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The role of oxygen diffusion in passive bioremediation of petroleum contaminated soils

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Abstract

In passive bioremediation of petroleum hydrocarbon contaminated soils, oxygen diffusion is the primary mechanism for supplying the oxygen which is required for microbial hydrocarbon biodegradation processes. It is the objective of this research to theoretically evaluate whether passive bioremediation can be a feasible treatment alternative for petroleum contaminated soils. In this paper we derive equations for the steady-state oxygen concentration profiles which are expected to develop as a result of simultaneous oxygen diffusion and consumption in hydrocarbon contaminated soils. These equations are used to estimate the maximum oxygen penetration distance and the total cleanup time for several environmental scenarios such as surface and subsurface soil contamination as well as contaminated soil piles. It was found that oxygen is expected to penetrate most contaminated soils for up to several meters if hydrocarbon biodegradation rates are similar to those measured during bioventing respiration tests, i.e. approximately 2.5–10 ppm TPH day^{-1}. Both the depth of oxygen penetration and the total passive bioremediation cleanup time were found to be strongly dependent on the magnitude of the diffusion coefficient for oxygen in soil (D_s). As expected, increased oxygen penetration distances and decreased cleanup times are associated with increased D_s values. Since the magnitude of D_s is inversely related to the soil moisture content, it is imperative to maintain moderately low soil moisture levels in order to maximize the effectiveness of passive bioremediation treatment. Passive bioremediation is expected to be a feasible and cost-effective treatment alternative for TPH contaminated soils in cases where the minimization of cleanup times is not a major remediation objective.

Keywords: Oxygen; Petroleum contaminated soil; Passive bioremediation

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1. Introduction

In most bioremediation projects involving hydrocarbon contaminated soils, environmental conditions are optimized (i.e. pH, moisture, fertilizer concentrations, aeration, etc.) in order to achieve maximum hydrocarbon biodegradation rates and thereby minimize overall cleanup times [1–4]. It has been shown, however, that hydrocarbon biodegradation proceeds in many cases without special soil amendments as long as oxygen is present [5–9]. For example, the success of bioventing as an effective cleanup technology for fuel contaminated sites is based on the fact that acceptable hydrocarbon biodegradation rates are achieved as long as sufficient quantities of oxygen are supplied to the indigenous soil microorganisms. While the active delivery of oxygen during bioventing is necessary to stimulate hydrocarbon biodegradation in deeper soil strata, it may be feasible to rely on passive oxygen transport mechanisms such as diffusion in cases where the hydrocarbon contamination is present in surficial soils or excavated soil piles.

Soil aeration has been the subject of intense research by soil scientists for more than a century [10,11]. It has been shown that the predominant mechanism for root zone aeration is passive diffusion while convective oxygen transport due to temperature and barometric pressure fluctuations or wind and rainfall effects is only of minor significance [10]. Surprisingly, very little attention has been focused on the role of oxygen diffusion during bioremediation of contaminated soils. Devinny and Islander [12] verified a simple oxygen diffusion model with laboratory data and found that oxygen diffusion limits the performance of land treatment units only in cases of high respiratory activity. Oxygen was found to penetrate the entire treatment zone (30 cm) when soil respiration rates were approximately $0.0035\,mg\,O_2\,l\,s^{-1}$.

It is the objective of this research to theoretically evaluate whether passive bioremediation can be a feasible treatment alternative for petroleum contaminated soils. In this paper we derive equations for the steady-state oxygen concentration profiles which are expected to develop as a result of simultaneous oxygen diffusion and consumption in hydrocarbon contaminated soils. These equations are used to estimate the maximum oxygen penetration distance and the total cleanup time for several soil contamination scenarios. In addition, empirical correlations are provided for estimating the magnitude of the oxygen diffusion coefficient and the microbial oxygen consumption rates in soils.

2. The oxygen transport equation for soils

The equation describing both oxygen diffusion and consumption within a soil matrix can be derived from Fick's Law and the oxygen conservation equation for soil gas [10]. Assuming steady-state conditions, the resulting equation for oxygen diffusion is

$$\frac{\partial^2 C}{\partial z^2} = \frac{r}{D_s} \tag{1}$$

where C is the soil gas oxygen concentration (mass of oxygen per volume of soil air), r

is the rate of oxygen consumption (mass of oxygen removed per unit volume soil per unit time) due to microbial activity, and D_s is the oxygen diffusion coefficient in soil. D_s can be related to the oxygen diffusion coefficient in air (D_a) according to

$$D_s = \tau_g D_a \tag{2}$$

where τ_g is the gas tortuosity factor ($\tau_g < 1$). Methods for estimating the magnitude of D_s for a given soil type are described in the next section.

The steady-state oxygen transport Eq. (1) may be used to determine the oxygen concentration profile $C(z)$ in the soil gas as a function of depth (z). The solution to Eq. (1) depends on the choice of boundary conditions and the magnitude of both the soil gas diffusion coefficient (D_s) for oxygen and the oxygen consumption rate (r). Details regarding the estimation or measurement of D_s and r are provided prior to the development of analytical solutions for the steady-state oxygen concentration profiles for three commonly encountered soil contamination scenarios.

3. Estimation of the oxygen diffusion coefficient (D_s) in soils

Ideally, the soil gas diffusion coefficient for oxygen (D_s) is measured for a particular field soil using laboratory or field methods [13–15]. Since the performance of these measurements is likely to be too time-consuming and expensive, it is in most cases simpler to use empirical models which relate the gas tortuosity factor τ_g (see Eq. (2)) to specific bulk soil properties which are relatively easy to determine. Numerous empirical models have been proposed (see [10,11] for a review on this subject) for relating the gas tortuosity factor τ_g to the volumetric air content α of a given soil. Because of its applicability over a wide range of α values [16], the Millington and Quirk [17] model is particularly useful for estimating the gas tortuosity factor:

$$\tau_g = \frac{\alpha^{10/3}}{\theta^2} \tag{3}$$

Porosity (θ) is defined as the volume of void space (= volume of soil gas and water) per total soil volume while volumetric air content (α) is defined as the volume of gas space per total volume of soil. Porosity (θ) and volumetric air content (α) may be computed for a specific soil if the bulk density (ρ_b), particle density (ρ_p) and moisture (μ) are known:

$$\theta = 1 - \frac{\rho_b}{\rho_p} \tag{4}$$

$$\alpha = \theta - \mu\frac{\rho_b}{\rho_{water}} \tag{5}$$

Bulk density ρ_b is defined as the mass of dry soil per total soil volume and may be estimated from the dry weight of a soil core sample [18]. Particle density ρ_p is the ratio of dry soil mass to unit volume of soil particles, the latter of which may be determined from the volume of water displaced by the soil particles [19]. Moisture content μ is

defined as the mass of water per mass of dry soil and may be determined by gravimetry with oven drying [20]. Finally, the density of water ρ_{water} is assumed to be $1\,g\,cm^{-3}$.

Using Eqs. (3)–(5), the soil gas diffusion coefficient (D_s) can now be calculated as a function of soil moisture content (μ) and porosity (θ):

$$D_s = \frac{\left[\theta + \frac{\mu\rho_p}{\rho_{water}}(\theta - 1)\right]^{10/3}}{\theta^2} \cdot D_a \tag{6}$$

Assuming that ρ_p and ρ_{water} are constant, a family of curves for D_s as a function of μ and θ can be plotted as shown in Fig. 1. As expected, the diffusion coefficient for oxygen in soil (D_s) increases with decreasing moisture content (μ) and increasing porosity (θ). Since many soils have a porosity of approximately 50% [21] and since microbial activity is present as long as the moisture content is at least 50% of field capacity [3], which translates into a μ value of 0.05–0.10 g water(g dry soil)$^{-1}$ for most soils [21], it is expected that D_s will range from approximately 0.005 to $0.04\,cm^2\,s^{-1}$ in most moderately moist (non-saturated) and microbially active soils. D_s values within this range are used for the computation of oxygen penetration distances and cleanup times in the soil contamination scenarios described below.

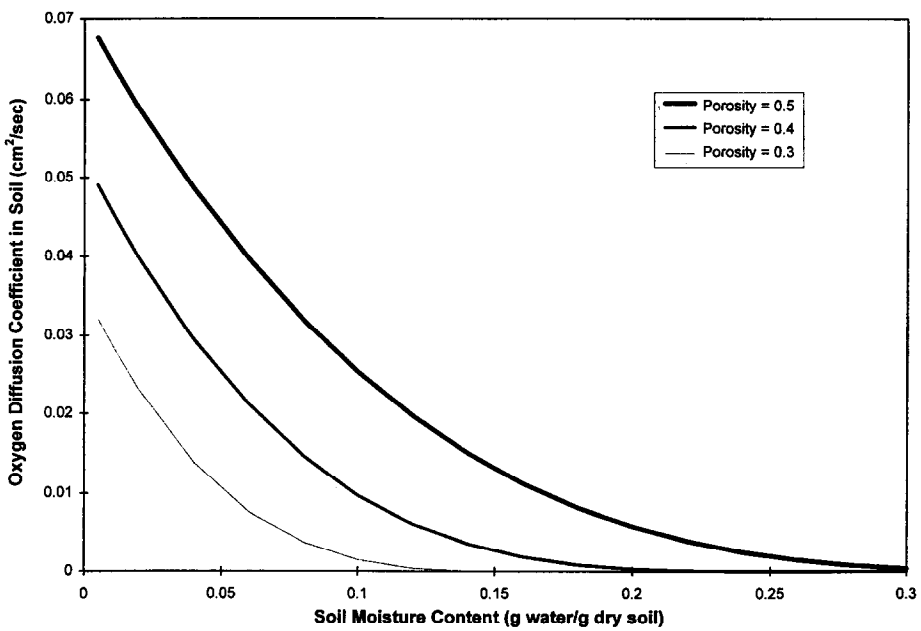

Fig. 1. Oxygen diffusion coefficient in soil (D_s) as a function of soil moisture content (μ) and porosity (ϕ) for a particle density (ρ_p) of $2.65\,g\,cm^{-3}$. The diffusion coefficient for oxygen in free air (D_a) is assumed to be $0.178\,cm^2\,s^{-1}$ [22].

4. Measurement or estimation of microbial oxygen consumption rates in soils

The magnitude of the microbial oxygen consumption rate (r) during hydrocarbon biodegradation is affected by numerous environmental parameters such as temperature, pH, oxygen levels, nutrient (N, P) concentrations, soil moisture, hydrocarbon types, microbial population densities, and soil type [23,24]. Since it is virtually impossible to predict the oxygen consumption rate in a particular contaminated soil, it is necessary to measure r either by *ex situ* laboratory respiration tests or *in situ* respirometry [25].

In cases where soil respirometry data are not available, it is possible to correlate the hydrocarbon biodegradation rate (r_{HC}) with the oxygen consumption rate (r) using the following stoichiometric relationship:

$$CH_2 + 1.5\,O_2 \rightarrow CO_2 + H_2O \tag{7}$$

For simplicity, it is assumed that all hydrocarbon (CH_2) is mineralized into carbon dioxide and water without (or only minimal) formation of biomass. Eq. (7) indicates that 1.5 mol oxygen per mol CH_2 hydrocarbon or equivalently 3.4 g oxygen (g hydrocarbon)$^{-1}$ are required for complete mineralization. Since in most cases the hydrocarbon biodegradation rate (r_{HC}) is reported as loss of hydrocarbon mass per dry soil mass per unit time, while the oxygen consumption rate (r) is based on the volume of moist soil, the correlation between r and r_{HC} must also include a term for bulk density:

$$r = 3.4\rho_b r_{HC} \tag{8}$$

Fig. 2 shows the distribution of TPH biodegradation rates (r_{HC}) in soils during

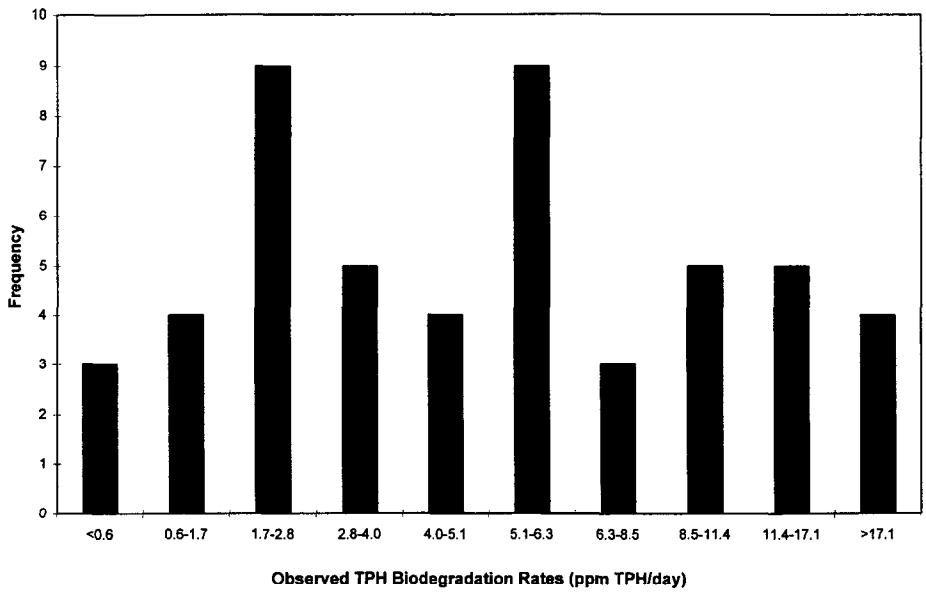

Fig. 2. Distribution of TPH (total petroleum hydrocarbon) biodegradation rates in soils during bioventing operations at 51 sites across the US. TPH biodegradation rates were calculated using the equation and oxygen consumption data given in [7].

bioventing operations at 51 sites across the US [7]. It can be seen that most *in situ* TPH biodegradation rates range from 2.5 to 10 ppm TPH day^{-1}. Consequently, TPH biodegradation rates within this range are used for the computation of oxygen penetration distances and cleanup times in the following three soil contamination scenarios.

5. Oxygen penetration distances and cleanup times in three contamination scenarios

5.1. Scenario I: oxygen diffusion into contaminated surface soil

A homogeneous layer of contaminated surface soil of thickness T is located above a clean (uncontaminated) layer of subsurface soil (see Fig. 3). The depth (z) of the soil is measured from the soil surface ($z = 0$). The concentration of oxygen at the soil surface ($C(z = 0)$) is constant and is equal to the atmospheric oxygen concentration C_0. The soil gas diffusion coefficient for oxygen (D_s) is constant throughout the contaminated soil layer, and no biodegradable organics are present in the clean subsurface soil layer (i.e. $r = 0$ for $z > T$). Finally, it is assumed that oxygen consumption by microbial processes

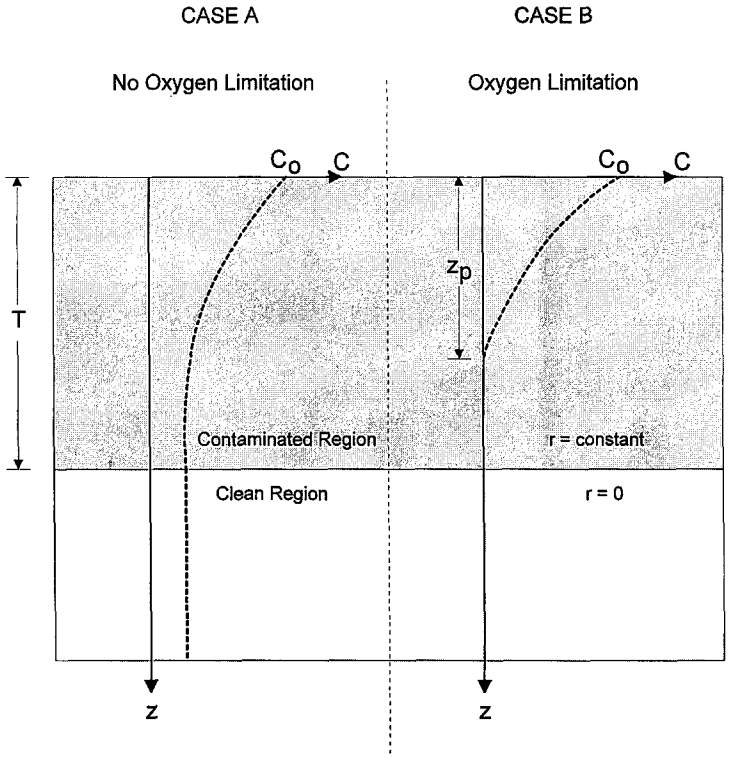

Fig. 3. Possible oxygen concentration profiles within a contaminated surface soil layer (scenario I).

occurs as long as any oxygen is present in the soil gas. Thus, if C is greater than zero, the oxygen consumption rate is constant and of magnitude r.

Depending on the ratio of oxygen diffusion rates to oxygen consumption rates, the following two hypothetical steady-state oxygen concentration profiles may develop in the contaminated surface soil (see cases A and B in Fig. 3).

5.1.1. Case A: the contaminated surface soil layer is fully oxygenated

If diffusional processes can supply more oxygen to the soil than can be consumed by soil microorganisms, the oxygen concentration profile reaches an asymptote ($C > 0$) at greater soil depths (see case A in Fig. 3). Since no microbial activities (i.e. oxygen consumption) are assumed to occur in the clean subsurface layer, there is no diffusional transport of oxygen from the contaminated to the clean soil layer. This translates into a so-called no-flux boundary condition, or equivalently, $dC/dz = 0$ at $z = T$.

Accordingly, it is possible to formulate the following two boundary conditions for case A:

(i) at $z = 0$,

$$C = C_0$$

(ii) at $z = T$,

$$\frac{dC}{dz} = 0$$

Using these boundary conditions, Eq. (1) may be integrated twice to obtain the steady-state solution for the oxygen concentration in the soil gas as a function of depth:

$$C(z) = C_0 + \frac{r}{D_s}\left(\frac{z^2}{2} - Tz\right) \tag{9}$$

Eq. (9) may be rewritten using the dimensionless parameters of relative soil gas concentration (C/C_0) and relative soil depth (z/T):

$$\frac{C(z)}{C_0} = 1 + \frac{rT^2}{D_s C_0}\left[\frac{1}{2}\left(\frac{z}{T}\right)^2 - \left(\frac{z}{T}\right)\right] \tag{10}$$

This equation indicates that a family of soil gas oxygen concentration profiles may be obtained as a function of the dimensionless parameter

$$k = \frac{rT^2}{D_s C_0} \tag{11}$$

Analysis of Eq. (10) reveals that no oxygen limitation exists within the soil layer (i.e. $C > 0$ for $0 < z < T$) as long as $k < 2$. If $k > 2$, the lower part of the contaminated soil layer will become oxygen limited and a distinct oxygen penetration distance (z_p) may be calculated (see case B below).

Since the rate of oxygen consumption is assumed to be constant ($= r$) whenever the soil gas oxygen concentration (C) is greater than zero, the flux of oxygen into the soil surface is directly related to the depth (T) of the oxygenated and microbially active soil layer:

$$J(z = 0) = rT \tag{12}$$

5.1.2. Case B: the contaminated surface soil layer is only partially oxygenated

If the rate of oxygen consumption by soil microorganisms is greater than the rate of oxygen diffusion into the soil, the oxygen concentration will decrease rapidly with depth as shown for case B in Fig. 3. Oxygen will penetrate only a limited distance z_p into the soil. At depths greater than the oxygen penetration distance ($z > z_p$), the oxygen concentration in the soil gas is zero. At steady-state, the mass flux of oxygen across the soil surface is equal to the mass of oxygen taken up in the microbially active zone, i.e.

$$J(z=0) = -D_s \frac{dC}{dz}(z=0) = rz_p$$

Accordingly, it is possible to formulate the following two boundary conditions for case B:

(i) at $z = 0$,

$$C = C_0$$

(ii) at $z = 0$,

$$\frac{dC}{dz} = -\left(\frac{r}{D_s}\right) z_p$$

Using these boundary conditions, Eq. (1) may be integrated twice to obtain the steady-state solution for the oxygen concentration (C/C_0) in the soil gas as a function of soil depth (z/z_p):

$$\frac{C(z)}{C_0} = 1 + \frac{rz_p^2}{D_s C_0}\left[\frac{1}{2}\left(\frac{z}{z_p}\right)^2 - \left(\frac{z}{z_p}\right)\right] \tag{13}$$

Since $C(z_p) = 0$, it follows that

$$\frac{rz_p^2}{D_s C_0} = 2 \tag{14}$$

Consequently, Eq. (13) can be simplified as

$$\frac{C(z)}{C_0} = 1 + 2\left[\frac{1}{2}\left(\frac{z}{z_p}\right)^2 - \left(\frac{z}{z_p}\right)\right] \tag{15}$$

where z_p is obtained from Eq. (14) according to

$$z_p = \sqrt{\frac{2D_s C_0}{r}} \tag{16}$$

Fig. 4 shows the computed oxygen penetration distance in contaminated surface soil as a function of the oxygen diffusion coefficient in soil (D_s) and selected TPH biodegradation rates (r_{HC}). It can be concluded that oxygen is expected to penetrate up to several meters into contaminated surface soils if TPH biodegradation rates are in the range from 2.5 to 10 ppm TPH day^{-1}.

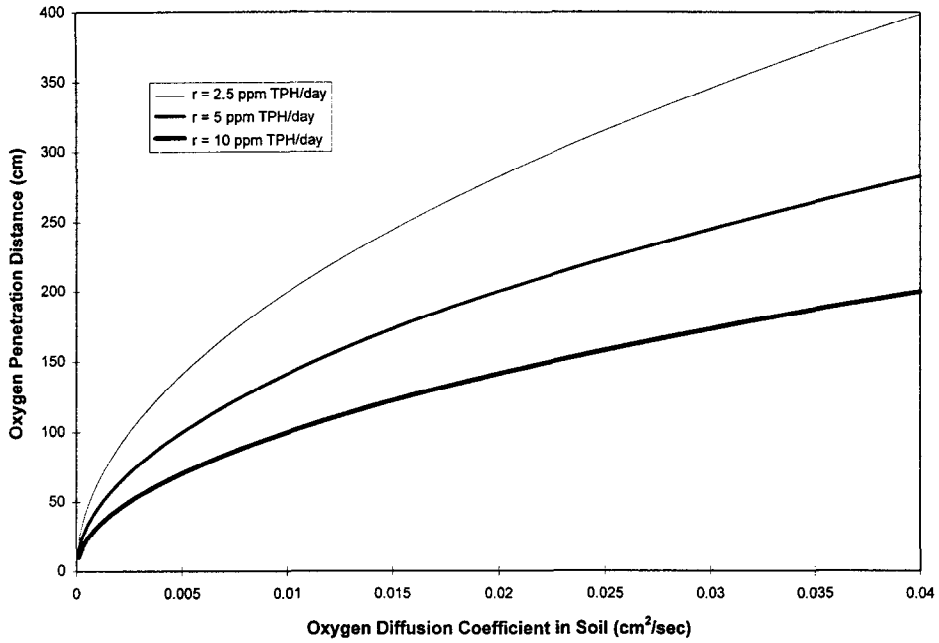

Fig. 4. Oxygen penetration distance (z_p) into contaminated surface soil (bulk density $\rho_b = 1.5\,g\,cm^{-3}$) as a function of the oxygen diffusion coefficient in soil (D_s) for different TPH (total petroleum hydrocarbon) biodegradation rates. The atmospheric oxygen concentration (C_0) is $294\,mg\,O_2\,(l\,air)^{-1}$.

Since the rate of oxygen consumption is assumed to be constant ($= r$) whenever the soil gas oxygen concentration (C) is greater than zero, the flux of oxygen into the soil surface is directly related to the depth (z_p) of the oxygenated and microbially active soil layer:

$$J(z = 0) = rz_p \tag{17}$$

5.2. Scenario II: oxygen diffusion into contaminated subsurface soil

This scenario is shown in Fig. 5 where a homogeneous layer of contaminated subsurface soil of thickness T (region II) is located beneath a clean (uncontaminated) surface soil layer of thickness L_0 (region I). The depth (z) of the soil is measured from the soil surface ($z = 0$). The concentration of oxygen at the soil surface ($C(z = 0)$) is constant and is equal to the atmospheric oxygen concentration C_0. The soil gas diffusion coefficient for oxygen (D_s) is assumed to be constant and the same in both the clean and contaminated regions (i.e. $D_s = D_s^{I} = D_s^{II}$), and no biodegradable organics are present in the clean surface soil layer (i.e. $r = 0$ for $0 < z < L_0$). Finally, it is assumed that oxygen consumption by microbial processes occurs in the contaminated subsurface soil layer as long as any oxygen is present in the soil gas. Thus, if C is greater than zero, the oxygen consumption rate in region II is constant and of magnitude r.

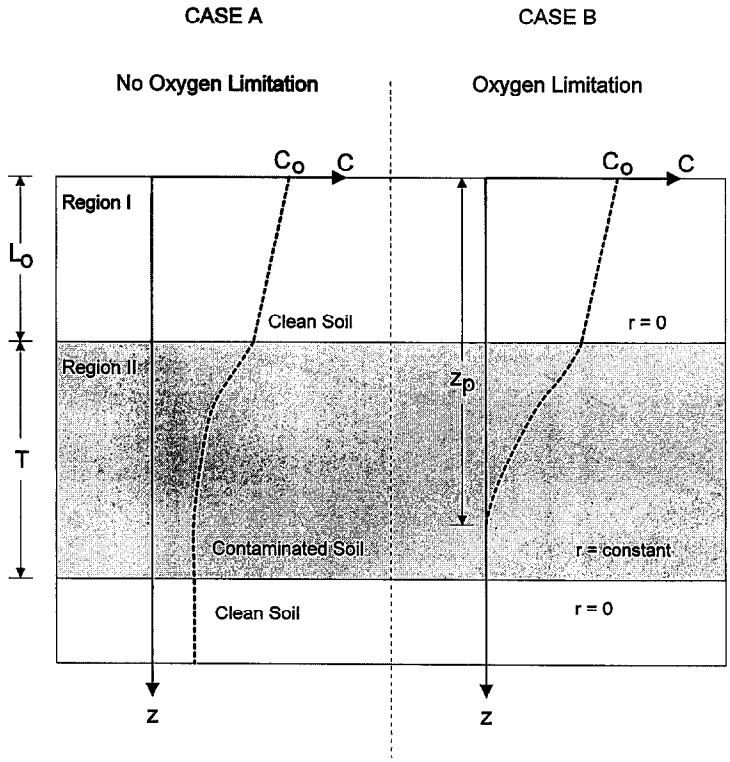

Fig. 5. Possible oxygen concentration profiles within a contaminated subsurface soil layer (scenario II).

Depending on the ratio of oxygen diffusion rates to oxygen consumption rates, the following two hypothetical steady-state oxygen concentration profiles may develop in the two soil regions (see cases A and B in Fig. 5).

5.2.1. Case A: the contaminated subsurface layer is fully oxygenated

If diffusion processes can supply more oxygen to the soil than can be consumed by soil microorganisms, the oxygen concentration profile reaches an asymptote ($C > 0$) in region II (see case A in Fig. 5). Since no microbial activities (i.e. oxygen consumption) are assumed to occur in the clean surface layer, a linear steady-state oxygen concentration profile will develop in region I.

The governing equation for $C^{\mathrm{I}}(z)$ within region I for $0 < z < L_0$ is given as

$$\frac{\partial^2 C^{\mathrm{I}}}{\partial z^2} = 0 \tag{18}$$

with boundary conditions:

(i) at $z = 0$,

$$C^{\mathrm{I}} = C_0$$

(ii) at $z = L_0$,

$$C^{I}(L_0) = C^{II}(L_0)$$

The governing equation for $C^{II}(z)$ within region II for $L_0 < z < L_0 + T$ is given as

$$\frac{\partial^2 C^{II}}{\partial z^2} = \frac{r}{D_s} \tag{19}$$

with boundary conditions:

(iii) at $z = L_0 + T$,

$$\frac{dC^{II}}{dz} = 0$$

(iv) at $z = L_0$,

$$D_s \frac{dC^{I}}{dz} = D_s \frac{dC^{II}}{dz}$$

Eqs. (18) and (19) are coupled via boundary conditions (ii) and (iv) and can be solved for the respective steady-state soil gas oxygen concentration profiles in each region:

$$\frac{C^{I}(z)}{C_0} = 1 - \frac{rT^2}{D_s C_0}\left(\frac{z}{T}\right) \tag{20}$$

$$\frac{C^{II}(z)}{C_0} = 1 + \frac{rT^2}{D_s C_0}\left[\frac{1}{2}\left(\frac{z}{T}\right)^2 - \left(\frac{L_0}{T} + 1\right)\left(\frac{z}{T}\right) + \frac{1}{2}\left(\frac{L_0}{T}\right)^2\right] \tag{21}$$

It should be noted that, if L_0 is set equal to zero, Eq. (21) reduces to Eq. (10) of scenario I. Since the rate of oxygen consumption is assumed to be constant ($= r$) whenever the soil gas oxygen concentration (C) is greater than zero, the flux of oxygen into the soil surface is directly related to the depth (T) of the oxygenated and microbially active soil layer:

$$J(z = 0) = rT \tag{22}$$

5.2.2. Case B: the contaminated subsurface soil layer is only partially oxygenated

If the rate of oxygen consumption by soil microorganisms is greater than the rate of oxygen diffusion into the soil, the oxygen concentration will decrease rapidly with depth as shown for case B in Fig. 5. Oxygen will penetrate only a limited distance z_p into the soil. At depths greater than the oxygen penetration distance ($z > z_p$), the oxygen concentration in the soil gas is zero. Since no microbial activities are assumed to occur in the clean surface layer, a linear steady-state oxygen concentration profile will develop in region I. Finally, at steady-state, the mass flux of oxygen into the contaminated soil layer (region II) is equal to the mass of oxygen taken up in the microbially active zone, i.e.

$$J(z = L_0) = -D_s \frac{dC^{II}}{dz}(z = L_0) = r(z_p - L_0)$$

The governing equation for $C^{I}(z)$ within region I for $0 < z < L_0$ is given as

$$\frac{\partial^2 C^{I}}{\partial z^2} = 0 \tag{23}$$

with boundary conditions:

(i) at $z = 0$,

$$C^{I} = C_0$$

(ii) at $z = L_0$,

$$C^{I}(L_0) = C^{II}(L_0)$$

The governing equation for $C^{II}(z)$ within region II for $L_0 < z < L_0 + T$ is given as

$$\frac{\partial^2 C^{II}}{\partial z^2} = \frac{r}{D_s} \tag{24}$$

with boundary conditions:

(iii) at $z = L_0$,

$$\frac{dC^{II}}{dz} = \frac{r}{D_s}(L_0 - z_p)$$

(iv) at $z = L_0$,

$$D_s \frac{dC^{I}}{dz} = D_s \frac{dC^{II}}{dz}$$

Eqs. (23) and (24) are coupled via boundary conditions (ii) and (iv) and can be solved for the respective steady-state soil gas oxygen concentration profiles in each region:

$$\frac{C^{I}(z)}{C_0} = 1 - \frac{r(z_p - L_0)^2}{D_s C_0}\left(\frac{z}{z_p - L_0}\right) \tag{25}$$

$$\frac{C^{II}(z)}{C_0} = 1 + \frac{r(z_p - L_0)^2}{D_s C_0}\left[\frac{1}{2}\left(\frac{z}{z_p - L_0}\right)^2 - \left(\frac{z_p}{z_p - L_0}\right)\left(\frac{z}{z_p - L_0}\right) + \frac{1}{2}\left(\frac{L_0}{z_p - L_0}\right)^2\right] \tag{26}$$

It should be noted that, if L_0 is set equal to zero, Eq. (26) reduces to Eq. (13) of scenario I. Since $C^{II}(z_p) = 0$, it follows from Eq. (26) that

$$z_p = \sqrt{\frac{2D_s C_0}{r} + L_0^2} \tag{27}$$

Fig. 6 shows the oxygen penetration distance $(z_p - L_0)$ into contaminated subsurface soil as a function of L_0 for different values of D_s. It can be seen that, even in the

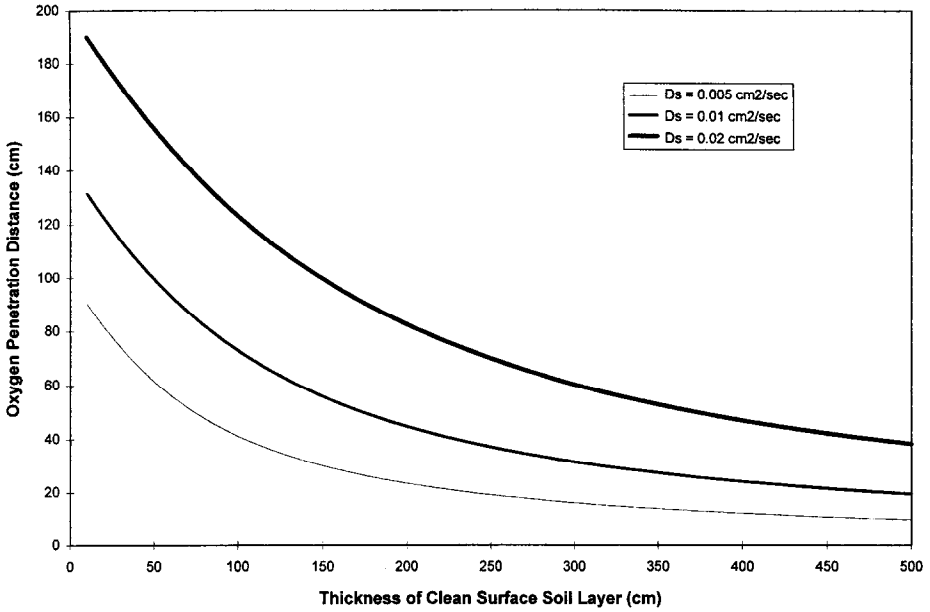

Fig. 6. Oxygen penetration distance ($z_p - L_0$) into contaminated subsurface soil (bulk density $\rho_b = 1.5\,g\,cm^{-3}$) as a function of clean surface soil layer thickness (L_0) for different D_s values. The total petroleum hydrocarbon biodegradation rate is $5\,ppm\,TPH\,day^{-1}$ and the atmospheric oxygen concentration is $294\,mg\,O_2\,(l\,air)^{-1}$.

presence of relatively thick clean surface soil layers, oxygen is expected to penetrate significant distances into the contaminated subsurface soil if the TPH biodegradation rate is $5\,ppm\,day^{-1}$. For example, even if the clean soil surface layer is 100 cm (3 ft) thick, oxygen is expected to penetrate approximately 73 cm into the contaminated subsurface soil layer given an oxygen diffusion coefficient (D_s) of $0.01\,cm^2\,s^{-1}$.

Eq. (27) is not only useful for calculating the oxygen penetration distance z_p, but also for determining whether, for a given set of conditions, the subsurface layer is fully (case A) or only partially (case B) oxygenated. If $z_p < L_0 + T$, region II is only partially oxygenated (case B). Consequently, using Eq. (27), the subsurface layer is only partially oxygenated if the following condition is satisfied:

$$\frac{rT^2}{D_s C_0} > \frac{2T}{2L_0 + T} \tag{28}$$

Otherwise, region II is fully oxygenated (case A).

Since the rate of oxygen consumption is assumed to be constant ($= r$) whenever the soil gas oxygen concentration (C) is greater than zero, the flux of oxygen into the soil surface is directly related to the depth ($z_p - L_0$) of the oxygenated and microbially active soil layer:

$$J(z = 0) = r(z_p - L_0) \tag{29}$$

5.3. Scenario III: oxygen diffusion into a soil pile

This scenario is shown in Fig. 7 where contaminated soil is placed in a spherical soil pile of radius R_t. Oxygen will diffuse only a limited distance $(R_t - R_p)$ into the soil pile and no oxygen will be present at any point where $R < R_p$.

The governing equation for the steady-state oxygen concentration profile within a spherical soil pile is given as

$$\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{dC}{dR}\right) = \frac{r}{D_s} \tag{30}$$

with boundary conditions:

(i) at $R = R_t$,

$$C = C_0$$

(ii) at $R = R_t$,

$$D_s\frac{dC}{dR}4\pi R_t^2 = r\cdot\int_{R_p}^{R_t}4\pi R^2\,dR$$

The second boundary condition represents the fact that the mass flux of oxygen into the soil pile is equal to the mass of oxygen taken up in the microbially active zone. Using both boundary conditions, Eq. (30) may be integrated twice to obtain the steady-state solution for the oxygen concentration in the soil gas as a function of the pile radius:

$$\frac{C(R)}{C_0} = 1 + \frac{r}{D_s C_0}\left[\left(\frac{R^2 - R_t^2}{6}\right) + \left(\frac{R_p^3}{3R} - \frac{R_p^3}{3R_t}\right)\right] \tag{31}$$

Since $C(R_p) = 0$, it follows that R_p can be obtained by solving the following equation:

$$\frac{R_p^3}{3R_t} - \frac{R_p^2}{2} = \frac{D_s C_O}{r} - \frac{R_t^2}{6} \tag{32}$$

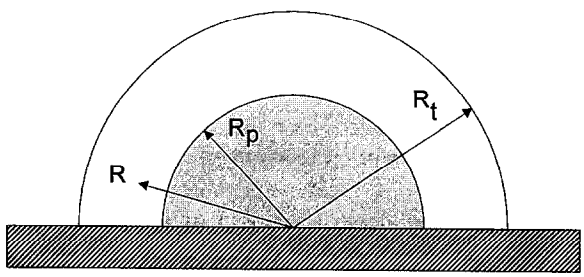

Fig. 7. Oxygen diffusion into a spherical soil pile of radius R_t (scenario III). Soil is oxygenated at any point where $R > R_p$.

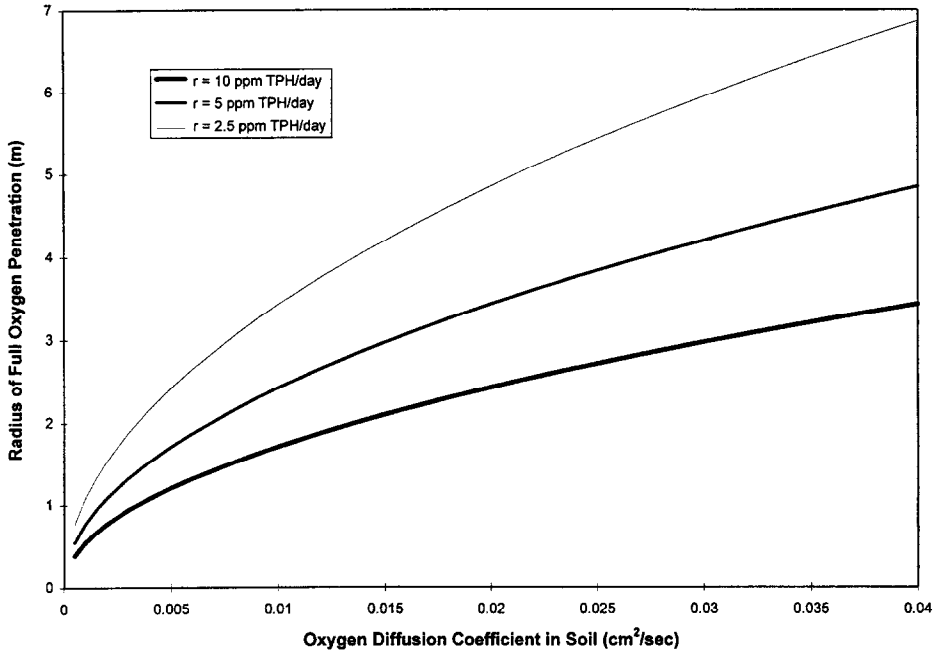

Fig. 8. Radius of full oxygen penetration as a function of D_s for different TPH biodegradation rates. The soil bulk density (ρ_b) is $1.5\,g\,cm^{-3}$ and the atmospheric oxygen concentration is $294\,mg\,O_2\,(l\,air)^{-1}$.

A soil pile is fully oxygenated if $R_p = 0$. Consequently, it follows from Eq. (32) that a soil pile is fully oxygenated if:

$$R_t \leq \sqrt{\frac{6\,D_s C_0}{r}} \tag{33}$$

Fig. 8 shows the radius of full oxygen penetration as a function of D_s for three different TPH biodegradation rates. According to these graphs it appears that most "real life" soil piles are expected to be fully oxygenated, particularly if the soil is well drained ($D_s > 0.01\ cm^2\ s^{-1}$) and TPH biodegradation rates are low ($r_{HC} < 10\,ppm\,TPH\,day^{-1}$), as is the case for unamended soils (see Fig. 2).

6. Estimation of cleanup times

The cleanup time ($\Delta t_{cleanup}$) for a specific oxygenated contaminated soil volume (or layer) depends on the initial hydrocarbon concentration ($C_{HC}^{initial}$) and the hydrocarbon biodegradation rate (r_{HC}) and can be computed as:

$$\Delta t_{cleanup} = \frac{C_{HC}^{initial}}{r_{HC}} \tag{34}$$

The hydrocarbon biodegradation rate (r_{HC}) may either be determined from biodegradation experiments or obtained from a correlation with measured oxygen consumption rates (r) according to Eq. (8) above. Assuming that (a) the soil contamination is homogeneous, i.e. $C_{HC}^{initial}$ is constant throughout the contaminated soil layer, (b) the hydrocarbon biodegradation rate is constant with respect to both contaminant location and time, and (c) biodegradation occurs as long as the oxygen concentration is greater than zero ($C > 0$), it follows that all hydrocarbon contamination will be removed from the oxygenated contaminated soil volume after the time interval $\Delta t_{cleanup}$.

The length of the total cleanup time ($t_{cleanup}$) for all hydrocarbon contamination at a given site is dependent on the thickness (T) and the oxygenation status (fully or partially oxygenated) of the contaminated region. If the contaminated region is fully oxygenated (case A in scenarios I or II, or Eq. (33) is satisfied in scenario III), the entire soil layer of thickness T is bioremediated within the cleanup time period $\Delta t_{cleanup}$. Therefore, the total cleanup time ($t_{cleanup}$) is equal to the cleanup time period ($\Delta t_{cleanup}$) for the fully oxygenated contaminated soil layer.

If the contaminated surface soil is only partially oxygenated (case B in scenario I), the oxygenated soil layer of thickness z_p will be bioremediated first. The total bioremediation time for this soil layer may be computed using Eq. (34). After all hydrocarbon contamination has been removed, oxygen must diffuse through the remediated (clean) soil layer of thickness z_p to reach hydrocarbon contamination in the deeper soil stratum. This situation can now be mathematically described by the equations given in case B of scenario II which deals with oxygen diffusion through a clean soil layer of thickness L_0 (equal to the z_p value calculated in the first step) into a region of contaminated subsurface soils. A new steady-state oxygen concentration profile will develop and a new oxygen penetration distance (L_1) may be computed according to Eq. (27):

$$L_1 = \sqrt{\frac{2 D_s C_0}{r} + L_0^2}$$

The thickness of the newly oxygenated soil layer is $\Delta L_1 = L_1 - L_0$. The cleanup time for this soil layer may be computed using Eq. (34). After all hydrocarbon contamination has been removed from this layer, oxygen must diffuse through a clean soil layer of thickness L_1 to reach hydrocarbon contamination in deeper soil strata. Again, a new oxygen penetration distance may be computed according to the general formula:

$$L_n = \sqrt{\frac{2 D_s C_0}{r} + L_{n-1}^2} \tag{35}$$

The thickness of the newly oxygenated layer is $\Delta L_n = L_n - L_{n-1}$. This process of bioremediating successively deeper soil strata continues until the entire contaminated region is cleaned, i.e. when $L_n > T$ (scenario I) or $L_n > T + L_0$ (scenario II). For additional clarification, Fig. 9 shows a representative illustration of successively oxygenated soil layers and the respective nomenclature for L_i and ΔL_i. The total number of successively bioremediated soil layers required for the cleanup of the entire contaminated region is $n + 1$ for scenario I and n for scenario II. If both $C_{HC}^{initial}$ and r_{HC} are

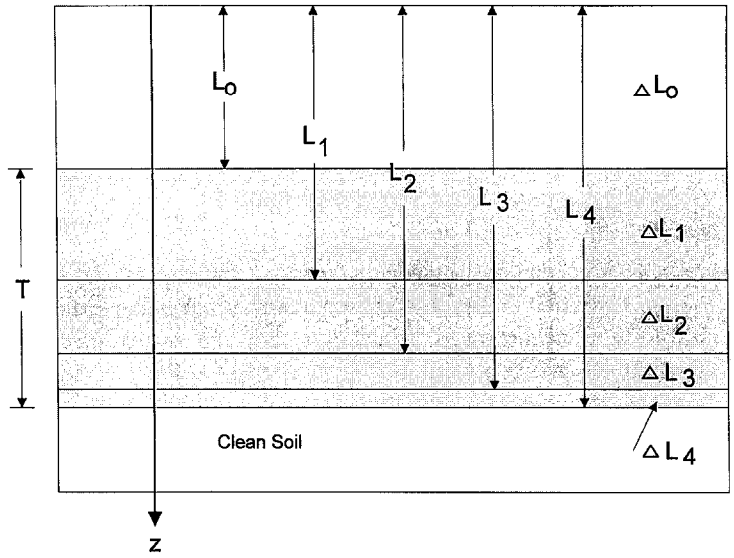

Fig. 9. Representative illustration of successively oxygenated soil layers.

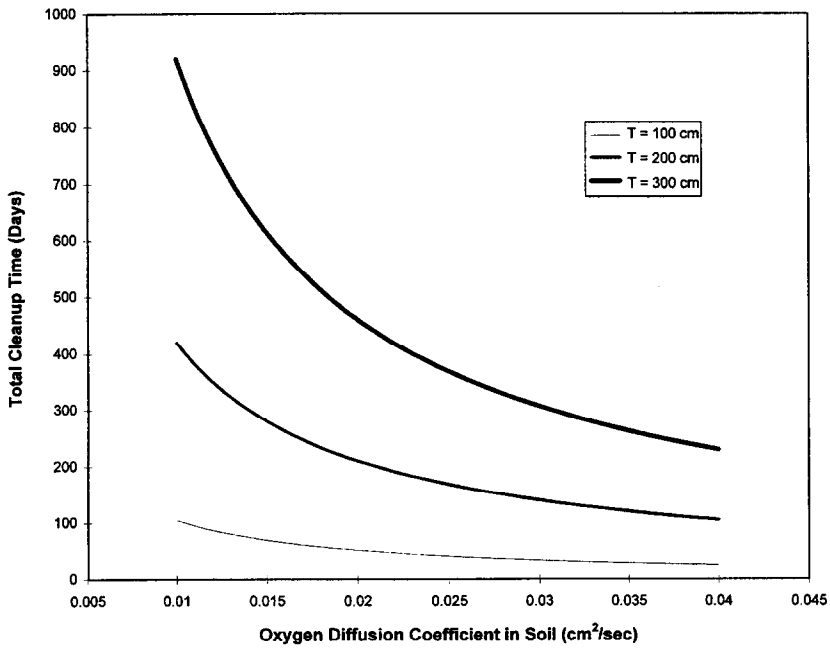

Fig. 10. Total cleanup time as a function of D_s for surface soils with three different depths (T) of hydrocarbon contamination. The initial hydrocarbon concentration is 1000 ppm TPH, the soil bulk density (ρ_b) is $1.5\,g\,cm^{-3}$, and the atmospheric oxygen concentration is $294\,mg\,O_2\,(l\,air)^{-1}$.

constant throughout the entire contaminated region, the cleanup time period ($\Delta t_{cleanup}$) for each oxygenated layer (ΔL_n) is the same and is given by Eq. (34). Consequently, the total cleanup time ($t_{cleanup}$) for all hydrocarbon contamination within a region is

$$t_{cleanup} = (n+1) \cdot \Delta t_{cleanup} \tag{36a}$$

for scenario I, and

$$t_{cleanup} = n \cdot \Delta t_{cleanup} \tag{36b}$$

for scenario II.

Fig. 10 shows the total estimated cleanup time as a function of D_s for surface soils with three different depths (T) of hydrocarbon contamination under conditions in which the overall bioremediation process is diffusion-limited, i.e. when successively deeper soil layers are bioremediated as shown in Fig. 9. The initial hydrocarbon concentration is 1000 ppm TPH. As expected, the total cleanup time was found to be inversely related to the magnitude of D_s. For example, the times required to passively bioremediate a 200 cm (T) thick layer of contaminated surface soil are 420, 210 and 105 days for D_s values of 0.01, 0.02 and 0.04 $cm^2\ s^{-1}$, respectively. In addition, the total cleanup time is proportional to T^2. For example, it takes four times longer to passively bioremediate a contaminated surface soil layer of 200 cm thickness than a 100 cm thick layer.

Finally, since $\Delta t_{cleanup}$ is affected by the magnitude of the initial hydrocarbon concentration (see Eq. (34)), the total cleanup times for an environmental scenario with different initial hydrocarbon contamination levels can easily be calculated by multiplying the cleanup times given in Fig. 10 by a factor which accounts for the difference in initial hydrocarbon concentrations. For example, all cleanup times given in Fig. 10 are twice as long if the initial hydrocarbon concentration is 2000 ppm instead of 1000 ppm.

7. Discussion and conclusions

Before introducing potential applications of the passive bioremediation approach it is necessary to address some of the assumptions which were used in the above derivations.

First, it was assumed that oxygen consumption due to microbial hydrocarbon biodegradation occurs at a constant rate (r) as long as the oxygen concentration (C) in the soil gas is greater than zero. It is conceivable that the hydrocarbon biodegradation rate (r_{HC}) decreases significantly or becomes zero if the oxygen concentration drops below a certain threshold values C_{th} (i.e. $r_{HC} = 0$ if $C < C_{th}$). In soil respirometry experiments involving crude oil contaminated soils [23] it was found that oxygen consumption rates remained constant if C was above 5% (data not shown). However, no attempts were made to investigate the effects of lower oxygen concentrations on r or r_{HC}. In an early study by Longmuir [26] it was found that the respiration rate of bacteria decreases at low aqueous dissolved oxygen concentrations. The half saturation constant (K_m) for oxygen was found to be in the range of 10^{-8} molar which is approximately 0.3×10^{-3} mg l^{-1} dissolved oxygen. According to these data, the oxygen consumption rate would be half the maximum rate if the dissolved oxygen concentration in the soil water is approximately 0.3×10^{-3} mg l^{-1}. Since soil water in equilibrium with atmospheric oxygen ($C_0 = 20\%$ (v/v) or 294 mg O_2 (l air)$^{-1}$) has a dissolved oxygen concentration of approximately 8 mg l^{-1}, it is obvious that a threshold concentration for oxygen

in the soil gas must be extremely small (i.e $< 0.001\%$ (v/v) using Henry's law). Devinny and Islander [12] modeled oxygen diffusion and microbial oxygen consumption in hydrocarbon contaminated soils and found that the choice of threshold concentration (C_{th}) did not have a significant effect on the overall model system characteristics. Consequently, these investigators also chose a threshold concentration of zero in all of their subsequent modeling work.

Second, it was assumed that the oxygen consumption rate (r) is zero in clean soil layers. Since most "clean" soil will contain some organic matter, it is expected that some background respiration will be present in uncontaminated soils, particularly in soils characterized by high organic matter content. The oxygen consumption rate of fertilized clean sand with a total organic carbon (TOC) content of 0.4% was found to be approximately 3.5×10^{-5} mg O_2 (kg soil s)$^{-1}$ [23]. This is equivalent to a hydrocarbon biodegradation rate of 1 ppm TPH day^{-1}. However it must be noted that most "clean" *in situ* soils are expected to have lower respiration rates since they have not been amended with fertilizers. In addition, the oxygen consumption rate (r) in clean soil layers may be significant if hydrocarbon vapors move from contaminated to clean soil regions. For example, Ostendorf and Kampbell [27] found that biodegradation activities in the clean vadose zone prevented the escape of volatile fuel hydrocarbons from the water table to the atmosphere. Consequently, if the clean soil layer contains significant amounts of biodegradable organic matter or is exposed to hydrocarbon vapors, the above equations may be modified by including terms for soil organic matter or hydrocarbon vapor associated respiration.

Third, in the calculation of cleanup times (Eq. (34)) it was assumed that, given enough time, all hydrocarbon contamination would be removed from the soil. This assumption holds primarily for light hydrocarbon fuels such as gasoline and jet fuels. It has been shown that heavier petroleum contaminants such as crude oils and heavy fuel oils (bunker C, motor oil, etc.) are not completely biodegraded even when optimal environmental conditions are present [28]. Consequently, a residual TPH fraction is likely to remain in the soil after bioremediation treatment has been completed. In addition, it should be noted that the TPH biodegradation rates given in Fig. 2 relate mainly to light hydrocarbon fuels. It is therefore expected that heavier hydrocarbons biodegrade incompletely and at lower rates compared to those given in Fig. 2.

Finally, the assumption that soil layers are homogenous with respect to properties such as porosity, moisture, hydrocarbon contamination, oxygen consumption rates, or diffusion coefficients (D_s) may be appropriate for disturbed and mixed soils (e.g. excavated soil piles), but is probably unrealistic for *in situ* soils which are often characterized by significant heterogeneities. If the above soil characteristics vary throughout the soil layer, a more complex numerical model (instead of the above analytical solutions) will be required to provide estimates for the oxygen penetration distance and passive bioremediation cleanup times. It should be noted at this point that clay lenses, which are known to impede convective air flow during bio/venting operations, are not necessarily a barrier to oxygen diffusion as long as the clay has a relatively low moisture content (see Fig. 1) because diffusion, unlike convection, is not affected by the size of the pores (diameter), but rather the magnitude of air-filled porosity α (see Eq. (3)).

Given that the use of these simplifying assumptions does not significantly affect the above estimates for oxygen penetration distances and cleanup times, it is clear that passive bioremediation may be a feasible treatment alternative for many petroleum contaminated soils. Both the depth of oxygen penetration as well as the total cleanup time are strongly dependent on the magnitude of the diffusion coefficient for oxygen in soil (D_s). Thus, in order to optimize the effectiveness of passive bioremediation, it is imperative that conditions be maintained which maximize D_s. This can most easily be accomplished by controlling the moisture content of the contaminated soil (see Fig. 1).

Passive bioremediation is expected to be particularly applicable in cases where the minimization of cleanup times is not a major remediation objective. Active bioremediation techniques (i.e. bioventing, land-treatment, composting) are commonly used to accelerate hydrocarbon biodegradation in order to reduce the leaching potential (i.e. groundwater impact) and thus the potential risk to environmental receptors. However, if leaching risks are insignificant (e.g. in highly weathered soils) or can be minimized by simple engineering measures, it may not be necessary to accelerate the biodegradation process. In these cases, passive bioremediation may be a feasible and cost-effective treatment alternative for reducing TPH concentrations in hydrocarbon contaminated soils.

Appendix A. Nomenclature

C	oxygen concentration in soil gas ($g\,l^{-1}$)
C_0	atmospheric oxygen concentration ($g\,l^{-1}$)
C_{HC}	hydrocarbon concentration in soil ($g\,TPH\,kg^{-1}$)
C_{th}	threshold concentration for oxygen ($g\,l^{-1}$)
D_a	diffusion coefficient for oxygen in air ($cm^2\,s^{-1}$)
D_s	diffusion coefficient for oxygen in soil ($cm^2\,s^{-1}$)
J	mass flux of oxygen across soil surface ($g\,cm^2\,s^{-1}$)
L_0	thickness of the clean soil layer (m)
L_i	thickness of the oxygenated (i.e. bioremediated) soil layer i (m)
n	number of successively bioremediated soil layers
ppm	$mg\,kg^{-1}$ soil
r	rate of oxygen consumption ($g(l\,s^{-1})$)
r_{HC}	TPH biodegradation rate ($mg\,TPH(kg\ soil\ day)^{-1}$)
R	radius within spherical soil pile (m)
R_p	radius of oxygenation within spherical soil pile (m)
R_t	total radius of the spherical soil pile (m)
T	thickness of contaminated soil layer (m)
$t_{cleanup}$	total cleanup time for all hydrocarbon contamination (days)
$\Delta t_{cleanup}$	cleanup time for a specific soil layer or volume (days)
TPH	total petroleum hydrocarbon
z	soil depth (m)
z_p	oxygen penetration distance (m)
α	soil volumetric air content ($l\,l^{-1}$)
μ	soil moisture ($kg\,kg^{-1}$)

θ	soil porosity ($1l^{-1}$)
ρ_b	soil bulk density (kgl^{-1})
ρ_p	soil particle density (kgl^{-1})
ρ_{water}	density of water (kgl^{-1})
τ_g	gas tortuosity factor

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