

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

II. Multi-component systems

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Abstract

Environmental contaminants are frequently encountered as mixtures of non-aqueous phase liquids (NAPLs). The dissolution of organic mixtures from the aquifer has been examined with and without biodegradation. Various physical processes involved have been quantified based on the assumptions that liquid–liquid and sorption equilibria are established at the beginning of each flushing; oxygen required for biochemical oxidation is completely consumed by the end of each flushing; and the rate of biochemical oxidation obeys the Monod kinetics for a multi-substrate system, characterized by an oxygen utilization factor. The mass fraction of any component remaining in the aquifer, its aqueous concentration, and the composition of the NAPL have been obtained as functions of the number of flushings (volume of the flushing solution/volume of the aqueous-phase voids). The results of the simulation with the model demonstrate that highly soluble components of the NAPL are mainly removed by the pump-and-treat mechanism while the components of extremely low solubility are unavailable to the microbes as substrates in a multi-component scenario. Bioremediation, however, transforms a significant proportion of the low solubility compounds after the more soluble components have been removed from the aquifer. The results also demonstrate that the rate of removal of compounds is retarded by the inclusion of a non-soluble component in the mixture.

1. Introduction

The dissolution of multi-component organic solvents has been investigated by many researchers. Burriss and MacIntyre [1] have studied the water solubility behavior of binary hydrocarbon mixtures. Various aspects of solubility of organic mixtures

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have been discussed by Banerjee [2] and Shiu et al. [3]. Mackay et al. [4] have presented the results of their theoretical and experimental studies on the equilibria and kinetics of the NAPL dissolution in groundwater. Dissolution of organic compounds from gasoline [5], diesel fuel [6] and coal tar [7] has also been investigated. Nevertheless, relatively little has been done on biodegradation of mixtures. Some experimental results regarding the biodegradation of organic mixtures have been presented by Mosteller and Reardon [8]. Multi-component solute systems also give rise to the concept of antagonistic or synergistic interactions between the solutes and the solid and aqueous phases [9]. These interactions have been found to result in competitive or cooperative sorption processes by Karickhoff et al. [10], Chio et al. [11], and Brusseau [12].

The dissolution and biodegradation of a single component NAPL is discussed in a companion article [13] by us. The persistence of single component organic compounds thus studied has limited application in field conditions where environmental contaminants are mostly present as mixtures. The behavior of a compound in any mixture is far from that predicted from the pure component data. The model proposed here discusses the dissolution and biodegradation of a mixture of immiscible liquids under the conditions of equilibrium dissolution and biodegradation. Any antagonistic or synergistic interactions between the solutes and the solid and aqueous phases are neglected in our model owing to relatively low concentrations of solutes in the aqueous phase.

2. Model description

The proposed model addresses the applicability of biodegradation aided, pump-and-treat technology for remediating aquifers contaminated by a mixture of NAPLs. Similar to the treatment for single component NAPLs [13], this model assumes that the residence time of the soil water in each flushing is sufficiently large so that all processes attain equilibrium. This includes sorption to solid surfaces, dissolution of the NAPL, and biochemical oxidation.

2.1. Dissolution equilibrium

If a liquid solute is present in equilibrium with its aqueous solution at constant temperature and pressure, the solute's chemical potential or fugacity is equal in both phases. According to the definition of fugacity, f_i [14],

$$f_i = x_{iN}Y_{iN}f_R = x_{iW}Y_{iW}f_R. \quad (1)$$

Raoult's law activity coefficients, Y_{iN} and Y_{iW} , characterize the degree of non-ideality experienced by the organic compound in the NAPL and aqueous phase; Y 's become equal to unity as the mole fractions, x_{iN} and x_{iW} , approach unity. When solute i is pure, Eq. (1) reduces to

$$x_{iW}^p = (x_{iN}^p Y_{iN}^p) / Y_{iW}^p. \quad (2)$$

Since the organic phase comprises a pure liquid, both x_{iN} and Y_{iN} are unity; therefore,

$$x_{iW}^p = 1/Y_{iW}^p. \quad (3)$$

For a mixture of compounds, Eq. (1) gives

$$x_{iW} = (x_{iN}Y_{iN})/Y_{iW}. \quad (4)$$

The saturation concentration of component i as a function of its solubility can be obtained from Eqs. (3) and (4) as

$$(x_{iW}/x_{iW}^p) = (x_{iN}Y_{iN}Y_{iW}^p)/Y_{iW}. \quad (5)$$

For convenience, Eq. (5) can be expressed as the concentration ratio

$$(C_{iW}/S_i) = (x_{iN}Y_{iN}Y_{iW}^p)/Y_{iW}. \quad (6)$$

For sparingly soluble organic substances, the activity coefficient in the aqueous phase can be assumed to remain constant because the logarithm of Y_{iW} varies approximately in proportion to $(1 - x_{iW})^2$ which is essentially constant at low values of x_{iW} [15]. In other words, assuming Y_{iW} to be constant implies that solute–solute interactions are negligible in comparison with solute–water interactions due to high dilution.

In the organic phase, Y_{iN} is assumed to be unity; this is equivalent to regarding the organic phase to be ideal. For systems of chemically similar compounds such as isomers or members of a homologous series, e.g. paraffin hydrocarbons, this is a valid assumption. With these simplifications, Eq. (6) becomes

$$(C_{iW}/S_i) = x_{iN}. \quad (7)$$

If the weight fraction of component i in a multi-component NAPL is represented by w_i , then

$$x_{iN} = w_i(M_{\text{avg}}/M_i). \quad (8)$$

Substituting Eq. (8) into Eq. (7), we obtain

$$C_{iW} = S_i w_i (M_{\text{avg}}/M_i). \quad (9)$$

2.2. Dissolution accompanied by biodegradation of the multi-component NAPL

Equilibrium dissolution accompanied by biodegradation of the multi-component NAPL can be modeled similar to single component systems [13]. Since the more soluble components of the NAPL will dissolve faster than the less soluble ones, the weight fraction of the components in the NAPL will change as flushings progress. This will result in changes in the average molecular weight and density of the NAPL. In what follows, for simplicity, the average molecular weight, M_{avg} , and density, ρ_{avg} , of the NAPL are assumed to remain constant during a particular flushing. The values computed at the end of the flushing are used in the subsequent flushing.

The initial condition for the present model is specified by the fact that the multi-component NAPL of known composition exists in equilibrium with the aqueous

phase. The first flushing simply involves flushing out the equilibrated aqueous phase. The total initial concentration of component i , $C_{iT,1}$, in the saturated water, soil, and NAPL is

$$C_{iT,1} = C_{iW,1}\varepsilon_{W,1} + C_{iS,1}\rho_B + \rho_{Navg,1}\varepsilon_{N,1}W_{i,1}. \quad (10)$$

The last subscript for the porosity, concentration, or weight fraction indicates the number of flushing cycles. The concentration of component i on the solid phase, C_{iS} , can be calculated from the linear isotherm

$$C_{iS,1} = K_{Di}C_{iW,1} = K_{Di}S_iW_{i,1}(M_{avg,1}/M_i). \quad (11)$$

The mass fraction of component i removed from the aquifer by the flushing of the aqueous phase, $MF_{iO,1}$, is given by

$$MF_{iO,1} = \frac{C_{iW,1}\varepsilon_{W,1}}{C_{iW,1}\varepsilon_{W,1} + C_{iS,1}\rho_B + \rho_{Navg,1}\varepsilon_{N,1}W_{i,1}}. \quad (12)$$

The mass fraction of component i remaining in the aquifer after the end of the first flushing, $MF_{iR,1}$, is

$$MF_{iR,1} = 1 - MF_{iO,1}. \quad (13)$$

From the second flushing cycle onwards, oxygen enriched water is injected into the aquifer which stimulates the aerobic biodegradation of the contaminants by the microbes. Biodegradation causes a decrease in the aqueous concentration of the contaminants, thereby promoting further dissolution of the NAPL. Biodegradation and dissolution result in shrinkage of the NAPL blobs and change in the weight fraction of components in the NAPL. Thereafter, the average molecular weight and average density of the NAPL for any P th flushing are computed by the following equations.

$$M_{avg,P} = \sum M_i W_{i,P-1}, \quad (14)$$

$$\rho_{Navg,P} = \sum \rho_{Ni} W_{i,P-1}. \quad (15)$$

The mass balance of component i for the second flushing yields

$$\begin{aligned} & \rho_{Navg,1} W_{i,1} \varepsilon_{N,1} + C_{iS,1} \rho_B \\ &= \rho_{Navg,2} W_{i,2} \varepsilon_{N,2} + C_{iW,2} \varepsilon_{W,2} + \frac{S_{O\varepsilon_{W,1}} \beta_{i,1}}{Y_i} + C_{iS,2} \rho_B. \end{aligned} \quad (16)$$

The consumption of oxygen by the microbes for biodegrading component i depends on the concentration of component i in the aqueous phase in accordance with the Monod kinetic model for a multi-substrate system, i.e.,

$$\frac{dC_{iW}}{dt} = - \frac{\mu_{max} C_{iW} X}{Y_S (K_S + \sum C_{iW})}. \quad (17)$$

This equation indicates that in a multi-substrate system, the rate of degradation of a substrate is a function of its aqueous concentration. For the P th flushing, the oxygen

utilization factor, $\beta_{i,P}$, is defined as

$$\beta_{i,P} = C_{iW,P} / \left(\sum C_{iW,P} \right). \quad (18)$$

Obviously,

$$\sum \beta_{i,P} = 1.0. \quad (19)$$

A mass balance equation similar to Eq. (16) can be written for each component in the NAPL, thereby giving us a set of n equations with $(n + 2)$ unknowns in the form of $w_{1,2}, w_{2,2}, \dots, w_{n,2}, \varepsilon_{W,2}$, and $\varepsilon_{N,2}$. Since the total porosity of the aquifer, ε_T , remains constant, the NAPL porosity, $\varepsilon_{N,2}$, can be expressed in terms of the aqueous phase porosity, $\varepsilon_{W,2}$, by resorting to the relation

$$\varepsilon_{N,2} = \varepsilon_T - \varepsilon_{W,2}. \quad (20)$$

The fact that the sum of the weight fractions of all components in the NAPL is unity yields

$$\sum w_{i,2} = 1.0. \quad (21)$$

Eq. (16), written for each of the n components, and Eqs. (20) and (21) comprise a set of $(n + 2)$ equations with $(n + 2)$ unknowns. The system of equations can be solved numerically for the new weight fractions and porosity values. The mass fraction of component i removed in the second flushing is

$$MF_{iO,2} = \frac{C_{iW,2} \varepsilon_{W,2} + (S_O/Y_i) \beta_{i,1} \varepsilon_{W,1}}{C_{iS,1} \rho_B + \rho_{Navg,1} w_{i,1} \varepsilon_{N,1}}. \quad (22)$$

Thus, the overall mass fraction of component i remaining in the aquifer at the end of the second flushing, $MF_{iR,2}$, is

$$MF_{iR,2} = (1 - MF_{iO,2}) MF_{iR,1}. \quad (23)$$

The above analysis remains unchanged in subsequent flushings of the aquifer until NAPL disappears in the Q th flushing.

2.3. Disappearance of the NAPL

Due to recursive biodegradation and flushing, the volume of the NAPL shrinks continuously and finally disappears in the Q th flushing, i.e., $\varepsilon_{N,Q} = 0$ and $\varepsilon_{W,Q} = \varepsilon_T$. C_{iW} can be evaluated through a mass balance on component i as follows:

$$\begin{aligned} & C_{iS,Q-1} \rho_B + \rho_{Navg,Q-1} \varepsilon_{N,Q-1} w_{i,Q-1} \\ &= C_{iS,Q} \rho_B + \frac{S_O \varepsilon_{W,Q-1} \beta_{i,Q-1}}{Y_i} + C_{iW,Q} \varepsilon_{W,Q}. \end{aligned} \quad (24)$$

Solving Eq. (24) yields a value of $C_{iW,Q}$ as

$$C_{iW,Q} = \frac{[K_{Di}S_i\rho_B w_{i,Q-1}(M_{avg,Q-1}/M_i)] + [\rho_{Navg,Q-1} w_{i,Q-1} \varepsilon_{N,Q-1}] - [S_O \varepsilon_{W,Q-1} \beta_{i,Q-1}/Y_i]}{(K_{Di}\rho_B) + \varepsilon_T} \quad (25)$$

The mass fraction of component i removed in the Q th flushing is

$$MF_{iO,Q} = \frac{(C_{iW,Q} \varepsilon_T) + S_O \varepsilon_{W,Q-1} \beta_{i,Q-1}/Y_i}{(K_{Di}S_i\rho_B w_{i,Q-1}(M_{avg,Q-1}/M_i) + (\rho_{Navg,Q-1} w_{i,Q-1} \varepsilon_{N,Q-1}))} \quad (26)$$

The overall mass fraction of component i remaining in the aquifer after the Q th flushing is then

$$MF_{iR,Q} = (1 - MF_{iO,Q}) MF_{iR,Q-1} \quad (27)$$

For any Z th flushing ($Z > Q$), the following equations are valid until the aqueous concentration of contaminant i vanishes or decreases to a safe level.

$$C_{iW,Z} = \frac{C_{iS,Z-1} \rho_B - (S_O \beta_{i,Z-1}/Y_i) \varepsilon_T}{K_D \rho_B + \varepsilon_T} \quad (28)$$

$$MF_{iO,Z} = \frac{C_{iW,Z} \varepsilon_T + (S_O \beta_{i,Z-1}/Y_i) \varepsilon_T}{C_{iS,Z-1} \rho_B} \quad (29)$$

$$MF_{iR,Z} = (1 - MF_{iO,Z}) MF_{iR,Z-1} \quad (30)$$

$$\beta_{i,Z} = C_{iW,Z} / (\sum C_{iW,Z}) \quad (31)$$

3. Model simulation

Two different mixtures of organic compounds are considered. One is a mixture of benzene, toluene, ethylbenzene, and xylene, i.e., the BTEX NAPL, and the other is a mixture of benzene, toluene, ethylbenzene, xylene, and phenanthrene, i.e., the BTEXP NAPL. The former is often encountered at sites of gasoline spill, and the latter, at sites contaminated with coal tar and gasoline. Table 1 lists the parameter values chosen for the simulations, and Table 2 the representative properties of the

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 in soil, f_{OC}	0.03

Table 2

Values of density, normalized partition coefficient, solubility in water, yield coefficient, and molecular weight for each contaminant^a

Contaminant	ρ_N (gm/cm ³)	K_{OC} (l/Kg)	S_{HC} (mg/l)	Y_i	Molecular weight
Benzene	0.895	85	1780	3.076	78
Toluene	0.875	151	537	3.13	92
Ethylbenzene	0.874	158	152	3.47	106
Xylene	0.87	210	162	3.47	106
Phenanthrene	1.179	22908	1	2.96	178

^a Values taken from Knox et al. [16], Lyman et al. [17], and US EPA [18].

contaminants. The data for xylene are the values averaged over those for *o*-, *m*-, and *p*-xylene.

4. Results and discussion

The results of simulation are plotted in Figs. 1–5 for the BTEX NAPL and in Figs. 6–9 for the BTEXP NAPL. The symbols which are shown to identify the results for specific compounds represent simulated values.

The mass fractions of components in the BTEX NAPL remaining in the aquifer as well as the mass fractions removed are plotted as functions of the number of flushings in Fig. 1. The effectiveness of biodegradation in enhancing the remediation rates is illustrated by comparing the case with equilibrium dissolution with the case with equilibrium dissolution and biodegradation. The total initial NAPL porosity is assumed to be 0.03, which corresponds to 6% saturation since total soil porosity is 0.5; also, each component is assumed to occupy an equal initial weight fraction of 0.25 in the NAPL. An inlet oxygen concentration of 100 mg/l has been considered here; this can be provided by adding hydrogen peroxide into the saturated zone. Some authors report degassing of H₂O₂ [19, 20] while others have reported microbial toxicity at 100 mg/l [21]. Thus, 100 mg/l represents an upper limit at which oxygen can be supplied effectively. The effectiveness of biodegradation is more pronounced for components having lower solubilities, such as ethylbenzene and xylene; dissolution removes a much greater proportion of the higher solubility components, e.g., benzene and toluene, in comparison with biodegradation. Unlike the case for a single component system, the decrease in the mass fraction of a contaminant in the multi-component system is non-linear. The rate at which the contaminant mass is removed from the aquifer decreases for benzene and toluene and increases for ethylbenzene and xylene. This occurs because components with higher aqueous solubilities dissolve faster, thus leaving behind lower-solubility components in the NAPL. Hence, the weight fractions of the lower-solubility components increase, thereby increasing their aqueous phase concentrations. Accordingly, the rates of removal of the lower-solubility components increase as flushing progresses.

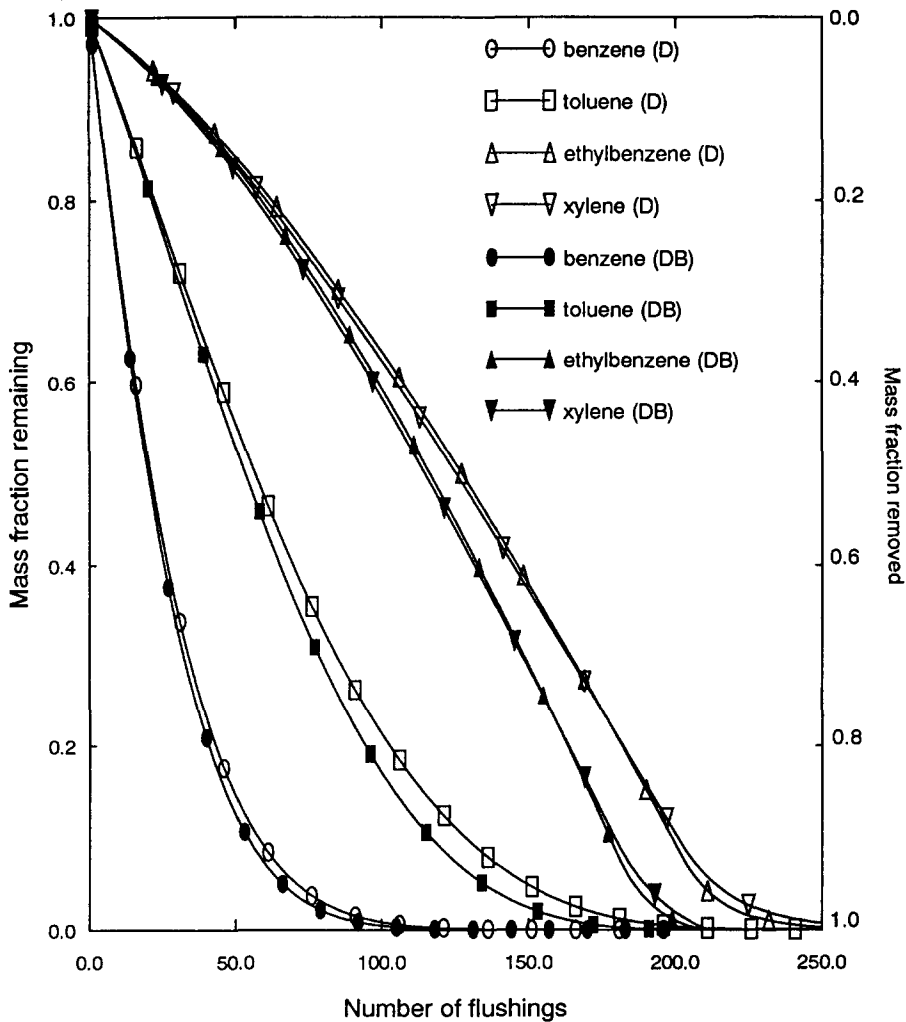


Fig. 1. Effectiveness of biodegradation in enhancing the remediation rates for an inlet oxygen concentration of 100 mg/l: D, dissolution only; DB, dissolution and biodegradation.

The variation of the weight fractions of the components in the NAPL is illustrated in Fig. 2. As expected, the weight fractions of ethylbenzene and xylene increase while the weight fractions of benzene and toluene decrease as the flushing progresses. The abscissa has data points only till flushing number 180 because the NAPL disappears at that point. The normalized aqueous concentration (the ratio of the aqueous concentration of the contaminant to its aqueous solubility when present as a pure component) is plotted as a function of the number of flushings in Fig. 3. The pattern of this figure is similar to that of Fig. 2 because the weight fraction of a component in the

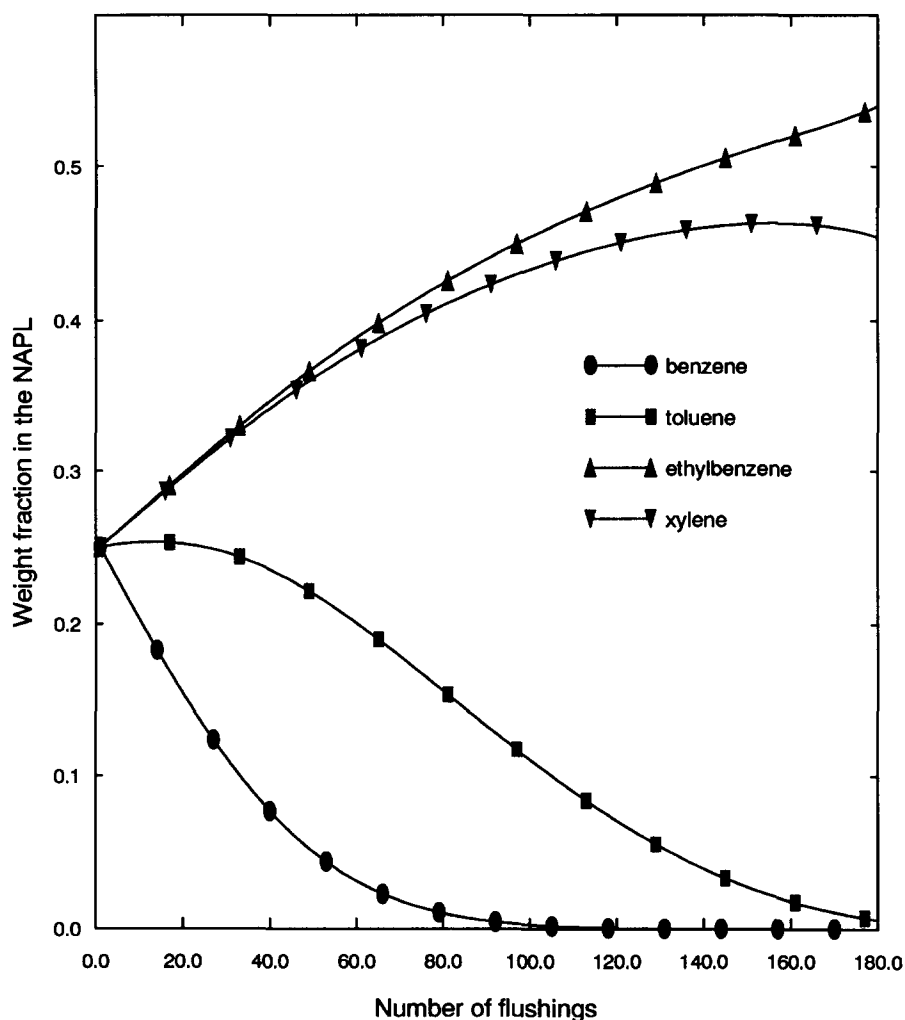


Fig. 2. Variation of the weight fractions of contaminants in the BTEX NAPL with the progress of dissolution accompanied by biodegradation for an inlet oxygen concentration of 100 mg/l.

NAPL governs its aqueous-phase concentration in accordance with Eq. (9). Hence, the aqueous phase concentrations of benzene and toluene decrease, while those of ethyl benzene and xylene increase until the NAPL disappears. After the NAPL disappears, tailing is exhibited by the contaminants, the extent of which is governed by the partition coefficients of the contaminants between the organic and aqueous phases. Since ethylbenzene and xylene have very similar partition coefficients, both exhibit similar behavior.

Fig. 4 compares the equilibrium dissolution and biodegradation of contaminants present in a multi-component system to those present as pure components. Two

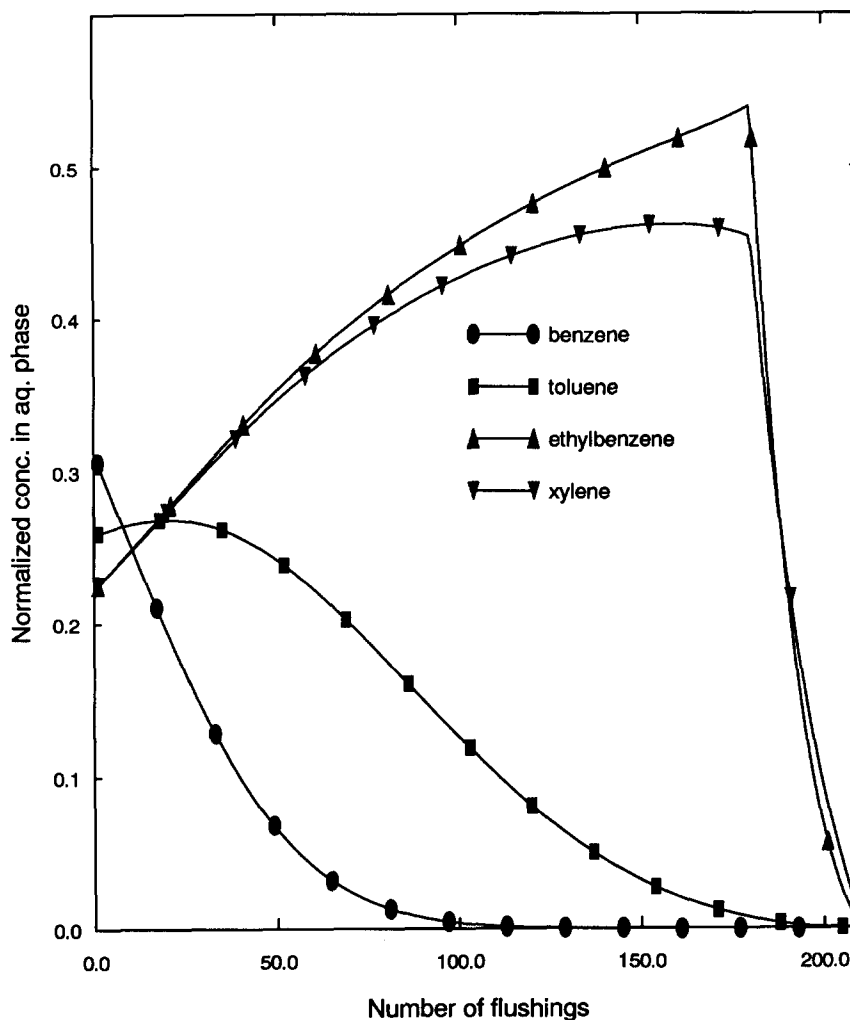


Fig. 3. Normalized aqueous concentrations of the components in the BTEX NAPL as functions of the number of flushings with the progress of equilibrium dissolution accompanied by biodegradation for an inlet oxygen concentration of 100 mg/l.

opposing factors are imposed in this illustration. Each pure component has been assigned an initial NAPL porosity of 0.03 which is equal to the porosity of the mixture. Thus, the initial mass of a component in pure form is four times its initial mass when it is present in the mixture. Each of the contaminants, however, can realize the maximum aqueous concentration when present as a pure component. The relative rate of removal of the contaminant in the two cases is thus dependent on which factor is predominant. Compounds with higher solubility, such as benzene and toluene, tend to disappear earlier when present in pure form, whereas compounds with lower

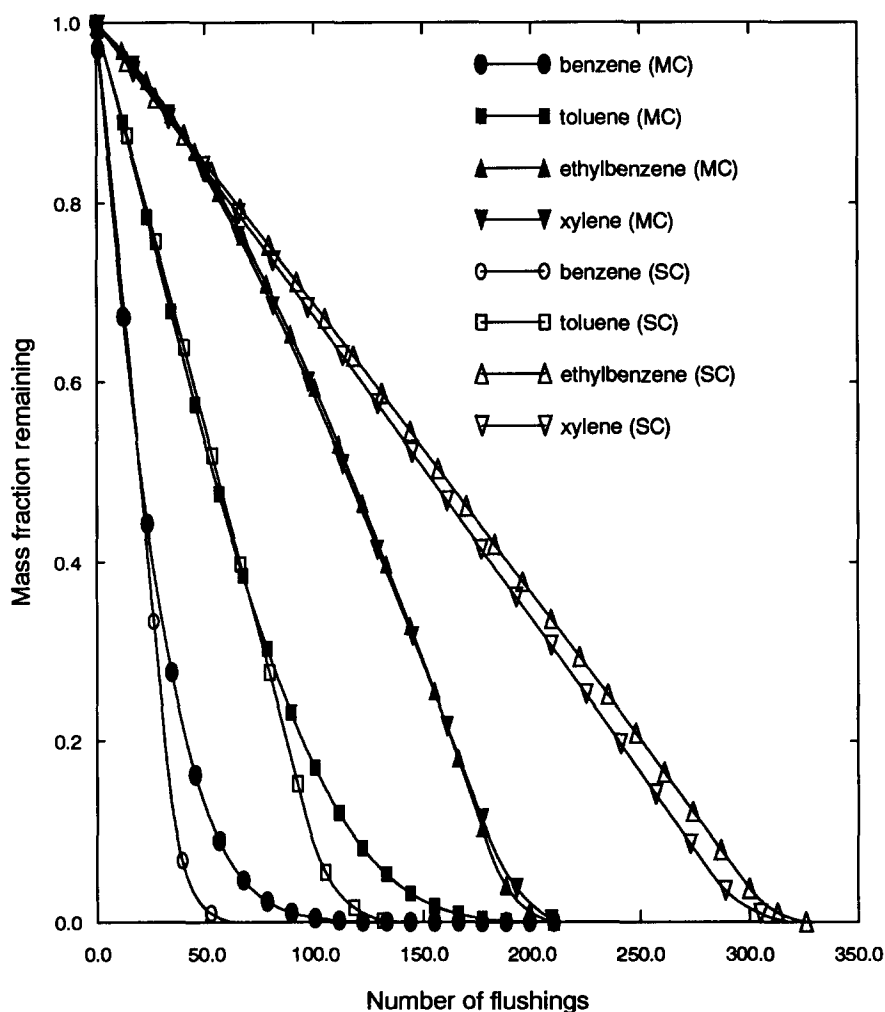


Fig. 4. Comparison of the rates of removal of the components in the BTEX NAPL with those of the respective components, each existing in pure form and initially occupying 6% of the void volume in the saturated zone ($\epsilon_{N,1} = 0.03$): MC, multi-component system; SC, single component system.

solubility, such as ethylbenzene and xylene, require fewer flushings when present in the multi-component NAPL. To equate the initial mass of each of the components in the two cases, the initial NAPL porosity of a pure component has been reduced by a factor of four in Fig. 5. Here, all the contaminants present as pure components disappear faster than when present in a multi-component NAPL.

As mentioned previously, Figs. 6–9 present the results for the BTEXP NAPL. Fig. 6 plots the mass fractions of various components of the NAPL remaining in the aquifer as functions of the number of flushings under the conditions of equilibrium

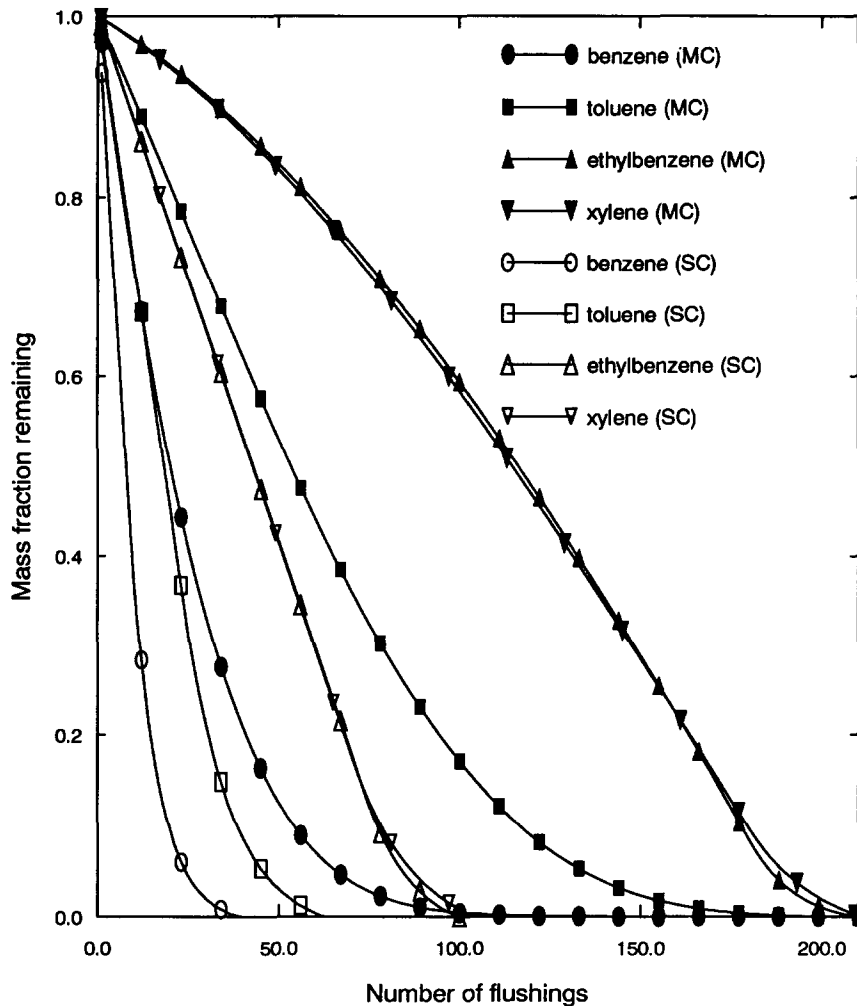


Fig. 5. Comparison of the rates of removal of the components in the BTEX NAPL with those of the respective components, each existing in pure form and initially occupying 1.5% of the void volume in the saturated zone ($\epsilon_{N,1} = 0.0075$): MC, multi-component system; SC, single component system.

dissolution and biodegradation. The total initial NAPL porosity is assumed to be 0.03, and each component is assumed to occupy an equal initial weight fraction of 0.2 in the NAPL. Again, an inlet oxygen concentration of 100 mg/l has been used for the simulation. While the rates of removal of benzene and toluene decrease with time, the rate of removal of phenanthrene increases progressively; however, the rates of removal of ethylbenzene and xylene first increase and then decrease. This phenomenon can be explained by resorting to Fig. 7 which plots the aqueous concentrations of individual components against the number of flushings. The weight fractions of benzene and

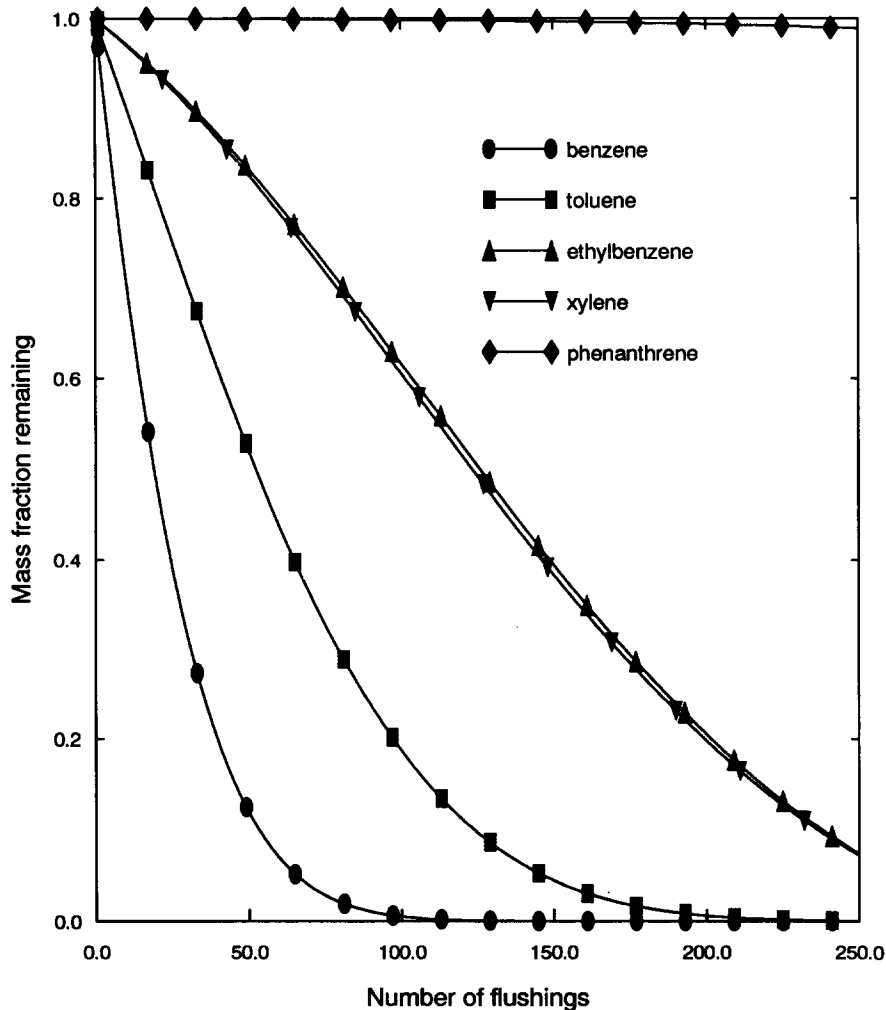


Fig. 6. Mass fractions of the components of the BTEXP NAPL remaining in the aquifer as a function of the number of flushings under the conditions of equilibrium dissolution accompanied by biodegradation for an inlet oxygen concentration of 100 mg/l.

toluene decrease continuously in the NAPL while the weight fraction of phenanthrene increases continuously in the NAPL owing to its extremely low solubility. Ethylbenzene and xylene, however, situate themselves between the two extremes. Their weight fractions first increase and then decrease. In accordance with Fig. 7, this leads to an increase followed by a decrease in the aqueous concentrations. Thus, the rates of removal of ethylbenzene and xylene vary as depicted in Fig. 6.

The rates of removal of contaminants in the BTEXP mixture are compared to those of the same components existing in the pure form in Fig. 8. Each pure component has

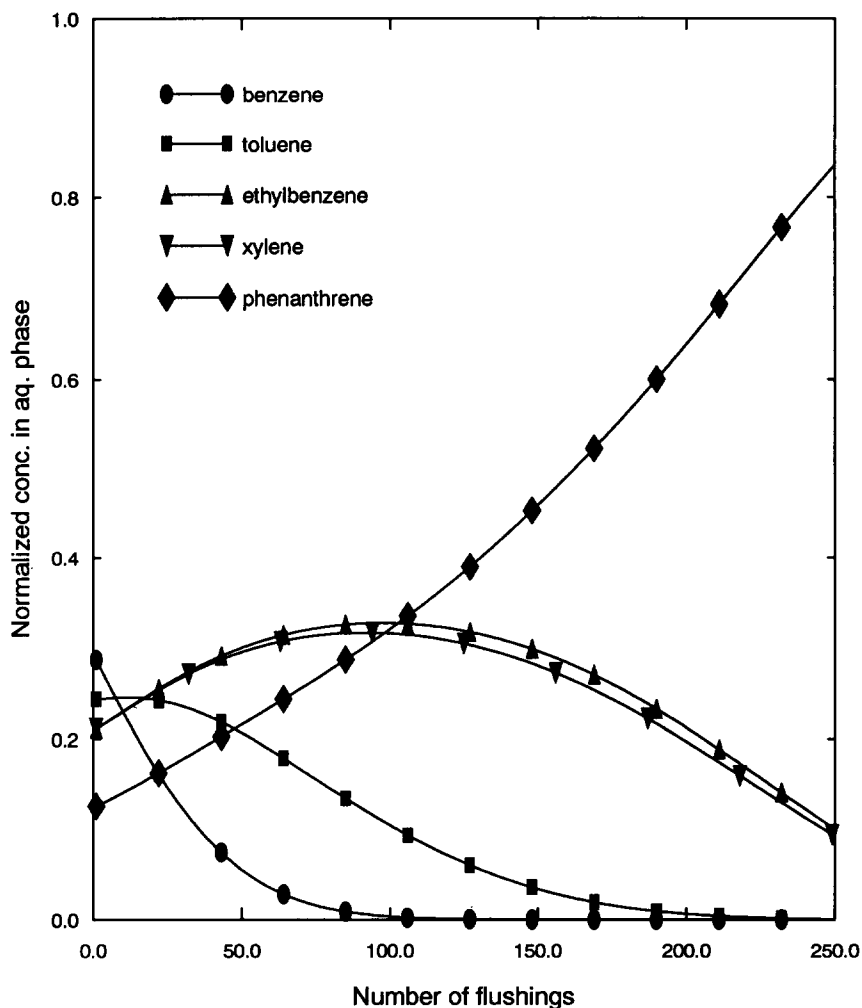


Fig. 7. Normalized aqueous concentrations of the components in the BTEXP NAPL as functions of the number of flushings with the progress of equilibrium dissolution accompanied by biodegradation for an inlet oxygen concentration of 100 mg/l.

been assigned an initial NAPL porosity of 0.03; thus, the initial mass of a contaminant in pure form is five times of that in the mixture. Again, benzene and toluene in pure form tend to disappear faster than those in the mixture, whereas the opposite is the case for ethylbenzene and xylene. The removal of phenanthrene has been depicted for the period when all other components are also present. During this period, pure phenanthrene disappears much faster than phenanthrene in the mixture. Naturally, all oxygen is consumed for biodegradation of phenanthrene in the absence of other compounds. In contrast, phenanthrene is hardly available when it coexists with other

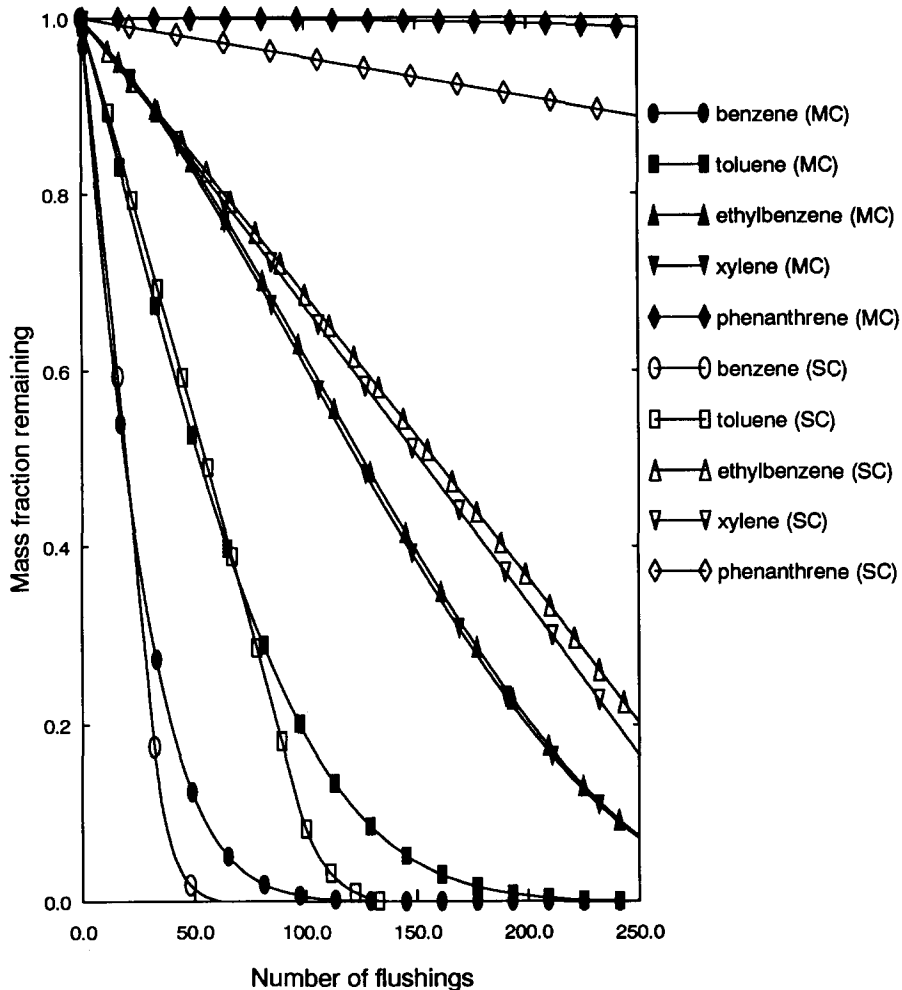


Fig. 8. Comparison of the rates of removal of the components in the BTEXP NAPL with those of the respective components, each existing in pure form and initially occupying 6% of the void volume in the saturated zone ($\epsilon_{N,1} = 0.03$): MC, multi-component system; SC, single component system.

components in a mixture owing to its extremely low concentration in the aqueous phase ($< 1 \text{ mg/l}$). Consequently, phenanthrene persists while the other compounds are being removed even when the inlet oxygen concentration is as high as 100 mg/l . However, after benzene, toluene, xylene, and ethylbenzene have been removed, the aquifer becomes a single-component system. In this scenario, biodegradation removes a substantial amount of phenanthrene from the aquifer. To illustrate the complete removal of phenanthrene in a reasonable number of flushings, Fig. 9 has been plotted with an initial NAPL porosity of 0.01. An inlet oxygen concentration has been set at

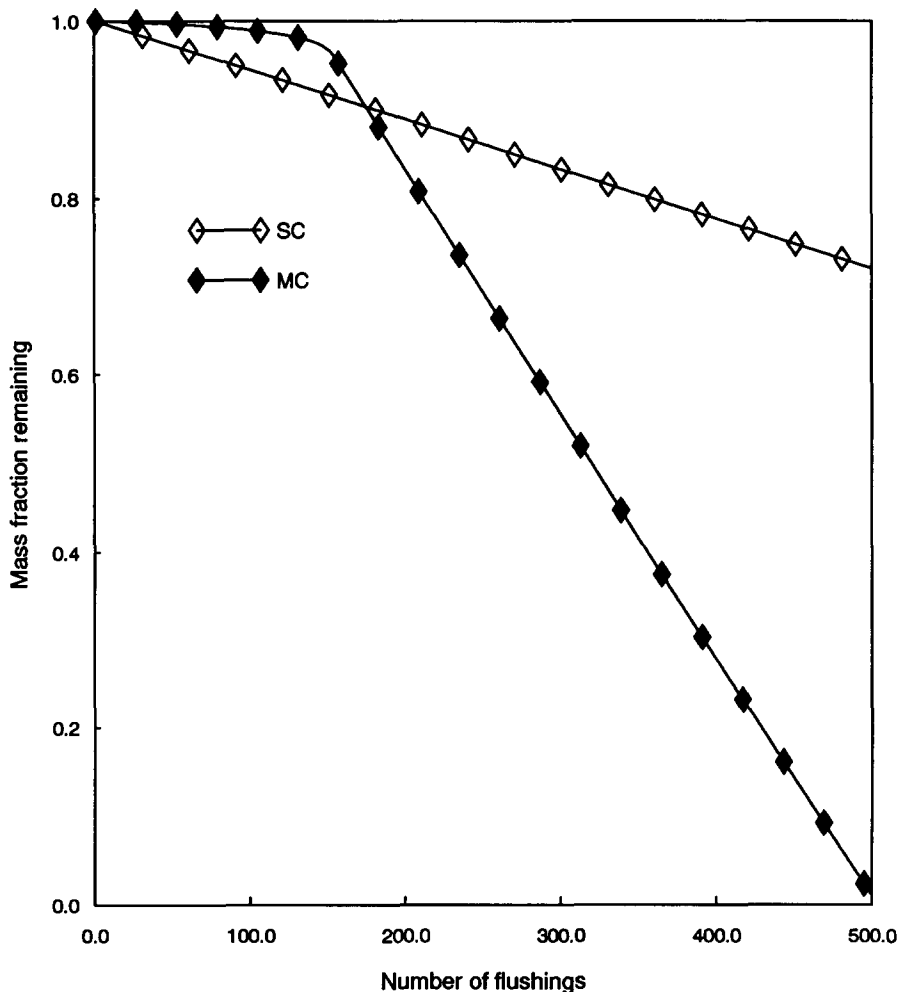


Fig. 9. Comparison of the rate of removal of phenanthrene in the BTEXP NAPL (MC) with that present in pure form (SC) for an inlet oxygen concentration of 40 mg/l; the NAPL occupies 2% of the void volume in the saturated zone ($\epsilon_{N,1} = 0.01$) in both cases (see Table 3).

40 mg/l in this simulation. This figure indicates that the final cleanup time for pure phenanthrene is longer than when it is present in a mixture.

Table 3 compares the number of flushings required to lower the aqueous concentration to 100 ppb when the contaminant exists in three different states, namely, as a pure component, in the BTEX NAPL, and in the BTEXP NAPL. The number of flushings have been calculated with and without the role of biodegradation. Benzene and toluene tend to disappear earlier when present as pure components while xylene and ethylbenzene disappear faster when present in a mixture. Nevertheless, the rates of

Table 3

Number of flushings required for site remediation of selected organic compounds for 2% NAPL saturation ($\epsilon_{N,1} = 0.01$) and three values of inlet oxygen concentration

Solute	Final conc. (ppb)	Pure component			BTEX ^a			BTEXP ^b		
		Inlet oxygen level (mg/l)								
		0 ^c	8	40	0	8	40	0	8	40
Benzene	100	86	61	49	90	88	84	99	98	91
Toluene	100	143	105	83	146	125	105	172	162	137
Ethylbenzene	100	244	186	152	158	131	107	259	207	154
Xylene	100	219	174	146	186	134	108	279	212	156
Phenanthrene	100	28 241	6968	1763	–	–	–	7686	1576	491

^a Mixture of equal initial amounts of benzene, toluene, ethylbenzene and xylene.

^b Mixture of equal initial amounts of benzene, toluene, ethylbenzene, xylene and phenanthrene.

^c An inlet oxygen concentration of zero corresponds to the case with no biodegradation.

removal of more soluble contaminants are greatly retarded by the inclusion of a component of extremely low solubility, e.g., phenanthrene, in the NAPL. Phenanthrene tends to disappear much faster when present in the BTEXP NAPL than when present as a single component because the initial starting mass of phenanthrene in the mixture is much lower. Finally, bioremediation appears to be the most important pathway for the removal of low solubility compounds from the aquifer.

Similar to the analysis for the single component NAPL systems, the results presented for the multi-component NAPLs are for an idealized situation where local phase equilibrium and complete biochemical oxidation have been assumed for each flushing. Contaminant dissolution from the trapped NAPL and desorption from the soil solids into the groundwater may be rate limited [22–26]. Also, the rate of biochemical oxidation in an aqueous solution may be controlled by the biochemical reaction rate [27]. Several other factors, such as heterogeneity in the porous media, nonuniform flow path, and microbial toxicity, if present, tend to prolong remediation times and must be taken into account in designing the system. The implications of the assumptions have been discussed in detail in a companion article [13].

5. Conclusions

The efficacy of the bioremediation aided pump-and-treat process in cleaning-up sites contaminated by a mixture of NAPLs has been analyzed by a relatively simple mass balance approach. The results of the analysis show that the soluble components of the NAPL are mainly removed by the pump-and-treat mechanism; however bioremediation is recommended as a “polishing step” to remove the trace contaminants not readily removed by the flushing process. Bioremediation transforms

a significant portion of the low solubility compounds after the soluble components have been removed. Removal of compounds is retarded by the inclusion of a non-soluble component in the NAPL mixture. The numerous simplifying assumptions of the proposed model limit it to predict the “most optimistic scenario”. The model, however, provides a simple conceptual view of site remediation: it can serve as a screening tool prior to the implementation of the bioremediation aided, pump-and-treat technology.

6. Nomenclature

$C_{iS,P}$	concentration of component i in the solid phase at the end of the P th flushing
$C_{iT,P}$	total concentration of component i at the end of the P th flushing
$C_{iW,P}$	concentration of component i in the aqueous phase at the end of the P th flushing
f_i	fugacity of component i
f_R	reference fugacity
f_{OC}	fraction of organic carbon in the aquifer soil
K_{Di}	partition coefficient of component i
K_{OCi}	octanol–water partition coefficient of component i
K_s	saturation constant
$M_{avg,P}$	average molecular weight of NAPL at the end of the P th flushing
M_i	molecular weight of component i
$MF_{iO,P}$	mass fraction of component i removed from the aquifer during the P th flushing
$MF_{iR,P}$	mass fraction of component i remaining in the aquifer at the end of the P th flushing
S_i	solubility of component i in the aqueous phase
S_O	inlet oxygen concentration into the aquifer
$w_{i,P}$	weight fraction of component i in the NAPL at the end of the P th flushing
x_{iN}	mole fraction of component i in the NAPL
x_{iW}	mole fraction of component i in the aqueous phase
X	concentration of microbial biomass
Y_i	stoichiometric coefficient (mass of oxygen consumed / mass of component i degraded)
Y_s	stoichiometric coefficient (mass of biomass formed / mass of contaminant degraded)
$\beta_{i,P}$	oxygen utilization factor for component i at the end of the P th flushing
Y_{iN}	activity coefficient of component i in the NAPL
Y_{iW}	activity coefficient of component i in the aqueous phase
$\varepsilon_{N,P}$	NAPL porosity (volume occupied by NAPL/total volume)
$\varepsilon_{W,P}$	aqueous phase porosity (volume occupied by aq. phase / total volume)
ε_T	total soil porosity
μ_{max}	maximum specific growth rate
ρ_B	bulk soil density

$\rho_{\text{Navg},P}$ average density of NAPL at the end of the P th flushing
 ρ_{Ni} density of component i

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