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Biodegradation Phenomena during Soil Vapor Extraction: Sensitivity Studies for Single Substrate Systems

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Biodegradation Phenomena during Soil Vapor Extraction: Sensitivity Studies for Single Substrate Systems

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ABSTRACT

Biodegradation phenomena may take place during soil remediation by vapor stripping. Mass transfer limitations are likely to occur due to transport of oxygen and the contaminant between the aqueous and gaseous phases. Sensitivity studies performed with a one-dimension model show that under optimal conditions biodegradation substantially reduces the cleanup time, especially when high removal percentages are desired, leading to lower treatment cost. A first series of runs without nutrient limitations showed that the system is relatively insensitive to changes in the major biological parameters when severe mass transfer limitations occur. Nutrient limitations may seriously impair the advantages derived from biodegradation, especially if they occur during the final stages of the cleanup.

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INTRODUCTION

A mathematical model was previously (1) presented for the biodegradation processes that may occur during soil vapor extraction (SVE). That model was able to follow the trends of the major features observed in those field experiments in which bioremediation was studied while SVE was being carried out. These are 1) a constant rate of biodegradation (zero order with respect to contaminant and biomass concentrations) (2–4), and 2) a very substantial increase in the contribution of biodegradation to the cleanup without serious increase in the total cleanup time when the gas flux through the soil was decreased tenfold (5, 6).

We proposed that those observations may be due to a relatively slow rate of oxygen transfer from the gas to the bulk aqueous phase, similar to the mass transfer limitations that have been observed for contaminant stripping during SVE. We therefore developed a nonequilibrium model in which contaminant and oxygen are present in a mobile gas phase and in an immobile aqueous phase; the biological processes are described by Monod kinetics. The model as originally developed includes a rather large number of parameters associated with biodegradation. It proved possible to make some simplifications without interfering with the ability of the model to generate satisfactory results, thereby facilitating its use in examining the coupling of bioremediation and SVE.

However, even the simplified model suffered from the fact that computer time requirements were quite large, with some runs taking more than 2 days on a microcomputer with a 12-MHz 80286 microprocessor and math coprocessor. This despite our restriction to a one-dimensional (column) model and use of the largest possible time increments Δt in the integrations. Our first efforts were therefore directed toward speeding up the algorithm through the inclusion of several approximations. Reductions of more than 95% in the computer run times were achieved for those situations which were most time-consuming, with errors introduced by the approximations being below 1%.

The present paper presents sensitivity studies performed with the complete model as described in our first paper (1). The very large number of parameters used in that model will interfere with its use for predictive analysis simply because collection of all the information needed on a case-by-case basis would be very expensive and time-consuming. Nevertheless, the rapid growth in the use of SVE and aerobic bioremediation and the savings that can be expected from improved design make the availability of a model which may provide better understanding of the process highly desirable. One can also hope that the information and insights developed may prove useful in the modeling of other techniques such as in-situ flushing and sparging in the saturated zone.

RESULTS AND DISCUSSION

The previous paper presented two series of runs in which the gas flux through the column was changed tenfold by decreasing the pressure gradient. Each series consisted of five runs with different lumped parameter mass transfer coefficients, ranging from $\lambda_C = 10^{-3}$ to $\lambda_C = 10^{-7}$ s^{-1}. (λ_C is the first-order rate constant for mass transfer of contaminant C between the vapor and the stationary phases.) The ratio of the oxygen and the contaminant mass transfer rate parameters was always taken as 2, approximately the ratio between the diffusivities of oxygen and the most common organic contaminants in the aqueous phase (7). Here we

TABLE 1
Default Values for the Parameters Used in Runs Presented in Figures

Column length (L)	50 cm
Column radius (r)	10 cm
Number of volume elements into which the column is partitioned (N)	10
Voids fraction associated with the mobile phase (ν)	0.2
Volumetric moisture content of the soil (ω)	0.2
Inlet pressure (P_{in})	1 atm
Outlet pressure (P_{out})	0.9 atm
Temperature (T)	15°C
Darcy's constant (K_D)	50 cm^2/atm·s
Soil density (ρ)	1.5 g/cm^3
Initial contaminant concentration ($M/\rho V$)	100 mg contaminant/kg soil
Initial biomass concentration (B)	10^{-3} mg/L
Henry's constant of contaminant (Kh_C)	10^{-3}
Henry's constant of oxygen (Kh_O)	30
Stoichiometric coefficient for substrate (n_C)	2 g substrate/g biomass
Stoichiometric coefficient for oxygen (n_O)	3 g oxygen/g biomass
Maximum velocity constant (K)	2×10^{-5} s^{-1}
Michaelis constant of substrate (K_C)	0.1 mg/L
Michaelis constant of oxygen (K_O)	0.1 mg/L
Die-off coefficient of biomass (K_B)	10^{-7} s^{-1}
For runs including one limiting nutrient (Figs. 11–15):	
Initial nutrient concentration (A_1)	3.0 mg/L
Stoichiometric coefficient for limiting nutrient (n_1)	0.1 g nutrient/g biomass
Michaelis constant for limiting nutrient (K_1)	0.1 mg/L

will use the results of the first series of calculations as standard runs against which the results of runs with different values of the various parameters will be compared in the sensitivity analysis. The default (standard) parameter values are given in Table 1. The reader is referred to our first paper (1) for a list of symbols used and the mathematical equations which constitute the model. For further comparison purposes we show here, in Figs. 1 and 2, the results obtained in two of the so-called standard runs conducted at high ($\lambda_C = 10^{-3}\ \mathrm{s}^{-1}$, $\lambda_O = 2 \times 10^{-3}\ \mathrm{s}^{-1}$) and low ($\lambda_C = 10^{-7}\ \mathrm{s}^{-1}$, $\lambda_O = 2 \times 10^{-7}\ \mathrm{s}^{-1}$) mass transfer coefficients.

We first study the effects of some of the parameters (the effective Henry's constant for the contaminant, Kh_C; the substrate to biomass stoichiometric coefficient, n_C; the λ_C/λ_O ratio; etc.) for a system having a single substrate present and having unlimited nutrients (such as nitrate and phosphate). Then, since these limitations are likely to occur, especially in systems in which large biodegradation contributions are desired and in which no addition of nutrients is made, we explore the influence of nutrients in the model.

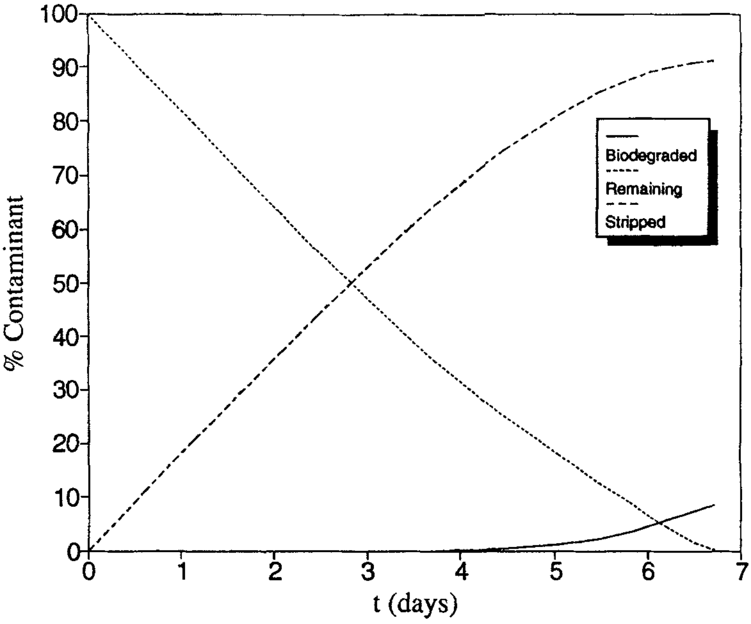

FIG. 1 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-3}\ \mathrm{s}^{-1}$; $\lambda_O = 2 \times 10^{-3}\ \mathrm{s}^{-1}$. See Table 1 for parameter values.

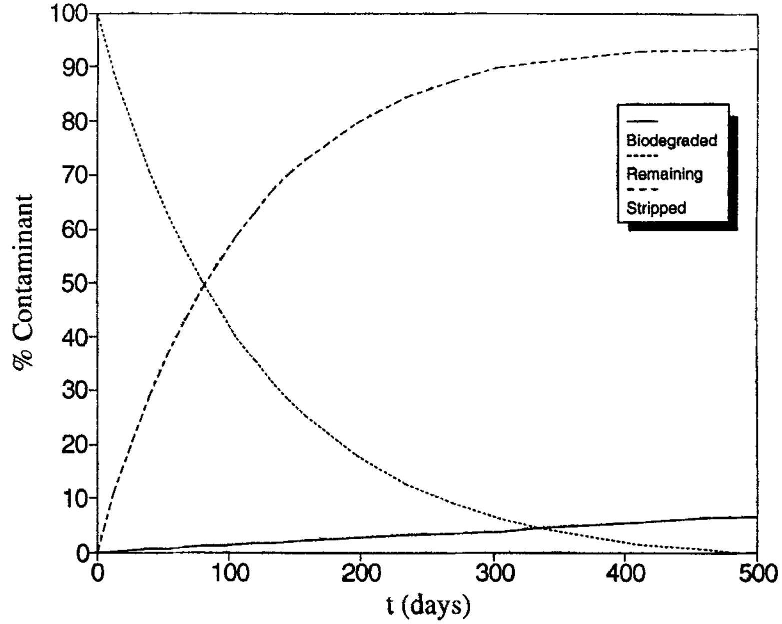

FIG. 2 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-7}\ s^{-1}$; $\lambda_O = 2 \times 10^{-7}\ s^{-1}$. See Table 1 for parameter values.

SENSITIVITY STUDIES WITHOUT NUTRIENT LIMITATIONS

Figure 3 shows the biodegradation contribution obtained for the standard runs and four more series performed in which the following parameters were varied singly: 1) the substrate to biomass stoichiometric coefficient, n_C; 2) the starting biomass concentration, B_0; 3) the effective Henry's constant of the contaminant, Kh_C; and 4) the maximum rate constant for biodegradation, K. In each of these series one parameter was varied while the others were all given their default values, listed in Table 1.

An increase of the *substrate to biomass stoichiometric coefficient* (n_C) from 2 to 4 g of substrate needed to generate 1 g of new biomass leads to a lower oxygen demand for biodegradation which in the absence of endogenous respiration is given by n_O/n_C rather than by the amount of oxygen needed to degrade substrate completely to CO_2 and H_2O. This allows larger contributions from the biological process under the oxygen-limited conditions that occur when very low values of the mass transfer

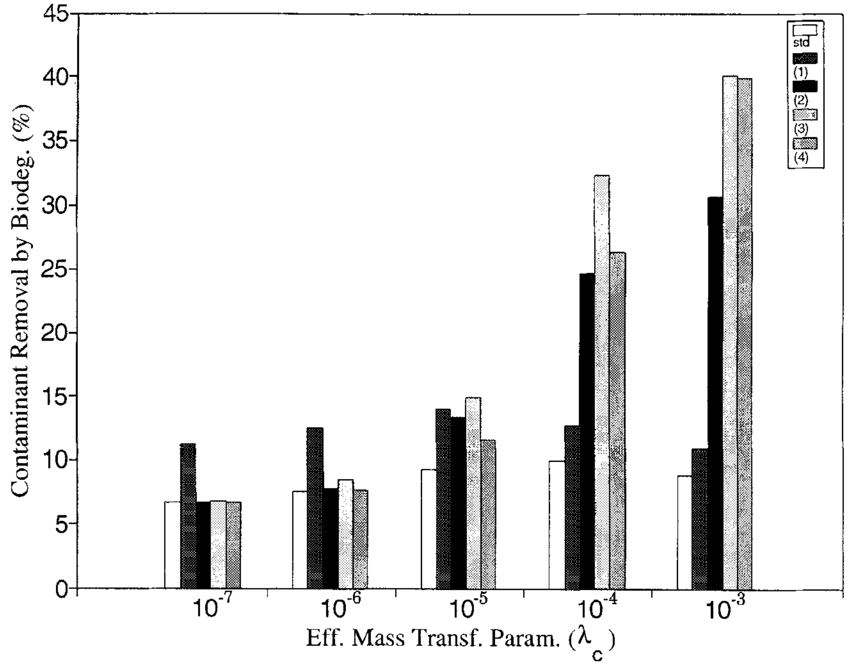

FIG. 3 Relative contribution of biodegradation to the cleaning process for different conditions ($\lambda_O = 2 \times \lambda_C$ for all the cases). (1): Stoichiometric coefficient for contaminant ($n_C = 2 \times$ standard; (2): Initial biomass concentration (B_0) = 100 × standard; (3): Effective Henry's constant (Kh_C) = 0.5 × standard; (4): Maximum growth rate (K) = 2 × standard. See Table 1 for standard parameter values.

rate parameter are used ($\lambda_C = 10^{-7}$ s^{-1}). For this value of the mass transport rate parameter the results obtained with $n_C = 4$ become quite similar to those of Fig. 2 (where $n_C = 2$), with biodegradation contribution increasing linearly with time, but the slope doubles as the n_C value is doubled, leading to a total cleanup time which is about 85% of that obtained for $n_C = 2$.

One might expect a similar increase in the relative contribution of biodegradation over the entire range of mass-transfer coefficient values, since an increase in the stoichiometric coefficient n_C leads to an equivalent increase in the variable usually known as the maximum substrate utilization rate (Kn_C in this work). Results presented in Fig. 3 show that this is not so, and that the increase of the relative contribution of biodegradation to the total cleanup is smaller for the higher values of the mass transfer rate coefficients since an induction period occurs during which biodegradation is negligible; most of the contaminant is stripped during this time (see Fig. 1).

This induction period, after which the biodegradation is noticeable, was discussed earlier (1) and is a result of the time needed for the development of a significant biomass population (from 1 μg/L to 1 mg/L). Nevertheless, increasing the *initial biomass concentration* from 1 to 100 μg/L of aqueous phase does not increase the biodegradation contribution when very low values of the mass transfer rate parameters are used. This is in agreement with the situation discussed previously and can be attributed to the limiting effect of oxygen availability. Of course, this controlling effect disappears as the mass transfer rate parameter increases, and substantially higher biodegradation rates can be obtained as a result of the lower induction periods which result from higher initial biomass concentrations. This is clearly seen from a comparison of Figs. 1 and 4.

A decrease in the *effective Henry's constant (dimensionless) for the contaminant*, Kh_C, from 10^{-3} to 5×10^{-4} leads to a decrease in the vapor stripping rate, so the relative contribution of biodegradation is expected to increase. For sufficiently high values of the mass transfer rate param-

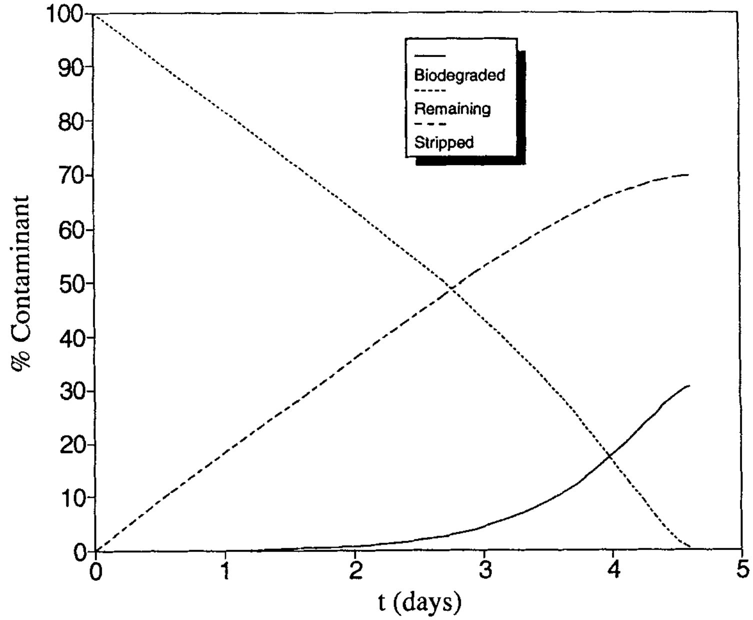

FIG. 4 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-3}\ \mathrm{s}^{-1}$; $\lambda_O = 2 \times 10^{-3}\ \mathrm{s}^{-1}$; $B_0 = 100 \times$ standard. See Table 1 for standard parameter values.

eters the process is governed basically by local equilibrium. (At $\lambda_C = 10^{-3}\ \mathrm{s}^{-1}$, indistinguishable results were obtained from the rigorous and the local equilibrium approximation models.) Figure 5 shows the results obtained in a run identical to the one presented in Fig. 1 except that the effective Henry's constant has been decreased by a factor of $\frac{1}{2}$. The induction periods until significant biodegradation takes place in the two runs are almost identical, but the amount of contaminant remaining at the end of the induction period for the run with smaller Kh_C is approximately twice as large as the amount remaining at the end of the induction period for the reference run. This ultimately results in a substantial increase in the contribution of biodegradation for the run with the reduced effective Henry's constant.

With regard to contaminant removal, stripping is diffusion limited at the two lowest values of λ_C in Fig. 3 and proceeds far from local equilibrium with regard to Henry's law. Therefore a moderate change in the effective Henry's constant does not cause significant differences in the driving force ($C^s - C^v/Kh_C$) for the stripping process since contaminant transport from the bulk immobile aqueous phase to the main gas stream

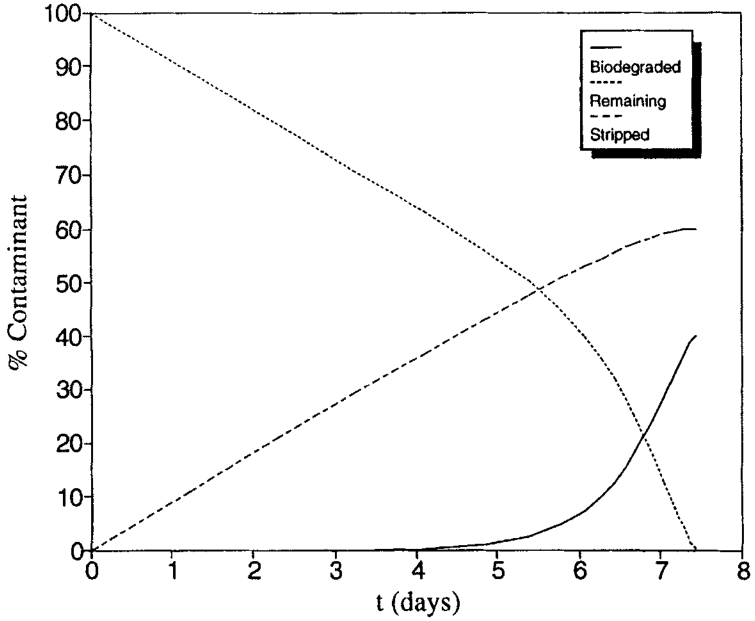

FIG. 5 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-3}\ \mathrm{s}^{-1}$; $\lambda_O = 2 \times 10^{-3}\ \mathrm{s}^{-1}$; $Kh_C = 0.5 \times$ standard. See Table 1 for standard parameter values.

is comparatively slow with respect to the rate of removal of contaminant by soil gas advection. Therefore the vapor contaminant concentration C^v is almost negligible in both cases and the driving force is approximately C^s. This is similar to the relatively small effect that was observed when a decrease in the air flow rate was tested under these conditions (1). Thus as diffusion-limited conditions appear, lower values of the contaminant vapor concentration should be expected in the stripped gas stream, but smaller differences will occur between contaminants of different volatility.

At high values of the mass-transfer rate parameters an increase in the *biodegradation kinetic constant* (K) from 2×10^{-5} to 4×10^{-5} s^{-1} leads to a major increase in the relative contribution of bioremediation. The effect is similar to that observed when the effective Henry's constant is decreased by a factor of $\frac{1}{2}$ (see Fig. 5), although about twice the time was needed in the later case for virtually complete remediation. The value of the maximum utilization rate (Kn_C) for this series is equal to the value resulting from the increase in n_C discussed above. But, as can be seen from comparison of Figs. 1 and 6, the induction period is now substantially lower, and when biodegradation starts to be noticeable a substantial

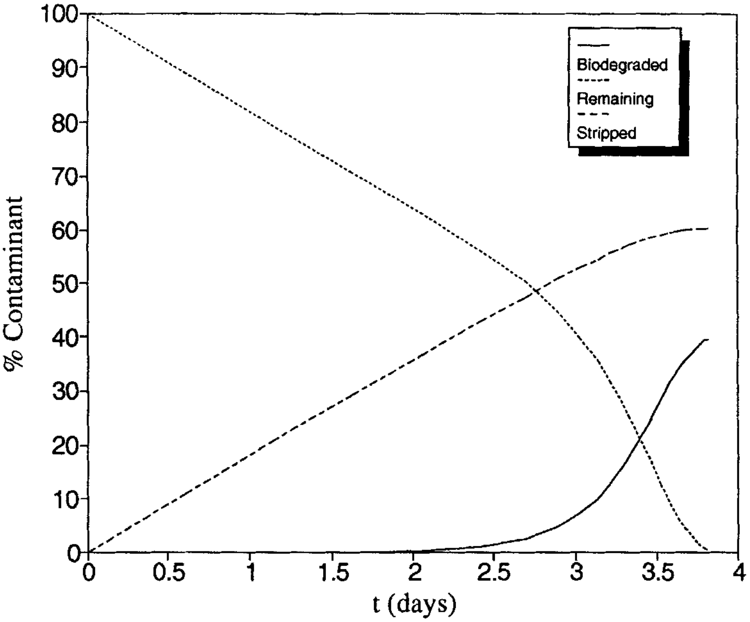

FIG. 6 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-3}$ s^{-1}; $\lambda_O = 2 \times 10^{-3}$ s^{-1}; $K = 2 \times$ standard. See Table 1 for standard parameter values.

amount of contaminant still remains in the column. This results in a much higher contribution of biodegradation to the cleanup, as can be seen in Fig. 3.

High values of *K* can also result in high oxygen consumption rates, so the dissolved oxygen concentrations reach lower levels even for high values of the oxygen mass transfer rate parameter ($\lambda_O = 2 \times 10^{-3}\ s^{-1}$). For moderately large values of the mass transfer coefficients ($\lambda_C = 10^{-4}\ s^{-1}$, $\lambda_O = 2 \times 10^{-4}\ s^{-1}$), the biodegradation rate is controlled by the dissolved oxygen supply rate, which yields a linear slope (instead of the exponential trend observed for Fig. 6) for biodegradation. This effect becomes increasingly noticeable as the mass transfer rate parameter λ_O decreases, giving rise to results indistinguishable from the standard run (in which all parameters are those given in Table 1) at the very small values of λ_O and λ_C used in the runs in Fig. 3.

As can be seen in Fig. 7, when the *microorganisms die-off coefficient*, K_B, was varied from 10^{-7} to $10^{-5}\ s^{-1}$, a substantial decrease in the rela-

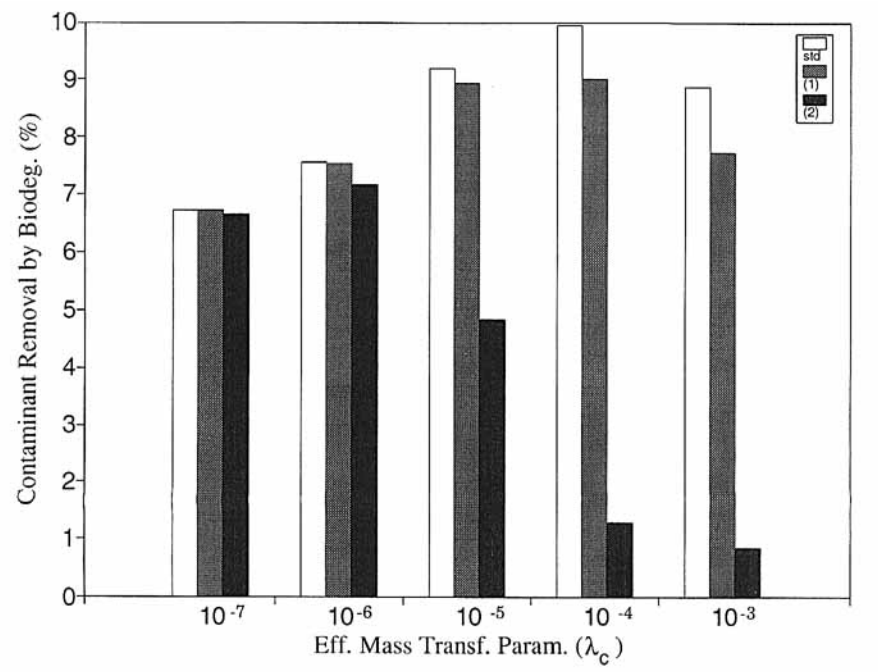

FIG. 7 Relative contribution of biodegradation to the cleaning process at different values of the die-off coefficient (K_B). ($\lambda_0 = 2 \times \lambda_C$ for all the cases.) (1): $K_B = 10 \times$ standard; (2) $K_B = 100 \times$ standard. See Table 1 for standard parameter values.

tive contribution of biodegradation was observed at the higher mass transfer rate parameter values where mass transfer kinetics are not significantly limiting. Substantial changes are seen as K_B values approach 10^{-5} s^{-1}. A better insight into this observation is obtained from Figs. 5 and 8, where results are presented for runs having the same value of the effective Henry's constant (5×10^{-4}) and K_B values of 10^{-7} and 10^{-5} s^{-1}, respectively. A longer induction period is observed at K_B values of the order of magnitude of the value used for the maximum rate constant, K (2×10^{-5} s^{-1}), at which the die-off term becomes comparable to the rate of biomass production under the nonlimited conditions that occur in the first stages of the remediation process. Here the biomass growth can be expressed as

$$dB/dt = (K - K_B)B \qquad (1)$$

so this result is not surprising.

As mass transfer limitation becomes more important (progressively decreasing values of λ_O in Fig. 7), changes in the K_B values are of less

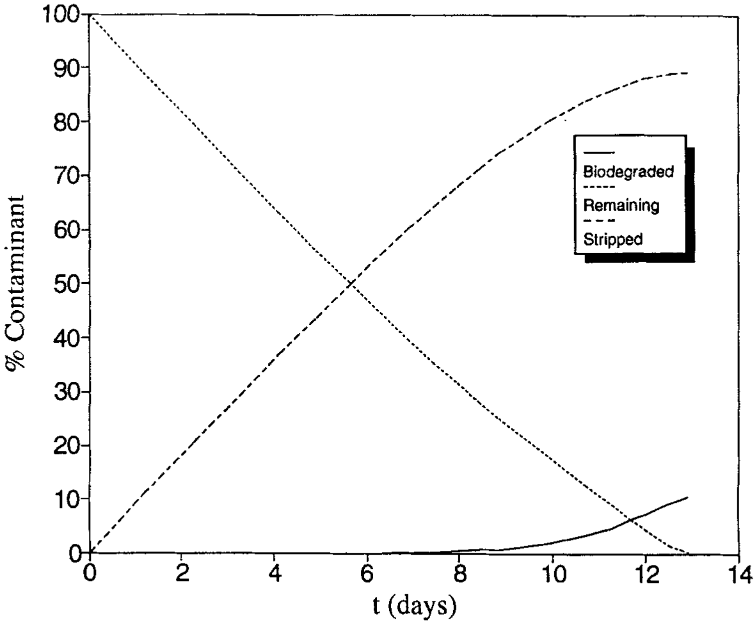

FIG. 8 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-3}$ s^{-1}; $\lambda_O = 2 \times 10^{-3}$ s^{-1}; $Kh_C = 0.5 \times$ standard; $K_B = 100 \times$ standard. See Table 1 for standard parameter values.

significance. An increase in rate of biomass death under these conditions (where no endogenous respiration is considered) would lead to a higher oxygen availability, giving rise to a counterbalancing increase of the biomass production term.

As indicated before, up to this point we have maintained a constant value of 2 for the *ratio of the mass transport rate parameters* λ_O/λ_C. However, we note that we are using effective instead of true vapor/liquid Henry's constants for the contaminant substrate in order to include sorption of the substrate on the soil. [This is a common procedure when linear partitioning between soil and aqueous phase may be assumed (8, 9).] As these sorption effects are not the same for oxygen and for substrate, it is not unlikely that a ratio λ_O/λ_C considerably greater than 2 could occur. We have therefore made some runs in which the ratio λ_O/λ_C has been varied from 2 to 200.

As can be seen from Fig. 9, at high values of the mass transfer rate parameters no increase of the relative contribution of biodegradation is

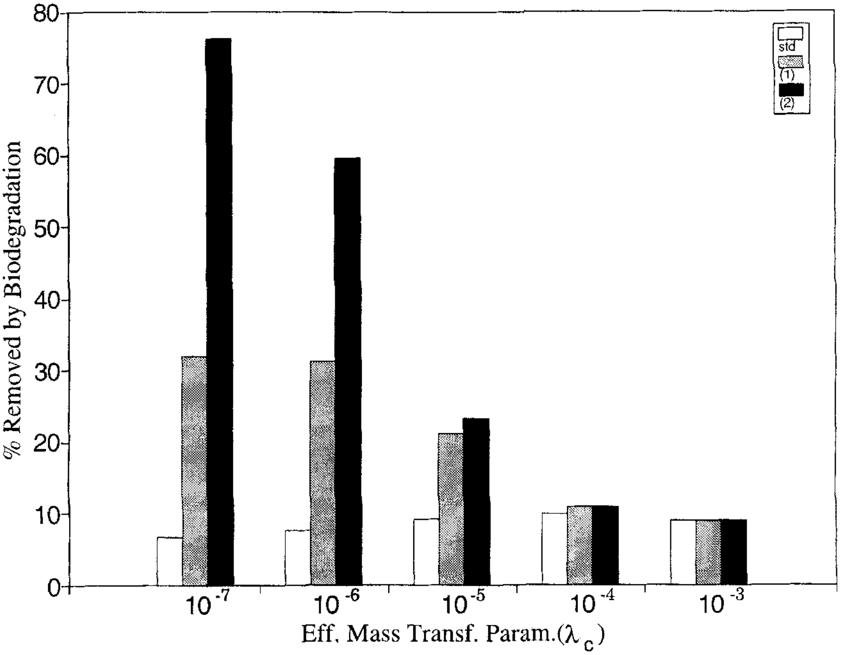

FIG. 9 Relative contribution of biodegradation to the cleaning process at different values of the λ_O/λ_C ratios (std): $\lambda_O/\lambda_C = 2$; (1): $\lambda_O/\lambda_C = 20$; (2): $\lambda_O/\lambda_C = 200$. See Table 1 for standard parameter values.

observed as the ratio λ_O/λ_C is increased simply because a high percentage removal by air stripping has been achieved before biodegradation starts to be significant, and under these conditions, biodegradation takes place without oxygen limitation. At lower values of the contaminant mass transfer rate parameters the stripping process slows down and the biodegradation contribution increases substantially as the dissolved oxygen supply increases. Oxygen control effects under such conditions are easily seen, as can be seen from the dramatic increase of the bioremediation contribution as the ratio λ_O/λ_C increases.

The cleanup times are also lowered substantially: from 43 MMs (500 days) obtained for $\lambda_O = 2 \times 10^{-7}$ s^{-1} (Fig. 2) to 21 MMs (245 days) for $\lambda_O = 2 \times 10^{-6}$ s^{-1} (Fig. 10) and to 5.3 MMs (61 days) for $\lambda_O = 2 \times 10^{-5}$ s^{-1}, always for 99.996% of contaminant removal. Thus, if adsorption effects are limiting the contaminant stripping rate, oxygen transport is not impaired to the extent modeled in previous runs. One notes that adsorbed contaminants may be degraded more slowly than free dissolved molecules (10). On the other hand, there are some reports on the ability of some microorganisms to produce extracellular polymers or biosurfactants to

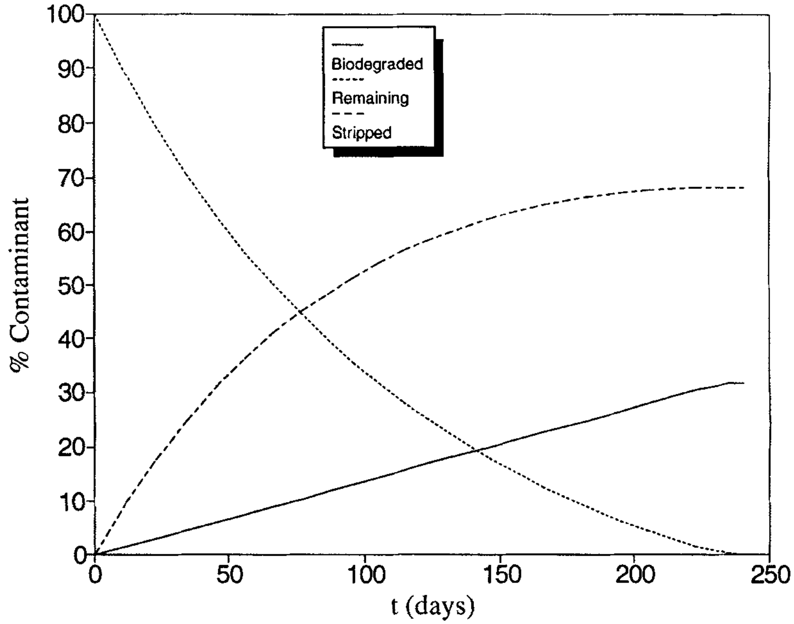

FIG. 10 Contaminant removal by stripping and biodegradation versus time. $\lambda_C = 10^{-7}$ s^{-1}; $\lambda_O = 2 \times 10^{-6}$ s^{-1}. See Table 1 for standard parameter values.

make adsorbed substances more readily available (11, 12). Therefore the contribution of biodegradation to the overall cleanup during SVE may be more important under conditions where the contaminant is fairly strongly adsorbed onto the soil, limiting the effectiveness of simple air stripping.

SENSITIVITY STUDIES WITH NUTRIENT LIMITATIONS

Although all the previous runs were performed assuming an excess of nutrients (such as nitrate and phosphate), one may expect to find some nutrient limitations in the soil being treated. Our model includes this (1), as do some other bioremediation models (References 13 and 14, for example), by means of another Monod-like factor. We also include a nutrient source term arising from biomass die-off, which could lead to nutrient turnover with or without oxygen consumption.

In this section we explore the following *three extreme situations*. 1) No nutrient turnover and no oxygen consumption from the dead biomass. 2) Nutrient is immediately available as cells die, but this release takes place without oxygen consumption. 3) Mineralization of the dead biomass releases nutrient and needs oxygen to be accomplished. Case 2 has been previously used by Kindred and Celia (15). Some other models include oxygen demand due to endogenous respiration by the addition of another Monod-like term (13, 16). We feel that additional insight to the process may be obtained by examining the three extreme situations described above since field parameters are not likely to be available.

All the following runs were performed with the parameter values given in Table 1 with a single limiting nutrient at an initial concentration of $A_1 = 3$ mg/L of aqueous phase; stoichiometric coefficient, n_1, of 0.1 g of nutrient needed to produce 1 g of new biomass; and a half saturation rate constant for the nutrient, K_1, of 0.1 mg/L.

In *Case 1*, the maximum amount of contaminant substrate which can be biologically removed is determined by the initial nutrient concentration and the stoichiometric coefficients. With the values used in our case, this is C^s_{max}(biodegradation) $= A_1 n_C n_1^{-1} = 60$ mg/L for the parameters in our example. Since the initial substrate concentration is 750 mg/L, one can biodegrade no more than 8% of the substrate initially present. Comparison of Figs. 10 and 11 shows clearly the effect of nutrient limitations in this case. Biodegradation under nutrient-limited conditions takes place while stripping is occurring at a maximum rate. The beneficial effect of biodegradation on the cleanup time is substantially lower than that observed even at lower biodegradation relative contributions in the absence of nutrient limitation (for instance, Fig. 2), and the cleanup time becomes very similar to that obtained in the absence of biodegradation. In these runs, for exam-

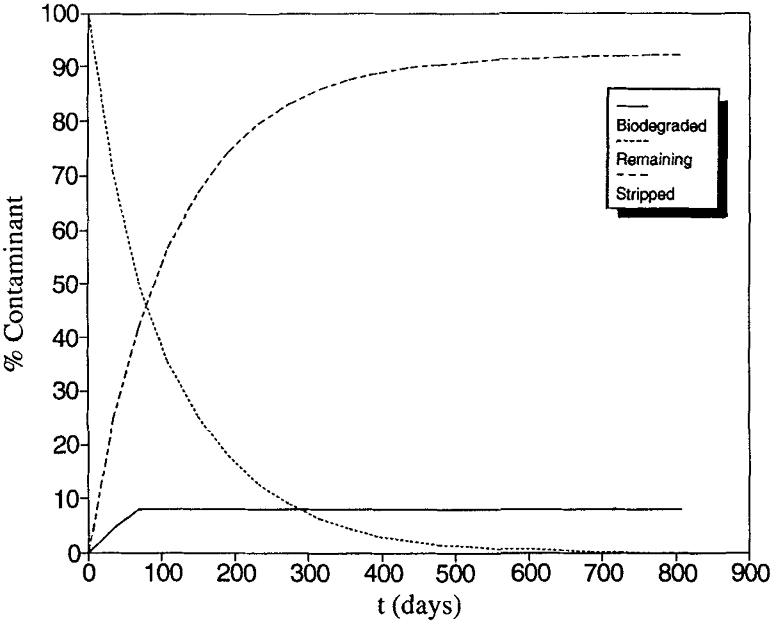

FIG. 11 Contaminant removal by stripping and biodegradation versus time in the presence of one limiting nutrient. $\lambda_C = 10^{-7}\ \mathrm{s}^{-1}$; $\lambda_O = 2 \times 10^{-6}\ \mathrm{s}^{-1}$. Nutrient is not returned upon biomass die-off (Case 1). See Table 1 for standard parameter values.

ple, the times necessary for 99.8% removal of contaminant differ by less than 2%, and the differences are smaller for higher percent removals.

In some runs where the relative contribution of biodegradation was lower than the 8% upper limit mentioned above, the effect of nutrient limitation was also appreciable, as seen when comparing Figs. 8 and 12. With large mass transfer rate parameters, stripping approaches local equilibrium behavior, and the cleaning process takes place first at the top (entrance) sections of the column. As biodegradation exhibits a significant induction period, its relative contribution is heterogeneously distributed over the column, varying from negligible at the top (where stripping is rapid and complete) to a value of 8% in the bottom compartments; the overall calculated relative contribution of biodegradation was 4.8%. Thus, the results shown in Figs. 8 and 12 are indistinguishable for the first 8×10^5 s (9 days) of the runs, showing different trends only as nutrient becomes exhausted in the contaminant-bearing compartments near the bottom of the column.

Case 2 runs, in which nutrients are released to the aqueous phase immediately upon cell die-off without requiring oxygen consumption, led to

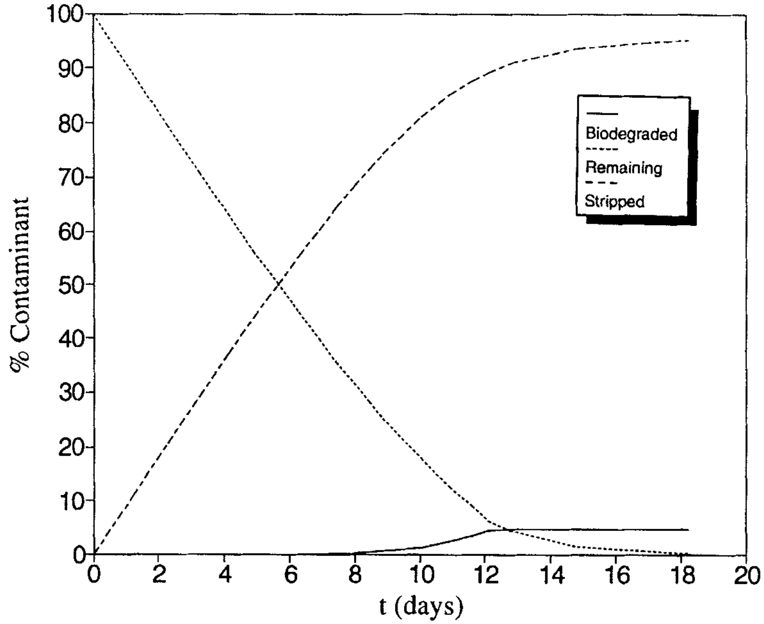

FIG. 12 Contaminant removal by stripping and biodegradation versus time in the presence of one limiting nutrient. $\lambda_C = 10^{-3}\ s^{-1}$; $\lambda_O = 2 \times 10^{-3}\ s^{-1}$; $Kh_C = 0.5 \times$ standard; $K_B = 100 \times$ standard. Nutrient is not returned upon biomass die-off (Case 1). See Table 1 for standard parameter values.

results falling between those obtained in the absence of nutrient limitations and those corresponding to Case 1. The rate of nutrient turnover is dependent on the value of the die-off coefficient K_B. Figure 13 shows the results obtained for Case 2 at the same conditions as the ones presented in Figs. 10 and 11 corresponding, respectively, to no nutrient limitations and Case 1 (nutrient not recycled).

As can be seen in Fig. 13, the cleanup time is about 25% larger than that obtained under conditions of no nutrient limitations (Fig. 10). The curve showing the biodegradation contribution in Fig. 13 exhibits two linear regions. The initial one corresponds to no nutrient limitations and oxygen mass transfer limited conditions. The second linear region begins after a biodegradation contribution of about 8%, which was the maximum contribution achievable for Case 1, where nutrient becomes limiting and is made available at a rate controlled by the value of K_B. The dissolved nutrient concentration remains below 1 μg/L, and the biomass population does not exceed the limit of 30 mg/L resulting from nutrient/biomass stoichiometry.

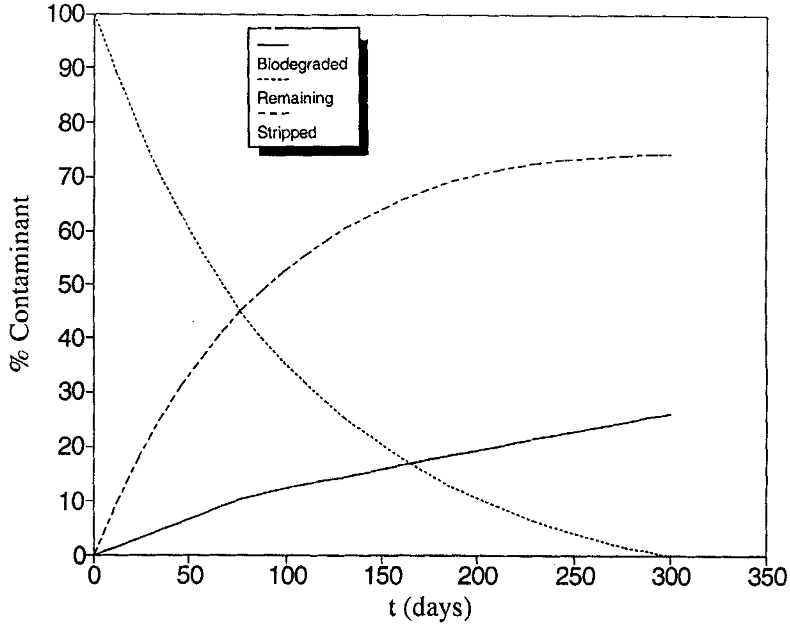

FIG. 13 Contaminant removal by stripping and biodegradation versus time in the presence of one limiting nutrient. $\lambda_C = 10^{-7}$ s^{-1}; $\lambda_O = 2 \times 10^{-6}$ s^{-1}; $K_B = 10^{-7}$ s^{-1} (standard). Nutrient is returned upon biomass die-off without oxygen demand (Case 2). See Table 1 for standard parameter values.

Runs were also performed for higher values of the die-off coefficient (K_B) after checking that these values do not affect significantly the results obtained under no nutrient limitations (Fig. 10) and Case 1 (Fig. 11), in agreement with our previous discussion regarding the effects of K_B when the process takes place under oxygen mass transfer limited conditions (Fig. 7). As K_B increases, nutrients are returned faster and the slope of the second linear region approaches that obtained for oxygen-limited conditions. Thus the cleanup time decreases toward the limiting value obtained in the absence of nutrient limitations (Fig. 10). At a K_B value of 10^{-6} s^{-1}, the nutrients are returned at a rate that gives a nutrient concentration always above 2 mg/L, at which concentration biodegradation may be considered to be of zero order with respect to the nutrient. The process is oxygen controlled and the biomass concentration remains between 5 and 10 mg/L. A die-off coefficient of 10^{-5} s^{-1} apparently leads to similar results, but here the biomass concentration remains at a value about one-tenth of the earlier value. The dissolved oxygen concentration has a value in the vicinity of K_O (0.1 mg/l), so the reaction order with respect to oxygen is somewhere around $\frac{1}{2}$.

When the values of the mass transfer rate parameters are large, the die-off coefficient K_B has a significant effect on the system, especially as the K_B value approaches that of K. This was mentioned above when the effect of the die-off coefficient was discussed (Figs. 5 and 8). Although a higher value of K_B means a higher availability of nutrients in a Case 2 situation, it also means a reduction in the net rate of formation of biomass. Figures 14 and 15 show the results obtained for runs performed under conditions identical to those corresponding to Figs. 5 and 8. A very low value of K_B (Fig. 14) leads to results similar to Case 1 since the rate of nutrient turnover is quite small compared to the stripping rates obtained for large mass transfer rate parameters. As K_B increases (Fig. 15), the biodegradation contribution approaches the situation of no nutrient limitations (Fig. 8).

For *Case 3* no lack of dissolved oxygen was observed in any of the runs performed using high values of the oxygen mass transfer rate parameter. Therefore it is not surprising that indistinguishable results were obtained

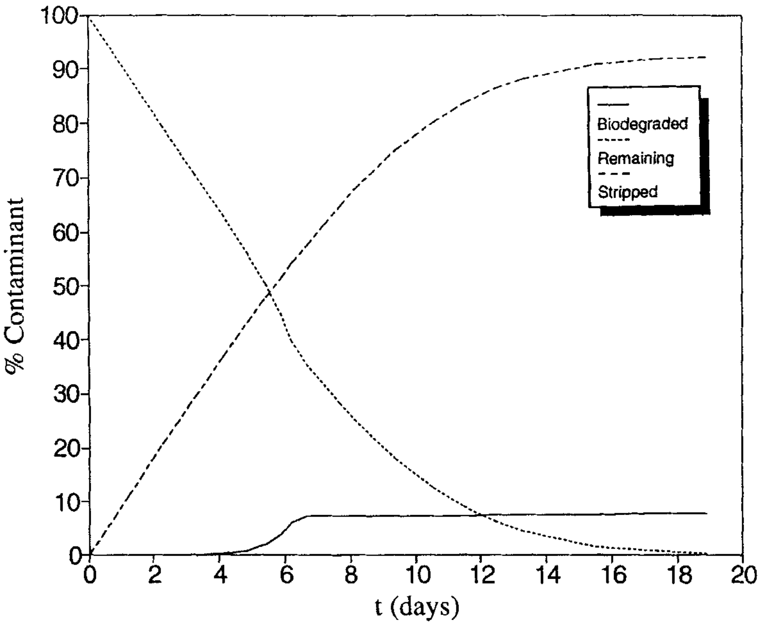

FIG. 14 Contaminant removal by stripping and biodegradation versus time in the presence of one limiting nutrient. $\lambda_C = 10^{-3}\ s^{-1}$; $\lambda_O = 2 \times 10^{-3}\ s^{-1}$, $Kh_C = 0.5 \times$ standard; $K_B = 10^{-7}\ s^{-1}$ (standard). Nutrient is returned upon biomass die-off without oxygen demand (Case 2). See Table 1 for standard parameter values.

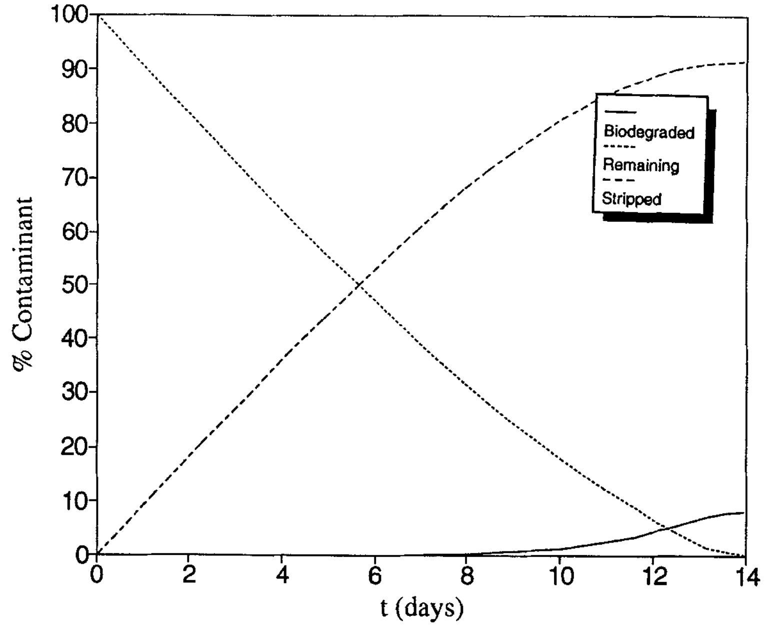

FIG. 15 Contaminant removal by stripping and biodegradation versus time in the presence of one limiting nutrient. $\lambda_C = 10^{-3}\ s^{-1}$; $\lambda_O = 2 \times 10^{-3}\ s^{-1}$, $Kh_C = 0.5 \times$ standard; $K_B = 100 \times$ standard. Nutrient is returned upon biomass die-off without oxygen demand (Case 2). See Table 1 for standard parameter values.

when running the model in the Case 3 situation and in Case 2 using the same conditions (Figs. 14 and 15).

The series of runs for Case 2 with the very low values of the mass transfer rate parameters (see Fig. 13) were also carried out for Case 3. The final cleanup times obtained when using a K_B value of $10^{-7}\ s^{-1}$ are very close in both cases, but a smaller slope is now observed in the first linear region where oxygen availability is controlling. On the other hand, this produces a decrease in the rate of nutrient consumption, so that this becomes a limiting factor later in the run, partially counterbalancing the previous effect. The run with a K_B value of $10^{-6}\ s^{-1}$, which was oxygen-controlled throughout the entire process for Case 2, gives in Case 3 a cleanup time about 20% larger than in Case 2 because of the additional oxygen requirements for biomass degradation. Finally, when a value of $10^{-5}\ s^{-1}$ was used for K_B, again a 20% increase in cleanup time was observed, so it may be concluded that the biodegradation process is oxygen-limited here, as it was for the case where $K_B = 10^{-6}\ s^{-1}$. Although higher oxygen concentrations were computed, the higher rate of die-off produces a significant decrease in the biomass concentration, as for Case 2.

CONCLUSIONS

The importance of the nonequilibrium mass transport processes between the immobile aqueous phase and the moving vapor phase that was found previously (1) is further documented in these sensitivity studies. The relative importance of other variables depends heavily on the values of the mass transport rate parameters. For instance, the initial microbial population can change by several orders of magnitude without noticeable variations in the contribution of biodegradation to the cleanup process when very small values of the mass transfer rate parameters are used.

On the other hand, the system is quite sensitive to variations in the initial microbial population when the mass transport process approaches local equilibrium behavior, as happens with large values of the mass transfer rate parameters. As a general observation, the system becomes less sensitive to changes in the other parameters as the mass transfer rate parameters decrease. Oxygen demand of the contaminant (oxygen consumed/contaminant degraded), which has been modified by changing the stoichiometric coefficient, n_C, is the only exception to this general rule, with system having mass transfer limitations being more sensitive to this parameter than those in which local equilibrium between aqueous and gaseous phases may be assumed.

Values of the mass transfer rate parameters for oxygen and the contaminant are related to their diffusivities in water systems, but may also be influenced by other factors of the system, such as sorption onto solids (probably more important for contaminant than for oxygen). If this happens, the biodegradation contribution may increase. This, of course, depends on the influence of sorption on the availability of the substrate to the microorganisms. Still, the very important limitation of oxygen availability arising from very small mass transfer rate parameters makes it reasonable to expect increases in the biodegradation rate as oxygen supply is improved, even if only aqueous-phase substrate is available for biodegradation.

The contributions of biodegradation may be severely hindered by limits on nutrient availability. Furthermore, even if the biodegradation contribution to remediation might otherwise be important, if nutrients are exhausted during the process, reductions in cleanup time may become almost negligible because biodegradation will occur mainly at the early stages of the process where stripping is most efficient. Nutrient addition as an aqueous solution over the treated soil may be implemented, but further studies on how such added nutrients reach those areas where they are most needed and how an increase in the soil moisture content affects other important parameters (such as the pneumatic permeability) should be considered. Water may accumulate in those areas which are less accessible to the advecting gas and make diffusion limitations more important.

System sensitivity to nutrient availability is also influenced by the mass transport rate parameters. If local equilibrium may be assumed, biodegradation effects will probably be more important in those soil regions that are further from the point of injection of fresh air, near which soil will be rapidly cleaned up by stripping. In this case, nutrient limitations may occur only in those areas that are cleaned up later in the process.

Some other phenomena that have not been considered in the model may occur and could have important influences on the process; these include clogging by biomass growth, the influence of the presence of other substrates, etc. Some of our conclusions may therefore need further critical studies, perhaps with two- or three-dimensional models. Our present results certainly support the belief that bioremediation and soil vapor extraction in combination are two very useful techniques for the cleanup of organic contaminants in the vadose zone. With proper design, one expects that improvements in the efficiency and cost effectiveness of both techniques will be forthcoming.

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