occupies 6% of the pore volume in the saturated zone.

bio-oxidation has been assumed to be oxygen-limited, the number of flushings required for achieving a final concentration of 1, 10 or 100 ppb remains invariant for a particular inlet oxygen concentration fed to the aquifer. An inlet oxygen concentration of 8 or 40 mg/l is sufficient to reduce the contaminant concentration to zero during a particular flushing.

Phenanthrene has not been included in Table 3 because of the enormous number of flushings required for its remediation. A sample calculation has shown that it takes 6968 flushings to lower the concentration of phenanthrene, initially present at 2% saturation, to 100 ppb with an inlet oxygen concentration of 8 mg/l. In the absence of bioremediation, the desired level of 100 ppb cannot be attained even after 8000 flushings.

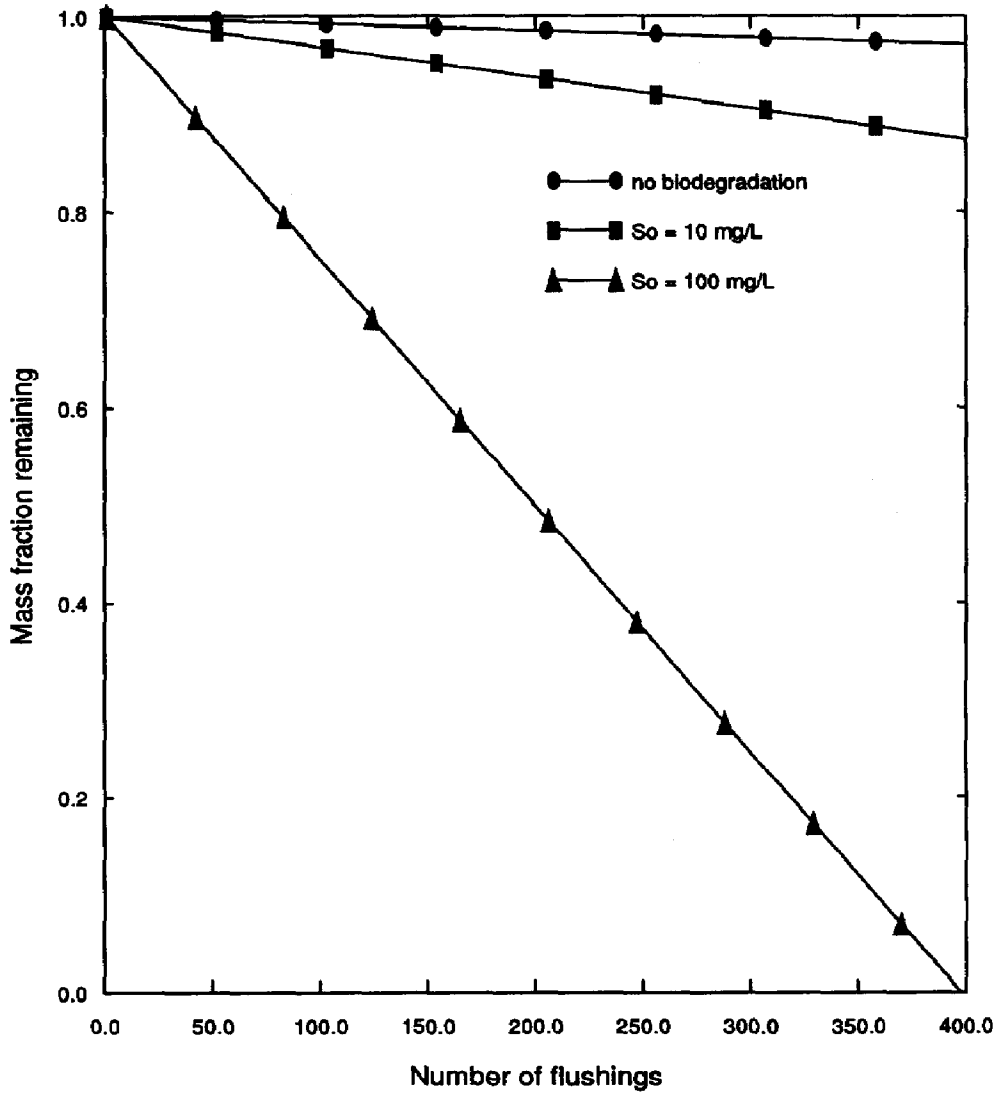

Fig. 8. Effectiveness of biodegradation in remediating a site contaminated with phenanthrene; the NAPL initially occupies 1% of the pore volume in the saturated zone.

Numerous simplifying assumptions have been made in developing the proposed model. The model assumes a homogeneous porous media in which idealized Darcian flow takes place in NAPL containing pores. In reality, however, by-passing of the aqueous phase might occur around the NAPL contaminated area due to heterogeneities or permeability differences. The flow through the contaminated region is assumed sufficiently slow to allow for phase and reaction equilibria to be approached. Contaminant dissolution from trapped ganglia of the NAPL into groundwater is often mass transfer limited [27–30]. As a consequence of the non-equilibrium, the aqueous phase contaminant concentration is less than the solubility limit. The rate of dissolution of immiscible liquid into the aqueous phase is also dependent on the pore

water velocity. Increasing this velocity enhances the dissolution rate and the flushing rate; at higher velocities, non-equilibrium conditions are expected to be encountered [31]. This model does not take into consideration the removal of NAPL droplets in ground water; this is a fair assumption when the trapped NAPL droplets exist in residual saturation. The present model also assumes local equilibrium for sorption/desorption processes. Nevertheless, some researchers in recent years have revealed that adsorption and desorption of organic solutes by aquifer materials may be rate limited. The rate-limiting mechanism could be hindered diffusion within the sorbent matrix [32], or slow diffusion of the solute through regions containing immobile water [33]. In field situations, intra-particle diffusion and sorption may limit the rate of biodegradation of a contaminant [34]. The rate of biodegradation in an aqueous solution may also be controlled by the rate of oxygen transfer, the contaminant concentration or the biochemical reaction rate [35]. Finally, the proposed model neglects any microbial toxicity to the microorganisms due to the presence of the NAPLs.

The non-equilibrium conditions further prolong the tailing behavior and result in delayed flushing of the contaminant. The rate of each flushing and the number of flushings per day depend on the soil characteristics and physical system design. Since considerable information is available on the mass transfer coefficients [28–30, 36, 37], diffusion coefficients [38, 39], and biodegradation rates [22, 40], it is possible to examine the appropriateness of the assumptions for various applications. When non-equilibrium conditions are encountered at regular flushing rates, the technique of pulsed pumping can be utilized. Pulsed operation is the cycling of the extraction or injection wells on and off in active and resting phases. The resting phase allows sufficient time for equilibrium concentrations to be reached in local ground water. The resting phase is followed by the active phase in which the contaminated ground water is removed at the maximum possible concentration. Keely [41] discusses certain design aspects of pulsed pumping operation. Another way to enhance the performance of pump-and-treat technology is through chemical solubility enhancement by surfactants which tend to decrease the interfacial tension between water and NAPL and increase the aqueous phase concentrations of the organic compounds. Palmer and Fish [42] provide a detailed discussion of chemical enhancement techniques. These methods are important for compounds with very low solubility, such as phenanthrene.

5. Conclusions

The results of the present work show that bioremediation can play a significant role in remediating sites contaminated by non-aqueous phase liquids. The importance of bioremediation is illustrated for attaining concentrations close to the drinking water standards for various contaminants. Bioremediation can serve as a 'polishing step' to eliminate contaminants not completely removed through the flushing process. Numerous simplifying assumptions have been made in developing the proposed model. The most important among them are equilibrium sorption, dissolution and

biodegradation, no substrate toxicity, homogenous and isotropic porous media, and idealized Darcian flow in NAPL containing pores. These assumptions enable the model to provide a simplified conceptual view of the site remediation of selected organic contaminants. The required number of flushings are expected to be larger than the values reported here. This model can be thought of as providing a useful upper bound with respect to the efficiency of bioremediation aided pump-and-treat technology. The model is simple and can be readily calculated on a microcomputer.

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