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A study of the dissolution rate-limited bioremediation of soils contaminated by residual hydrocarbons

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Abstract

The widespread release of organic chemicals in the environment frequently leads to groundwater contamination with non-aqueous phase liquids (NAPLs) because many of these organic chemicals are barely soluble in water. Understanding the mechanisms of transport and biotic transformation is essential for successful design and implementation of remedial strategies for contaminated soils. A model describing the biodegradation of the contaminants in NAPL–groundwater systems has been developed in this paper. Numerous field data and experimental results have indicated that the non-wetting fluids of the NAPLs in groundwater are trapped, i.e., completely surrounded by the wetting aqueous phase. In the present model, therefore, the NAPLs are treated as discrete blobs, while the aqueous phase is considered to be continuous. Interactions between the two liquid phases are incorporated into the governing equations for the aqueous phase. The rates of dissolution and desorption are assumed to be of the first order. Only aerobic growth of microorganisms is taken into account. This paper focuses on situations in which dissolution is the main rate-limiting factor. An investigation has been carried out on the rates of biodegradation of some common petroleum components such as benzene, ethyl-benzene, toluene, and xylene in the four-phase system. The effects considered are those of the mass-transfer area, specific growth rate of biomass, and velocity of pore-water flow.

1. Introduction

Manufacture, transportation, and utilization of organic chemicals have brought about frequent occurrences of soil contamination with non-aqueous phase liquids (NAPLs) because many organic chemicals are only sparsely soluble in water. The NAPLs released into the subsurface are long-term threats to our drinking water supplies as their components gradually dissolve into groundwater [1, 2]. Bioremediation is an innovative technology that depends on the indigenous soil microorganisms to transform or mineralize the organic contaminants. This technology has the potential to be a cost-effective clean-up method [3, 4].

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Theoretical studies to date have not generated sufficient information to enable us to eliminate uncertainties when bioremediation is applied to situations involving two immiscible liquid phases. Difficulties of simulating the bioremediation of soils with an organic phase stem from the complexities of soil pore structures, residual organic distribution, and microbial processes. Interfacial area for mass transfer and accessibility of nutrients and oxygen to microbes may play important roles in the biotic depletion of the contaminant. The majority of previous modeling efforts assumes that every fluid phase is spatially continuous (see, e.g., Refs. [5, 6]). Numerous field data and experimental results have indicated that when distributed as blobs of various sizes in groundwater, the non-wetting NAPLs are trapped, i.e., completely surrounded by the wetting phase (aqueous solution) [7, 8]. Due to surface tension, these blobs remain stable under a significant pressure gradient [9]. By assuming that an equilibrium is instantaneously attained, the concentration in one phase can be directly expressed in terms of that in the other phase. The equilibrium models which take into consideration both dissolution and biodegradation have predicted the lower or upper limits of the clean-up time for bioremediation [10–12]. Studies of the mass transfer processes in multiphase porous media have revealed that local equilibrium may be hardly reached in many cases [13, 14]. Laboratory investigations have shown that biodegradation is capable of reducing the aqueous concentration and further increasing the mass transfer driving force [15, 16]. Hence, it is necessary to describe various phenomena involved in bioremediation of soils contaminated by the NAPLs more precisely and accurately than achieved previously to gain insight into them.

This paper proposes a model which includes contaminant depletion and microbial growth in saturated porous media with organic, aqueous, and soil phases. In the model, interfacial area is determined from known parameters on the basis of certain assumptions, and interfacial mass transfer is characterized by a kinetic approach. Effects of the contaminant solubility, NAPL blob size distribution, and agitation of the aqueous phase are discussed. Microbial growth with or without substrate inhibition is numerically studied.

2. Theoretical consideration

The system under consideration, which can be in situ, on-site or off-site, comprises four phases including a solid phase which forms a rigid porous medium, an aqueous phase flowing in the pore space of the medium, a non-aqueous phase or the organic phase, and a microbial phase which is generally the indigenous soil microorganisms. From a spill or leaking tank of organic materials, NAPLs may move downward in the soil and spread in the groundwater; clay lenses may attenuate this movement. Because of the surface tension, the non-wetting phase, which is usually the organic phase in an organic–water system, is trapped as discrete blobs under residual saturation conditions.

In bioremediation, any of the following processes may constitute the rate-controlling step or steps: dissolution of organic components from the NAPL phase into the aqueous phase, adsorption–desorption of the contaminant between the solid and aqueous phases, convection–dispersion of the solute in the aqueous phase, and

microbial assimilation of the contaminant. The rate of microbial growth depends on the concentrations of nutrients and electron acceptor which is usually oxygen. It is well known that microorganisms form colonies on surfaces and that both floating cells and surface-attached colonies are involved in the transformation of the contaminant [17]. Furthermore, excessive concentrations of some organic chemicals may be toxic to microorganisms even though these organics are potential food sources for the microbes. A typical example is ethanol which is a germicide at high concentrations and is readily biodegradable at low concentrations. Various xenobiotic chemicals such as halogenated organics may disrupt cell membranes and cell functions [18, 19]; however, they may undergo biodegradation in soils along pathways that include gratuitous metabolism or cometabolism [20].

3. Model development

The system is assumed to be a layer of saturated well-mixed isotropic soil with evenly distributed residual NAPLs in the pores. The trapped NAPLs consist of discrete blobs without bulk movement and interaction among them. Sufficient nutrients and oxygen are supplied either by direct aeration (air sparging) or addition of nutrients and oxygen enriched solution, e.g., hydrogen peroxide solution [21]. The aqueous phase is considered to be continuous where the solute transport equation can be derived from the conservative law of mass. The dissolution flux of an individual NAPL blob is integrated into the governing equation for the aqueous solute. The contaminant adsorbed by the solid phase is assumed to be evenly distributed on the surface of the soil particles; and the rates of adsorption and desorption are of the first order. A model has been developed to describe mass transfer in saturated porous media with two immiscible liquid phases [22]. The present work extends this model to incorporate bioremediation under the following assumptions.

1. The NAPL blobs are spherical, evenly distributed in the soil, and of equal size. In reality, the shapes and size distribution of NAPL blobs are extremely complex and thus essentially impossible to precisely describe and measure
2. The NAPL blobs neither break nor coalesce.
3. The NAPL phase contains only a single NAPL component.
4. The adsorption–desorption between the NAPL and solid phases is neglected because the residual NAPL saturation is low; furthermore, the organic phase is usually a non-wetting phase in an organic–water system [23, 24]. Nevertheless, mass exchange between the aqueous and solid phases is included.
5. The biomass concentration involved in the transformation includes the colonies on the surfaces of the solids and the floating cells in the aqueous phase, whose concentrations obey a linear adsorption equilibrium relation.
6. The microbial growth in the aqueous phase and on the solid surface, which depends on the dissolved contaminant concentration, is significant.

The NAPL volume fraction, ε^{α}, is a function of the volume of individual NAPL blob, v, and the number of NAPL blobs per unit volume of the soil, λ, i.e.,

$$\varepsilon^{\alpha} = \lambda v \tag{1}$$

(The notations appearing in this and other equations are fully elaborated in Section 7.) The NAPL volume fraction and the volume of a NAPL blob change with time as the contaminant dissolves. Since the blob is assumed to be spherical, we have

$$v(t) = \tfrac{4}{3}\pi R^3 \tag{2}$$

and the surface area-to-volume ratio, σ, is

$$\sigma = 3/R. \tag{3}$$

The mass flux from a NAPL blob to the aqueous phase is considered to be proportional to the concentration difference in the aqueous phase. Thus, the rate of dissolution of the NAPL is expressed as

$$\rho^{\alpha}\frac{\mathrm{d}R}{\mathrm{d}t} = -k_{\mathrm{n}}\gamma(C_{\mathrm{sat}} - C^{\beta}) \tag{4}$$

where γ accounts for the effect of actual mass transfer area of a NAPL blob, i.e., the area contacting with the aqueous phase. A mass balance over the aqueous phase for the contaminant gives

$$\frac{\mathrm{d}(\varepsilon^{\beta}C^{\beta})}{\mathrm{d}t} = -\frac{\varepsilon^{\beta}}{Y}r_i + [a - 4\pi\lambda(1-\gamma)R^2]k_{\mathrm{l}}\left(\frac{q^{\mathrm{s}}}{K_{\mathrm{ls}}} - C^{\beta}\right) + 4\pi\lambda\gamma R^2 k_{\mathrm{n}}(C_{\mathrm{sat}} - C^{\beta}). \tag{5}$$

In this equation, the term on the left-hand side signifies the accumulation of the contaminant in the aqueous phase, and the first, second and third terms on the right-hand side represent the contributions attributable to the biochemical reaction, adsorption or desorption, and dissolution of the contaminant, respectively. A mass balance for the contaminant adsorbed to the soil is

$$\rho^{\mathrm{s}}(1-\varepsilon)\frac{\mathrm{d}q^{\mathrm{s}}}{\mathrm{d}t} = -[a - 4\pi\lambda(1-\gamma)R^2]k_{\mathrm{l}}\left(\frac{q^{\mathrm{s}}}{K_{\mathrm{ls}}} - C^{\beta}\right). \tag{6}$$

The growth and endogenous metabolism of microbes are taken into account in the mass balance for biomass, which is

$$\frac{\mathrm{d}(R_{\mathrm{b}}\varepsilon^{\beta}C_{\mathrm{b}})}{\mathrm{d}t} = \varepsilon^{\beta}r_i - R_{\mathrm{b}}\varepsilon^{\beta}k_{\mathrm{d}}C_{\mathrm{b}}. \tag{7}$$

According to assumption 3, the retardation factor for the biomass concentration is defined as

$$R_{\mathrm{b}} = 1 + \frac{\rho K_{\mathrm{db}}}{\varepsilon^{\beta}} \approx 1 + \frac{\rho K_{\mathrm{db}}}{\varepsilon}. \tag{8}$$

The mass transfer coefficient for dissolution is given by [25]

$$Sh = \frac{k_{\mathrm{n}}(2R)}{D} = 2.0 + 0.6Re^{1/2}Sc^{1/3} = 2.0 + 0.6\left(\frac{2Ru}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3}. \tag{9}$$

Two forms of biomass growth kinetics are considered. One of them, the Monod model, is of the form

$$r_i = R_b C_b \left(\frac{\mu_m C^\beta}{K_1 + C^\beta} \right) \tag{10}$$

and the other, the substrate inhibition model,

$$r_i = R_b C_b \left[\frac{\mu_m C^\beta}{K_1 + C^\beta + (C^\beta)^2 / K_2} \right]. \tag{11}$$

The initial conditions at $t = 0$ are

$$C^\beta = C_{sat}$$

$$C_b = C_{b0}$$

$$q^s = q_0^s = C_{sat} \times K_{ls}$$

$$R = R_0$$

4. Numerical methods

The governing equations of the model, (4)–(7), are coupled ordinary differential equations that have been solved by the second-order modified Euler method with source term linearization [26]. The results are compared with available experimental data of toluene dissolution in a glass-bead column without biodegradation [27]. The model predictions agree well with the experimental data as indicated in Fig. 1 where only mass transfer is taken into consideration [22].

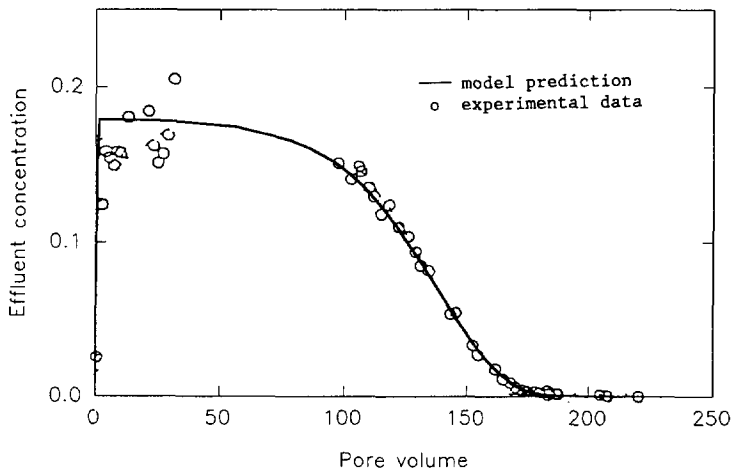


Fig. 1. Comparison of the predicted values of the dimensionless effluent concentration based on the model to the experimental data from Geller [27] for $U = 5$ m/d.

Table 1
Parameter values for numerical simulation

Paramater	Value	Ref.
a	50 cm^2/cm^3	[31]
C_{b0}	1×10^6 cells/g soil	[32]
C_{sat}	10–500 ppm	[2]
D	1×10^{-5} cm^2/s	[25]
K	0.25 C_{sat}	[33]
K_2	500 ppm	[33]
K_{db}	2 cm^3/g	[34]
k_l	1×10^{-5} cm/s	[28]
K_{ls}	1 cm^3/g	[28]
R_0	0.05–0.4 cm	[35]
u	0–100 cm/h	[2]
Y	1.0 g/g	[34]
γ	0.05–0.9	[8]
ε	0.4	[31]
ε_0^α	0.05	[24]
μ_m	0.01–0.3 h^{-1}	[33]
ν	1.0037×10^{-2} cm^2/s	[25]
ρ^α	1 g/cm^3	[2]
ρ^β	1 g/cm^3	[31]
ρ^s	2.5 g/cm^3	[31]

Parameter values taken or estimated from the literature for the simulation are listed in Table 1. The overall mass balance has been verified for each computation, and the numerical error for each case has been determined to be less than 1%.

5. Results and discussion

A typical bioremediation process, together with the parameter values, is illustrated in Fig. 2. Various normalized concentrations or fractions are plotted as functions of time. In the figure, $C_b^* = [\rho^\alpha \varepsilon_0^\alpha + (\varepsilon - \varepsilon_0^\alpha) C_{sat} + \rho K_{ls} C_{sat}] Y$ is the maximum attainable concentration of biomass from the contaminant concentration in the soil bed. The contaminant concentration in the aqueous phase becomes very low after a short period of time, thus indicating that the mass transfer driving force for dissolution is substantial, and the process is far from local equilibrium; i.e., it is basically rate-limited by dissolution. The biomass concentration increases rapidly at first; it reaches a maximum value and then decreases because of the low aqueous contaminant concentration and the endogenous metabolism.

Microbial growth with substrate inhibition is plotted in Fig. 3 for the same parameter values. Comparing Figs. 2 and 3 indicates that the dissolution of the contaminant ends at 25 d without substrate inhibition (Fig. 2) and at 26 d with

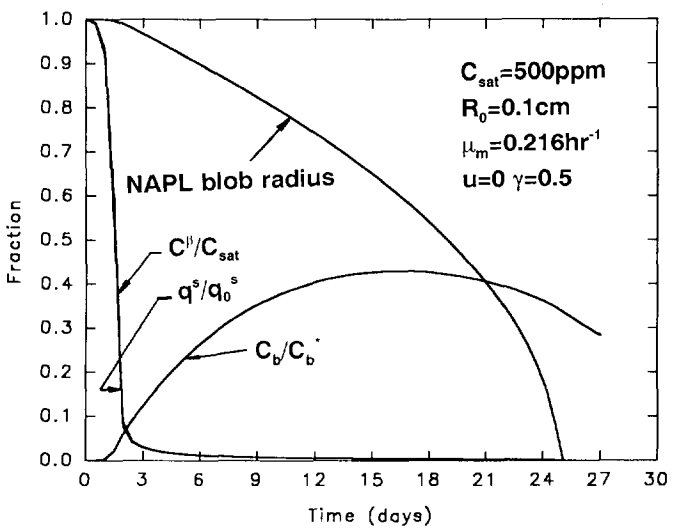


Fig. 2. A typical bioremediation process which is rate-limited by dissolution.

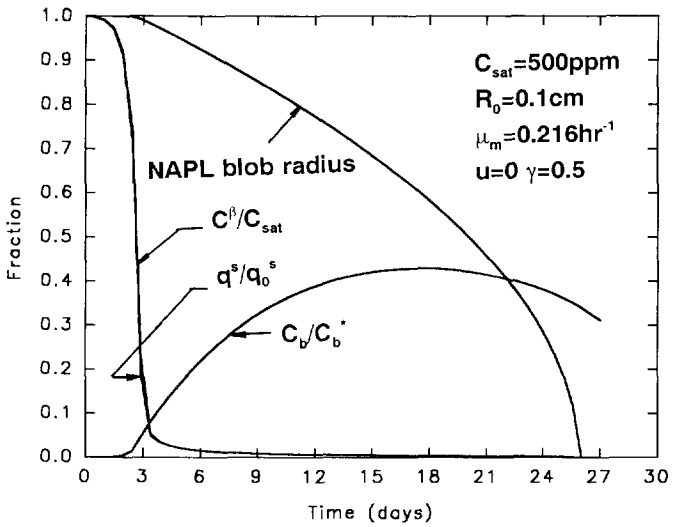


Fig. 3. Simulated bioremediation results for microbial growth kinetics based on Eq. (11) which includes substrate inhibition.

substrate inhibition (Fig. 3). This implies that substrate inhibition does not significantly affect the process under the dissolution rate-limiting condition.

The results in Figs. 4–9 are obtained with the Monod model of microbial growth. Note that Figs. 4–8 plot numerically obtained results as discrete points; these results

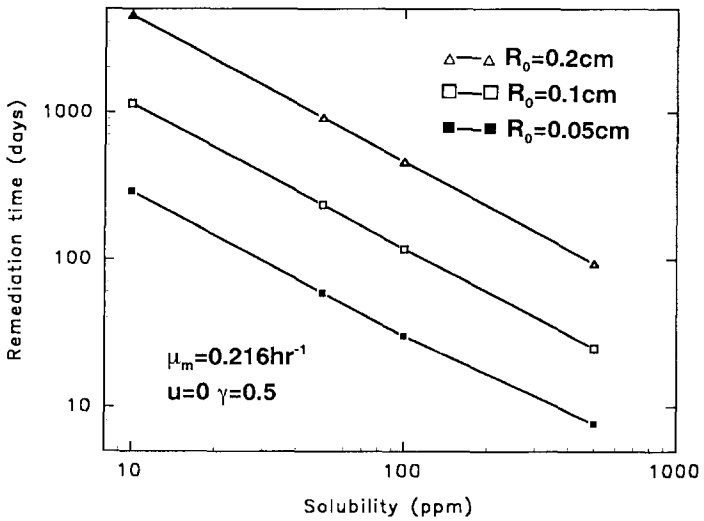


Fig. 4. Remediation time as a function of contaminant solubility for various initial NAPL blob radii.

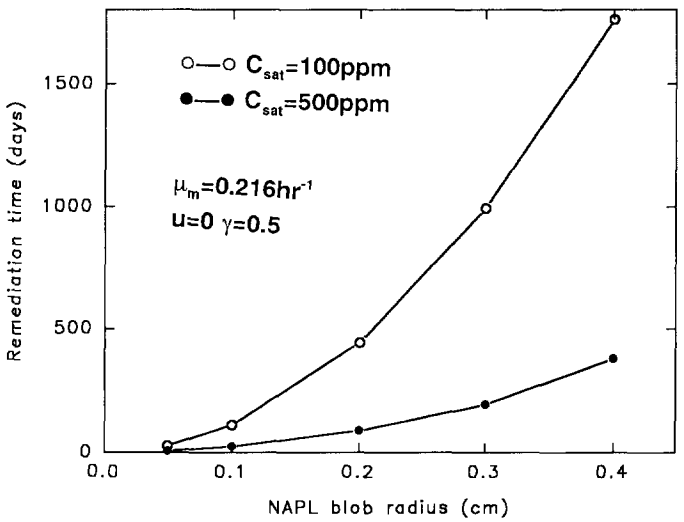


Fig. 5. Remediation time as a function of initial NAPL blob radius for two contaminant solubilities.

are not compared to any experimental data. The remediation time, i.e., the time for the total amount of the contaminant including those in the aqueous, NAPL, and solid phases to decrease to 0.1% of the original amount, is plotted logarithmically for different contaminant solubilities in Fig. 4. Lowering the solubility of the contaminant

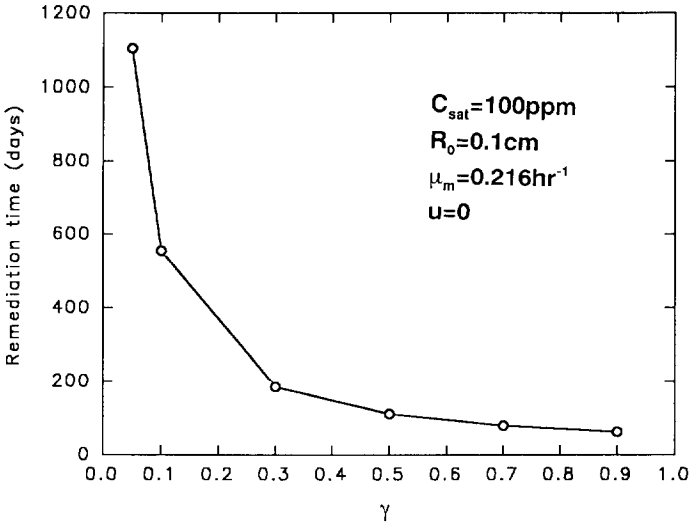


Fig. 6. Remediation time vs. NAPL aqueous-contacting ratio: the larger the ratio, the greater the NAPL blob surface exposed to the aqueous phase.

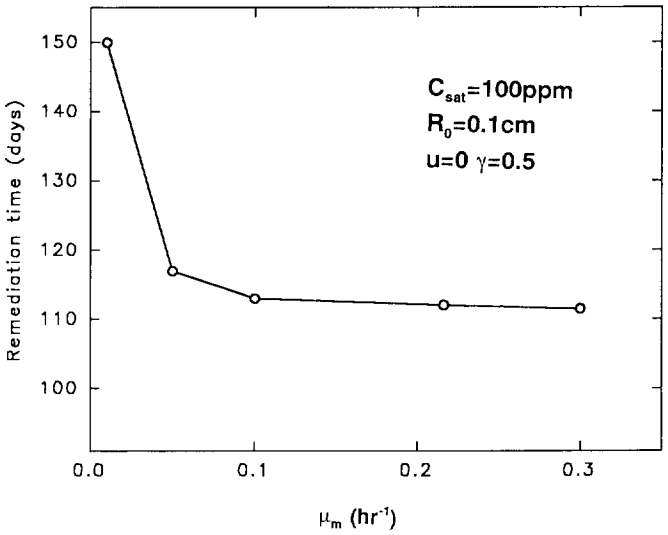


Fig. 7. Remediation time vs. maximum specific growth rate of biomass.

reduces the dissolution flux and prolongs the remediation time. Fig. 4 reveals that the logarithm of remediation time decreases linearly with that of solubility under the dissolution rate-limiting condition.

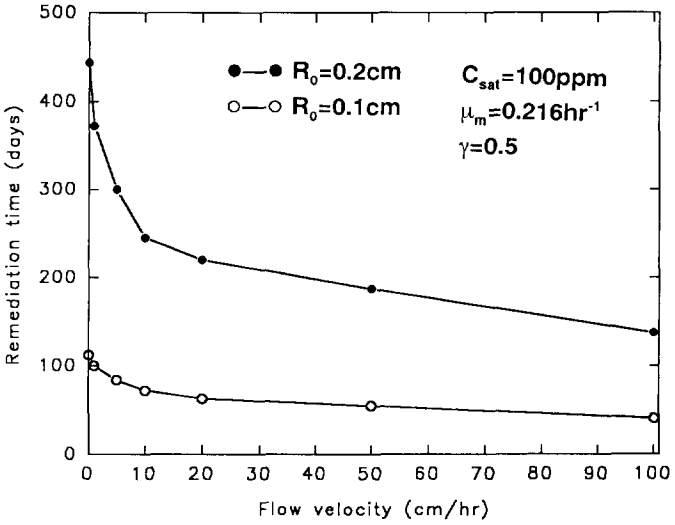
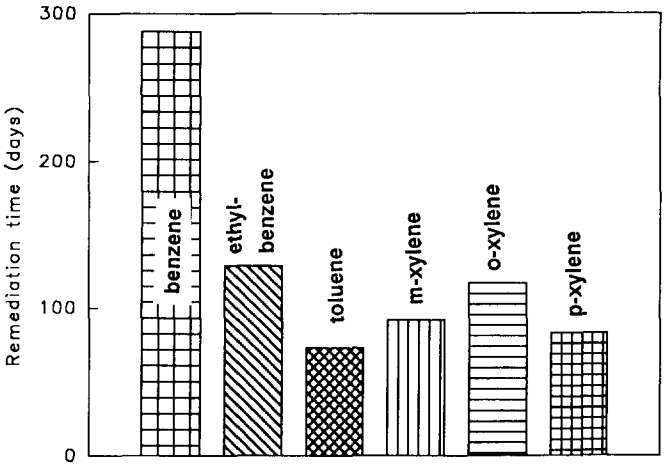


Fig. 8. Remediation time as a function of pore-water flow velocity for two initial NAPL blob radii.



	benzene	ethyl-benzene	toluene	m-xylene	o-xylene	p-xylene
density (kg/L)	0.878	0.867	0.867	0.86	0.88	0.86
solubility(mg/L)	1780	152	515	175	175	198
μ_m ($10^{-3}hr^{-1}$)	2.31	6.94	8.33	11.9	6.94	11.9
dissolution rate-limited?	no	yes	almost no	yes	yes	yes

Fig. 9. Comparison of the bioremediation processes for BETX.

In Fig. 5, the remediation time is presented as a function of the initial NAPL blob radius for two contaminant solubilities. For the same amount of contaminant, the larger the initial NAPL blob size, the longer the remediation time, as expected. The remediation time increases non-linearly with the initial NAPL blob radius. A remediation time of 2.5 d is predicted for both contaminant solubilities provided that local equilibrium prevails among the NAPL, aqueous and solid phases. Thus, the results for very small blob radii approach those obtained by assuming phase equilibrium. The size distribution of NAPL blobs is determined by pore sizes as well as other factors. Frequently, the larger the pores, the larger the NAPL blobs. Factors such as hydraulic shear stress, emulsification, and dissolution also contribute to the size distribution.

The ratio of the aqueous contacting area to the whole surface area of a NAPL blob, γ, profoundly influences the rate of dissolution. The larger the ratio, the greater the surface area of the NAPL blob exposed to the aqueous phase, and consequently, the total dissolution flux. In other words, under the dissolution rate-limiting condition, the larger the ratio, the shorter the remediation time; see Fig. 6. The mass transfer area of a blob with a complex shape, e.g., fingers or chains, can be represented by a combination of γ and the surface areas of spherical blobs varying in size.

Fig. 7 elucidates the effect of the maximum specific growth rate, μ_m. Under the dissolution rate-limiting condition, μ_m plays a less important role as shown in the figure; the curve becomes almost flat at $\mu_m > 0.1\ h^{-1}$. For a very low maximum specific growth rate ($\mu_m < 0.05\ h^{-1}$), the process is rate-limited by both dissolution and growth.

The remediation time is plotted against the pore-water flow velocity in Fig. 8; the former decreases with the increase in the latter. To optimize this technology requires trading-off between the remediation time and the energy required to achieve the flow velocity. Air sparging can provide oxygen for aerobic biodegradation and increase pore-water flow in the aquifer; pumping is an alternative. In general, pore-water flow can enhance the rate of mass transfer.

The remediation times for benzene, ethyl-benzene, toluene, and xylenes (BETX) are compared in Fig. 9. The radius of the NAPL blobs is 0.1 cm initially. The maximum specific growth rates, densities, and solubilities of BETX are taken from [29, 30]. Among these data, the maximum specific growth rates that appear to be exceedingly low have been estimated from the disappearance rates of BETX in groundwater [29]. These maximum specific growth rates depend on various factors including temperature, pH, and characteristics of the growth media. Hence, the results given in Fig. 9 should be regarded as a highly simplified representation of BETX remediation.

The exceedingly low maximum specific growth rates mentioned above would have led to growth rate-limiting situations. Nevertheless, it has proved not to be the case as delineated so far. This is not surprising; in fact, dissolution rate-limiting situations can be found in the bioremediation of ethyl-benzene and xylenes.

6. Conclusions

A model has been proposed to describe transport and biotransformation involved in bioremediation of soils contaminated with an organic phase. The model includes

mass transfer and batch kinetics in a four-phase system. The results of simulation reveal that the contaminant concentrations in the different phases are far from those obtained under equilibrium conditions and that the kinetic modeling approach predicts a clean-up time-scale appreciably different from that of an instantaneous equilibrium model.

The rate of dissolution is one of the significant rate-limiting factors in the remediation of soils contaminated with trapped NAPLs. A low dissolution flux may severely hinder clean-up efforts even in a favorable microbial environment with sufficient oxygen and nutrient supply. The dissolution rate-limiting situation is not uncommon in the remediation of subsurface soils contaminated with an organic phase. Under the dissolution rate-limiting condition, the impact of substrate inhibition is negligible; the effect of maximum specific growth rate is insignificant; the greater the interfacial area for dissolution, the faster the clean-up; the lower the NAPL solubility or the larger the initial NAPL blob size, the longer the remediation time; and the relation between the logarithm of remediation time and that of solubility is approximately linear.

7. Nomenclature

a	interfacial area of the soil grains per unit volume of the soil bed, L^2/L^3
C	concentration in the aqueous phase, M/L^3
C_{b0}	initial biomass concentration, M/L^3
C_{sat}	solubility of the substance in water, M/L^3
D	aqueous diffusion coefficient, L^2/t
k_d	decay constant for biomass, $1/t$
k_l	mass transfer coefficient of adsorption–desorption between the aqueous and solid phases, L/t
K_{ls}	partition coefficient, L^3/M
k_n	mass transfer coefficient for the dissolution of the contaminant, L/t
K_1	saturation constant, M/L^3
K_2	substrate inhibition constant, M/L^3
K_{db}	partition coefficient of biomass concentration, L^3/M
q	concentration in the solid phase, M/M
r_i	reaction rate defined by Eq. (10) or (11)
R	radius of the NAPL blob, L
R_b	retardation factor for biomass concentration
Re	Reynolds number ($=2Ru/\nu$)
Sc	Schmidt number ($=\nu/D$)
Sh	Sherwood number ($=2Rk_n/D$)
t	time, t
v	volume of the NAPL blob, L^3
Y	yield factor of biomass growth, M/M

Greek letters

γ	ratio of the aqueous contacting area to the surface area of the NAPL blob
ε	void fraction of the soil bed
ε^{α}	NAPL phase volume fraction
ε^{β}	aqueous phase volume fraction
λ	number distribution of NAPL blobs, $1/L^3$
μ_m	maximum specific growth rate of biomass, $1/t$
ρ	density, M/L^3
σ	surface-area-to-volume ratio of the NAPL blob, $1/L$

Subscript

0	initial value

Superscript

α	NAPL phase
β	aqueous phase
s	solid phase

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