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Biodegradation Phenomena during Soil Vapor Extraction. III. Sensitivity Studies for Two Substrates

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ABSTRACT

In the bioventing technique, soil vapor extraction (SVE) is used to promote aerobic biodegradation of contaminants in the vadose zone. Kinetics limited by mass transport of the contaminant and/or oxygen through the aqueous phase to the microorganisms and of contaminant to the gaseous phase may be expected during field operation. Sensitivity studies were performed with a one-dimension model for two substrates showing competitive inhibition, following Monod's kinetics. The mass transfer limitations were represented by means of lumped parameters, and results for high and low values of these parameters were compared. Under kinetics severely limited by mass transport processes, biodegradation occurs at a rate given by the availability of dissolved oxygen, and important contributions of biological degradation to the overall cleanup are expected if oxygen is not utilized exclusively for the oxidation of other substances than the target contaminant. For relatively fast mass transport kinetics the system becomes quite sensitive to a rather large number of parameters, but important reductions in the remediation time will usually occur if high removal percentages are mandated.

INTRODUCTION

Bioremediation of contaminated soils is usually based on the optimization of the subsurface environmental conditions to obtain complete detoxi-

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fication of the contaminants within a reasonable period of time. Oxygen availability is probably the most important limiting factor, and different oxygen carriers have been employed in field operations. Table 1 shows the oxygen concentration contained in those carriers more frequently used in field operations.

Soil vapor extraction (SVE) is now one of the commonly used technologies for the cleanup of volatile contaminants from the vadose zone. In SVE operation, volatile organic compounds (VOCs) are transferred from various phases in the soil to an air stream; this, in turn, generally needs treatment before discharge, treatment that accounts for approximately 50% of the total costs.

Bioventing (1) uses designs similar to those of SVE, modified to get a maximum contribution of the biological processes to the remediation. These biological processes are evaluated in field operations by means of oxygen balances (2), which have been reported as giving promising results (3–5).

A mathematical model for SVE with biodegradation of contaminants from unsaturated soils was presented earlier (6) and described in detail. The model is one-dimensional, so simulates operation of a laboratory column; however, one expects that the dependence of the modeling results on the various parameters should give insight and at least qualitative information about the operation of SVE wells in which biodegradation is taking place. The reader is Reference 6 for background information on the modeling and a discussion of the relevant literature.

A subsequent paper (7) discussed the dependence of the simulations on the various parameters which appeared in the model for the case in which a single contaminant substrate was present. The effects of kinetics limited by mass transport of the contaminant and/or oxygen through the bulk aqueous phase to the microorganisms (biodegradation) and of contaminant to the gaseous phase (SVE) were explored. Generally, during the latter part of the process, as contaminant concentration decreases, the effi-

TABLE 1
O_2 Supplied by Different Carriers to Subsurface Bioremediation

Carrier	(mg O_2)/(kg carrier)
Air-saturated water	10
Oxygen-saturated water	50
2000 mg/L H_2O_2 solution	1,000
Air	250,000

ciency of stripping decreases also, while biodegradation may continue to remove substantial quantities of contaminant. This may result in very marked reductions in cleanup times, particularly if high levels of cleanup are mandated. Sensitivity studies of the major variables involved in the process showed that their effects are strongly dependent on the values of the mass transfer rate parameters.

The study just discussed involved the degradation of only a single substrate, while most of the situations in which SVE is used involve more than a single contaminant. Often a wide range of compounds may be present, as is the case when one is dealing with petroleum hydrocarbons such as gasoline or jet fuel (see, for instance, Refs. 8–10 on mixtures). In the present paper we therefore extend the model to the case where there are two substrates. The first paper in this series (6) gives the conceptual details of the model, the notation, and the differential equations which are used.

The introduction of a second substrate increases the already large number of parameters which must be assigned, so one is even more limited than before in the extent to which the model can be explored in sensitivity studies. Still, comparison of results for different situations may be helpful in giving a better understanding of the biological processes taking place when SVE is being carried out in most field applications.

When two substrates are present, the rate of utilization of each of them may depend on the presence of the other in several ways. The simplest type of interaction one can consider is that which arises from the finite aqueous concentrations of the nutrients (ammonium, phosphate, . . .) or electron acceptors (oxygen, nitrate, . . .). Certainly the oxygen which is utilized in the oxidation of Substrate A is not available for the oxidation of Substrate B. The model explored here includes these types of interactions, and mass balances were used as a first check when debugging programs.

A second type of interaction between two substrates is cometabolism. In this, a substrate may be degraded by microorganisms that do not get any benefit from the process. Therefore, in order to maintain or increase the population of microorganisms, a different carbon source must also be available. A very interesting example of cometabolism is the breakdown of chlorinated solvents (TCE, DCE, 1,1,1-TCA, etc.) by methanotrophic bacteria (11, 12), in which both oxygen and methane are supplied. Processes of this kind may be easily represented with the model.

The concentration of microorganisms able to biodegrade the target substrate may depend on the presence of other substrates in two opposite ways: Growth of biomass may take place by virtue of one or more of the various substances present which are being biologically oxidized, so the

removal of a target substrate may be favored by the presence of other substrates even in cases in which cometabolism as defined above is not occurring. On the other hand, the presence of some substances may increase the rate of microbial die-off if these compounds exhibit toxicity above a threshold value. Inclusion of these effects is also possible with the model discussed here.

Another type of interaction between two substrates C_1 and C_2 is known as noncompetitive inhibition, which may be represented by a factor in, say, the rate expression for the consumption of C_1, which decreases with increasing concentration of C_2. Such a factor might be $\{1/[1 + (C_2/C_2^\circ)^n]\}$. This type of inhibition is often used to describe the rate of nitrate utilization as an electron acceptor by facultative bacteria in the presence or absence of oxygen (for instance, Ref. 13). This approach has also been proposed as a way of limiting the growth of biomass when a very high concentration of microorganisms is present (for example, Ref. 14). We have not included these interactions in our model here, but there is no mathematical difficulty in doing so, and such changes could be very easily introduced into the computer algorithm.

When one considers Monod kinetics, competitive inhibition may be expressed in the equation for biomass production (for example) as

$$\frac{\partial B}{\partial t} = K_{\max} B \frac{\alpha_1 \dfrac{C_1^s}{K_{C1}} + \alpha_2 \dfrac{C_2^s}{K_{C2}}}{1 + \dfrac{C_1^s}{K_{C1}} + \dfrac{C_2^s}{K_{C2}}} \tag{1}$$

This form (with appropriate changes in notation) is widely used in the literature. It is to be preferred over the alternative

$$\frac{\partial B}{\partial t} = K_{\max} B \left[\frac{\alpha_1 C_1^s}{K_{C1} + C_1^s} + \frac{\alpha_2 C_2^s}{K_{C2} + C_2^s} \right] \tag{2}$$

because it is not only consistent with the case in which either the C_1 or the C_2 aqueous concentration is negligible, but is consistent with the situation in which C_1 and C_2 are very similar substrates (identical substrates in the extreme case). Equation (2) predicts rates of biomass growth and substrate utilization which are too large for this situation.

RESULTS

Several series of runs have been performed in order to check the sensitivity of the system to the presence of a second substrate under almost no mass transfer limitations and also under rather slow oxygen and con-

taminant mass-transfer kinetics between the aqueous and gaseous phases. We have chosen here as initial conditions and model parameters values which we have earlier concluded (6, 7) were typical of those regarded by workers in the field as representative. These were also selected so as to yield significant contributions of the biological processes to the overall cleanup in order to make the effects of the second substrate more evident. Default parameters are given in Table 2.

Runs with large mass transfer coefficients ($\lambda_{C1} = 1 \times 10^{-3}$ s^{-1}; $\lambda_O = 2 \times 10^{-3}$ s^{-1}), in this paper have an effective Henry's constant for the first substrate of 0.5×10^{-3}, instead of 1.0×10^{-3}, the default value used in the previous papers. Runs performed using the higher value of the Henry's constant lead to rather low contributions of the biological processes to the overall cleanup, because by the time the population of microorganisms was large enough to make a significant contribution to the cleanup, simple stripping had removed almost all the contaminant. A

TABLE 2
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 Substrate 1 concentration ($M/\rho V$)	100 mg contaminant/kg soil
Initial Substrate 2 concentration ($M/\rho V$)	100 mg contaminant/kg soil
Initial biomass concentration (B)	10^{-3} mg/L
Henry's constant of first substrate (K_{H1})	10^{-3}
Henry's constant of oxygen (K_{HO})	30
Stoichiometric coefficient for Substrates 1 and 2 (n_C)	2 g substrate/g biomass
Stoichiometric coefficient for oxygen (n_O)	3 g oxygen/g biomass
Maximum rate of biomass growth with the best substrate (K)	4×10^{-5}s^{-1}
Relative maximum rate of biomass growth with Substrate 1 (α_1)	0.5
Michaelis constant of Substrate 1 (K_{C1})	0.1 mg/L
Michaelis constant of oxygen (K_O)	0.1 mg/L
Stoichiometric coefficient for endorespiration	1.1 g oxygen/g dead biomass
Die-off coefficient of biomass (K_B)	10^{-6}s^{-1}

run carried out with one substrate present, with the lower value of the effective Henry's constant and the other parameters as given in Table 2, led to a biodegradation contribution of 38%.

When very low mass transfer coefficients were chosen we have used a value of the Henry's constant of 1.0×10^{-3}, which was the most commonly used value in the previous papers. We found, however (7), that under these severely limited mass transfer conditions, runs for Henry's constants of 1.0×10^{-3} and 0.5×10^{-3} give almost indistinguishable results, so one can compare results of the two series with different mass transfer coefficients as if they had the same effective Henry's constant. Here the biodegradation processes were limited mostly by the availability of dissolved oxygen. We showed that under these conditions one is likely to have a ratio between the mass transfer coefficients (λ_O/λ_{C1}) higher than the ratio between diffusivities of the substances in water, which is approximately 2. This will happen when the kinetic limitations are related to adsorption processes which will probably affect the organic substances and oxygen in a different way. For a run carried out for one substrate, values of the mass transfer coefficients of $\lambda_C = 10^{-7}\ s^{-1}$ and $\lambda_{O1} = 2 \times 10^{-6}\ s^{-1}$, and all the other parameters with the values given in Table 2, we obtained a contribution of the biological processes to the remediation of 27%.

To examine the impact of variations in each of the most important parameters, we studied in the present paper the effect of competitive inhibition by means of a nonvolatile second substrate. Competitive inhibition factors of the type shown in Eq. (1) were included in all of the differential equations in which biomass was being formed, substrates consumed, and nutrients consumed.

For the first set of runs the concentration of the second substrate, C_2^s, was held constant by using a value for α_2 (the ratio of the maximum rate of biomass growth on Substrate 2 to the maximum rate of growth on the best substrate possible) of zero. Under these conditions the second substrate competes with the first for enzymatic sites in the microorganisms, but is then not metabolized. Figure 1 presents the calculated times required for 99.996% removal of Substrate 1 and the contribution of biodegradation to the process (expressed as a percentage of the total removal). As explained before, these runs were made with large values of the mass transfer rate parameters ($\lambda_C = 10^{-3}\ s^{-1}$, $\lambda_O = 2 \times 10^{-3}\ s^{-1}$) and an effective Henry's constant (K_{H1}) of 5×10^{-4} (dimensionless). All other parameter values are given in Table 2. In Fig. 1 it is seen that very high values of C_2^s/K_{C2} result in total inhibition of the biodegradation of the first substrate, so that removal of Substrate 1 is entirely by SVE. As

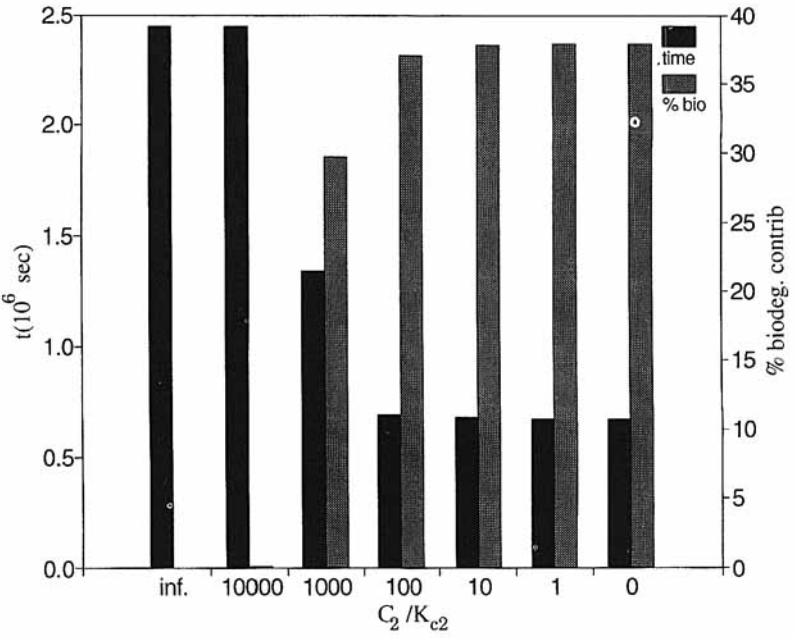

FIG. 1 Substrate 1 theoretical cleanup time for 99.996% removal and relative biodegradation contribution in the presence of a nonvolatile, nonbiodegradable ($\alpha_2 = 0$) competitive inhibitor. ($K_{HC1} = 5 \times 10^{-4}$; $\lambda_{C1} = 10^{-3}\ s^{-1}$; $\lambda_O = 2 \times 10^{-3}\ s^{-1}$). See Table 2 for other parameter values.

C_2^s/K_{C2} decreases to values of 1000 or less, Substrate 1 is able to compete for sites, and its biodegradation becomes important.

A similar series was done in which the half saturation constant for the first substrate, K_{C1} was increased from 0.1 to 10 mg/L; the results were very similar to those shown in Fig. 1, except that they corresponded to values of C_2^s/K_{C2} $1/100$th as large as those given in Fig. 1. As one would expect, the less strongly Substrate 1 is adsorbed on enzymatic sites (the larger the value of K_{C1}), the more readily is its biodegradation inhibited by competing Substrate 2. This result should be valid for any system for which the competitive inhibition model is valid as long as there are no other limiting substances (nutrients, toxins, oxygen, etc.).

In the work reported here we are principally concerned with the effects of mass transfer limitations of the biological and stripping processes. In the first set of runs, just described, the mass transfer rate parameters were rather large. In the second set, for comparison purposes, the same

parameter values were used as in the first set except that values of the mass transfer rate parameters were selected to make mass transfer limitations rather severe yet still admit the possibility of a fairly substantial contribution to the cleanup processes from biodegradation.

The results presented in Fig. 2 were obtained with a value of K_{C1} of 0.1 mg/L (so initially $C_1^s/K_{C1} = 7500$). The mass transfer rate parameters used in this second set are $\lambda_{C1} = 10^{-7}\ s^{-1}$, $\lambda_O = 2 \times 10^{-6}\ s^{-1}$. λ_O/λ_{C1} has been increased to 20, as discussed above. The drastic decreases of the mass transfer rate parameters in Fig. 2 as compared to Fig. 1 have correspondingly increased the remediation times, as expected; the runs summarized in Fig. 2 are all severely mass transport limited.

Moreover, a substantial difference is seen with respect to results given in Fig. 1 in the way in which the two substrates interact. We see that the relative contribution of biodegradation to the overall cleanup is not sensitive to the presence of the second substrate up through values of $C_2^s/K_{C2} < 10^3$ for the lower values of the mass transfer coefficients (Fig.

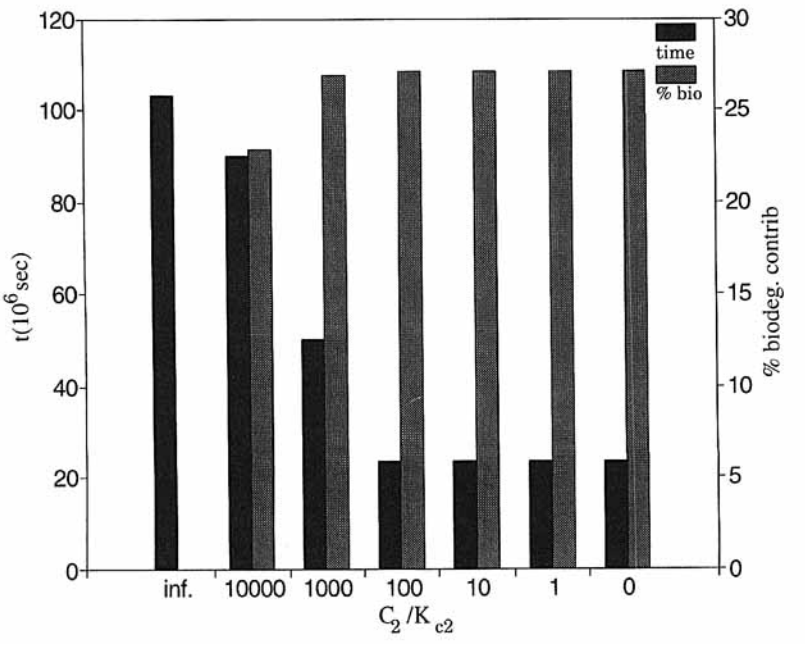

FIG. 2 Substrate 1 theoretical cleanup time for 99.996% removal and relative biodegradation contribution in the presence of a nonvolatile, nonbiodegradable ($\alpha_2 = 0$) competitive inhibitor. ($\lambda_{C1} = 10^{-7}\ s^{-1}$; $\lambda_O = 2 \times 10^{-6}\ s^{-1}$). See Table 2 for other parameter values.

2), and only up through values of C_2^s/K_{C2} of 100 for the larger values (Fig. 1). This may be due to the fact that the relative biodegradation contribution to the overall cleanup remains more important under these mass-transfer limited conditions because during most of the process dissolved oxygen continues to be limiting Substrate 1 utilization more stringently than the inhibition resulting from the high value of C_2^s/K_{C2}; the system is therefore less sensitive to changes in C_2^s/K_{C2}. Nevertheless, the decreases in cleanup time derived from this biological contribution are not as large for the higher values (10^4) of C_2/K_{C2} as they were in most other situations for two reasons. First, the rate of C_1 utilization is approaching first-order behavior with respect to the contaminant at higher concentrations ($C_1 < K_{C1}(1 + C_2^s/K_{C2})$, instead of just $C_1 < K_{C1}$ with no competitive inhibition), and second, the value of the equivalent first-order coefficient is smaller (given by $[K_{max}\alpha_1 n_{C1}]/K_{C1}(1 + C_2^s/K_{C2})]$ instead of $K_{max}\alpha_1 n_{C1}/K_{C1}$). This means that the tailing effect found when no biodegradation occurred is not avoided under these circumstances, and the biological process at the latter stages of the cleanup process is as slow as the already poorly performing stripping, proceeding also with first-order kinetics with respect to the contaminant. Therefore, the presence of a substance which inhibits the biological phenomena may be just as damaging here as it was when large mass transfer coefficients were used, even if large biodegradation contributions to the cleanup are reached.

When another series similar to the one presented in Fig. 2 was carried out for K_{C1} values of 10 mg/L ($t = 0$, $C_1/K_{C1} = 75$), compared to $K_{C1} = 0.1$ mg/L ($t = 0$, $C_1/K_{C1} = 7500$) for the earlier set, results were similar, but for values of C_2^s/K_{C2} 100 times smaller than those found with the earlier series (shown in Fig. 2) just as was observed for the large values of the mass transfer coefficients.

The results summarized in Figs. 1 and 2 correspond to a situation in which the second substrate underwent neither stripping nor biodegradation, but was only adsorbed to an active enzymatic site in the microorganisms. This would be a particularly unfavorable case, corresponding, perhaps, to adsorption of an inorganic ion or highly nonvolatile and biorefractory organic to the enzymatic sites. A more favorable alternative case is where Substrate 2 is relatively similar to Substrate 1 in its chemical and biological properties, and can therefore be removed, like Substrate 1, by stripping and biodegradation. This will be studied in the following section using for comparison purposes the runs obtained in the previous Figs. 1 and 2, for values of C_2/K_{C2} of 10^4 and 10^3.

Thus, one member of the third series of runs uses the same set of parameters as were used in the first set (shown in Fig. 1), except that the value of the biomass growth factor for Substrate 2, α_2, has been changed from

0.0 to 0.5, which is the same as the value of α_1 used in this and the earlier runs. These results were obtained using the large values of the mass transfer coefficients, $\lambda_O = 2 \times 10^{-3}\ s^{-1}$ and $\lambda_{C1} = 1 \times 10^{-3}\ s^{-1}$. Results of both runs are shown in Fig. 3. In this figure the initial value of C_2^s is 750 mg/L, $K_{C2} = 0.075$ mg/L and $\alpha_2 = 0.5$ and 0.0 as indicated. Substrate 2 is still assumed to be nonvolatile. For the run where Substrate 2 is susceptible to biodegradation, the contribution of biodegradation to the removal of Substrate 1 is 33% as compared to 0.1% (not noticeable in the figure) when the second substrate is neither volatile nor biodegradable, and the time required for virtually complete removal of Substrate 1 is reduced by a factor of slightly less than one half.

Figures 4 and 5 present results for $C_2^s = 750$ mg/L, $K_{C2} = 0.75$ mg/L and $C_2^s = 75$ mg/L, $K_{C2} = 0.075$ mg/L, respectively (also for the larger values of the mass transfer coefficients used in Fig. 1, $\lambda_C = 10^{-3}$, $\lambda_O = 2 \times 10^{-3}$), again for values of $\alpha_2 = 0.0$ and 0.5. For these values of the parameters the amounts of residual Substrate 1 show rather similar time dependences during most of the course of the remediation, with significant differences arising only during the last stages of the removals.

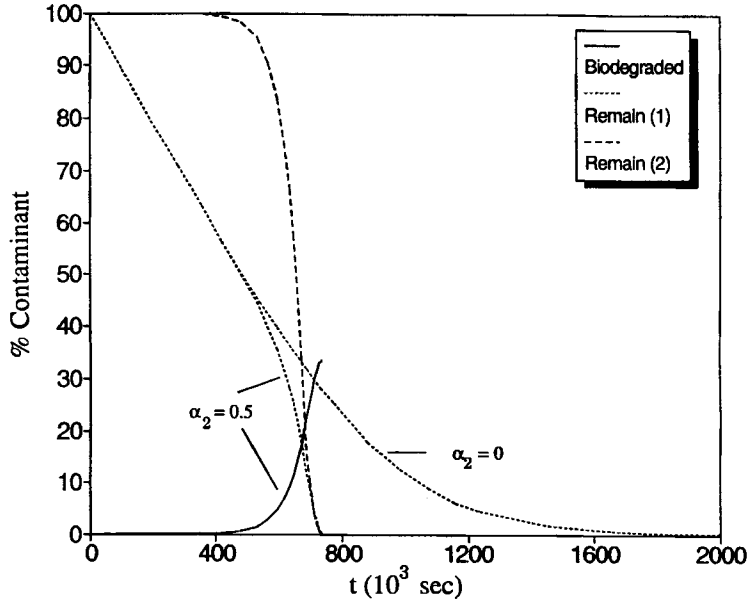

FIG. 3 Contaminant removal by stripping and biodegradation versus time, for $\alpha_2 = 0$ and $\alpha_2 = 0.5$. ($C_2^s = 750$ mg/L; $K_{C2} = 0.075$ mg/L; $K_{HC1} = 5 \times 10^{-4}$; $\lambda_{C1} = 10^{-3}\ s^{-1}$; $\lambda_O = 2 \times 10^{-3}\ s^{-1}$). See Table 2 for parameter values.

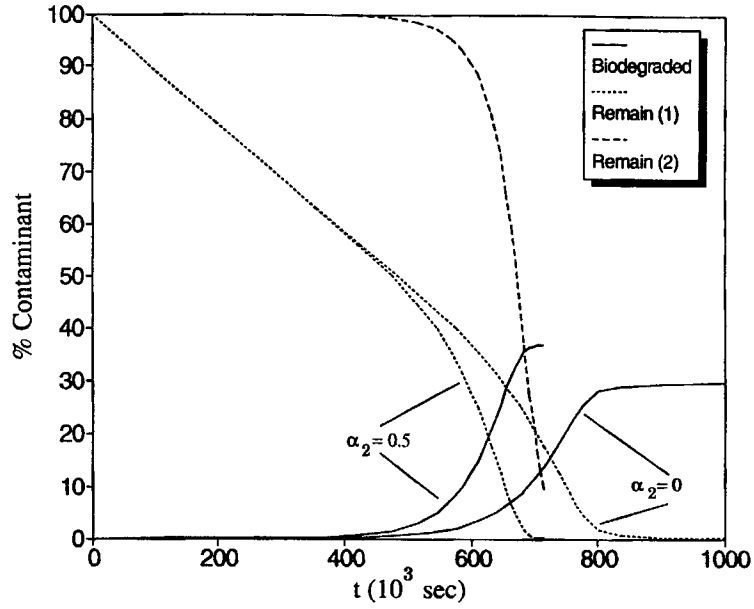

FIG. 4 Contaminant removal by stripping and biodegradation versus time, for $\alpha_2 = 0$ and $\alpha_2 = 0.5$. ($C_2^s = 750$ mg/L; $K_{C2} = 0.75$ mg/L; $K_{HC1} = 5 \times 10^{-4}$; $\lambda_{C1} = 10^{-3}$ s^{-1}; $\lambda_O = 2 \times 10^{-3}$ s^{-1}). See Table 2 for parameter values.

These results were obtained with the assumption that there are no limitations on the growth of biomass except for the availability of substrates and oxygen. In those situations in which large amounts of substrates are removed by biodegradation (particularly for $\alpha_2 = 0.5$ in Figs. 3 and 4), this leads to extremely high microbial populations. At this point, several phenomena will probably become limiting, such as a decrease in air flux due to a decrease in the pneumatic permeability of the soil by bacteria clogging, and additional mass transport limitations associated with the appearance of relatively thick biofilms. Neither of these are included in the present model.

As before, we are particularly interested in the differences in the behavior of these systems resulting from variations in the mass transport kinetics. Figure 6 presents results obtained under conditions identical to those used in the run shown in Fig. 3, except that the mass transport rate parameters for the run shown in Fig. 6 are $\lambda_C = 10^{-7}$ s^{-1}, $\lambda_O = 2 \times 10^{-6}$ s^{-1}, while in Fig. 3 these are $\lambda_C = 10^{-3}$ s^{-1} and $\lambda_O = 2 \times 10^{-3}$ s^{-1}, respectively. The results are considerably different; biodegradation of Substrate 1 in Fig. 6 is considerably slower during most of the process if Substrate

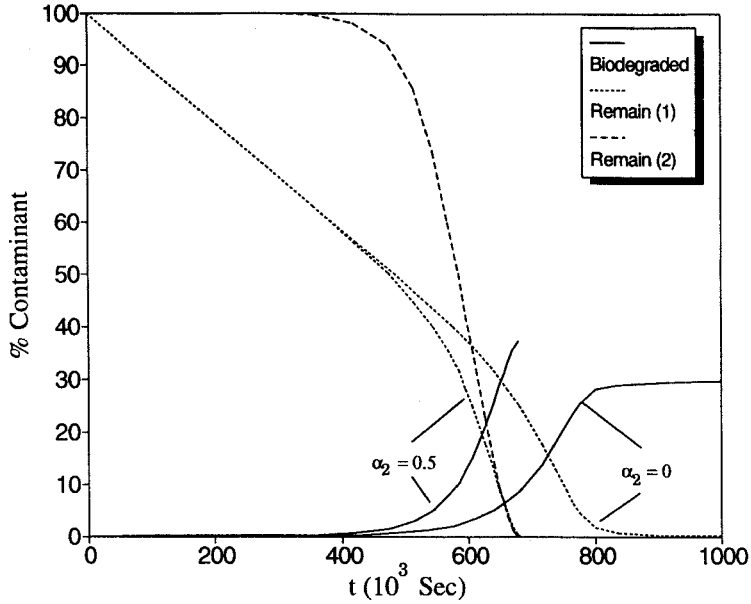

FIG. 5 Contaminant removal by stripping and biodegradation versus time, for $\alpha_2 = 0$ and $\alpha_2 = 0.5$. ($C_2^s = 75$ mg mg/L; $K_{C2} = 0.075$ mg/L; $K_{HC1} = 5 \times 10^{-4}$; $\lambda_{C1} = 10^{-3}\ s^{-1}$; $\lambda_O = 2 \times 10^{-3}\ s^{-1}$). See Table 2 for parameter values.

2 is biodegradable, due to the additional oxygen demand exerted by the degradation of Substrate 2. Only when the concentration of Substrate 1 has become relatively low (>95% removal) does its biodegradation become severely inhibited competitively by the presence of Substrate 2.

This inhibition is particularly important if Substrate 2 is not also being degraded along with Substrate 1 (i.e., $\alpha_2 = 0.0$). As a consequence of such competitive inhibition, even when the contribution of biodegradation in the intermediate stage of the run is reduced by a factor of a third (for $\alpha_2 = 0.5$) compared to its contribution when $\alpha_2 = 0.0$, the time required for virtually complete cleanup (99.996%) is less in the former case because of the partial elimination of the competitive inhibitor by biodegradation.

Nevertheless, cleanup times for both these runs are more than three times the cleanup time obtained when one has no competitive inhibition and no oxygen demand from a second substrate. For this last case, where oxygen availability alone is limiting the removal of Substrate 1, the cleanup time is about 2.3×10^7 seconds (270 days). Note that the results obtained when there is no competitive substrate present are almost indistinguishable from those for $\alpha_2 = 0.0$ (shown in Fig. 6) for the first 2.0×10^7 seconds

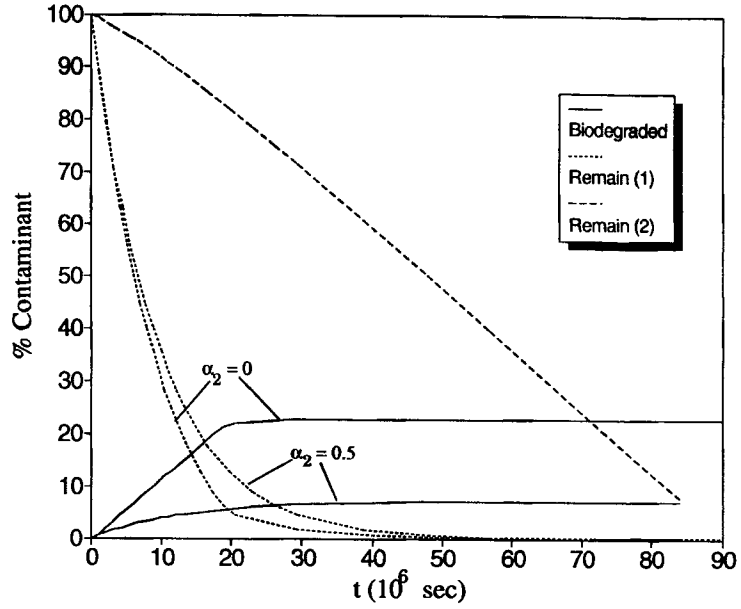

FIG. 6 Contaminant removal by stripping and biodegradation versus time, for $\alpha_2 = 0$ and $\alpha_2 = 0.5$. ($C_2^s = 750$ mg/L; $K_{C2} = 0.075$ mg/L; $\lambda_{C1} = 10^{-7}$ s^{-1}; $\lambda_O = 2 \times 10^{-6}$ s^{-1}). See Table 2 for parameter values.

(230 days). Thus, oxygen demand is the variable of maximum concern when mass transfer kinetics limitations are severe, especially if one does not require very high percent removals.

Figures 7 and 8 present results of runs made for parameter values identical to those used in making the runs plotted in Figs. 4 and 5, respectively, except that the mass transfer coefficients have been greatly reduced (again from $\lambda_C = 10^{-3}$ s^{-1} and $\lambda_O = 2 \times 10^{-3}$ s^{-1} to $\lambda_C = 10^{-7}$ s^{-1} and $\lambda_O = 2 \times 10^{-6}$ s^{-1}). Our comparison of these runs is fairly similar to that in the previous paragraph. Here, however, the similarity between the run for which the second substrate is present and $\alpha_2 = 0.0$, and the run in which the second substrate is absent extends out to more than 99% removal of Substrate 1, after which biodegradation of Substrate 1 occurs at a very low rate. This further control of the oxygen demand is related to the lower value of C_2/K_{C2}, as was pointed out in the discussion of Figs. 1 and 2. On the other hand, if the inhibitor requires oxygen ($\alpha_2 = 0.5$) and very high percentage removal is needed, it is of importance to be able to estimate the period during which a significant amount of Substrate 2, the inhibitor, will remain present. The run presented in Fig. 7 for $\alpha_2 =$

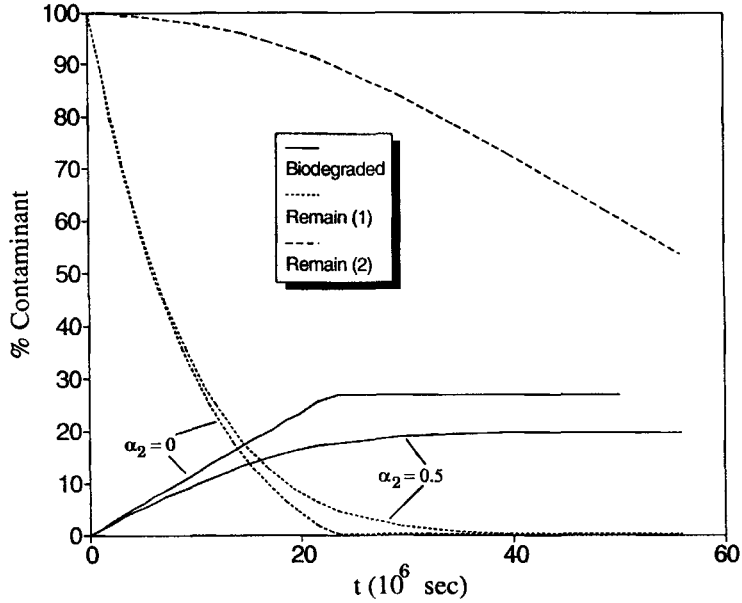

FIG. 7 Contaminant removal by stripping and biodegradation versus time, for $\alpha_2 = 0$ and $\alpha_2 = 0.5$. ($C_2^s = 750$ mg/L; $K_{C2} = 0.75$ mg/L; $\lambda_{C1} = 10^{-7}\ s^{-1}$; $\lambda_O = 2 \times 10^{-6}\ s^{-1}$). See Table 2 for parameter values.

0.5 is the only one leading to longer cleanup times than the run with $\alpha_2 = 0.0$. In the early stages of the process here, oxygen is being consumed by Substrate 2 as well as by Substrate 1. In the later stages the concentration of Substrate 1 is low, so inhibition by the adsorption of Substrate 2 on the enzymatic sites becomes limiting. This is especially severe if C_2 is large.

The difference between the theoretical cleanup times (99.996% removal) for runs with $\alpha_2 = 0.5$ seen in Fig. 7 (cleanup time 5.6×10^7 seconds, 650 days) and Fig. 8 (cleanup time 2.8×10^7 seconds, 320 days), which have the same value of C_2/K_{C2}, is due to the greater initial concentration of Substrate 2 during the run plotted in Fig. 7 (750 mg/L compared to 75 mg/L). If the inhibitor is demanding oxygen ($\alpha_2 = 0.5$) and very high removal efficiency is needed, it will be of considerable importance to know the period during which a significant amount of this substance, which is causing the inhibition of contaminant removal, will last.

In the runs performed with these low values of the mass transfer rate parameters the microbial population remains at quite reasonable values (<5 mg/L of aqueous phase) during the whole process, so no effects are

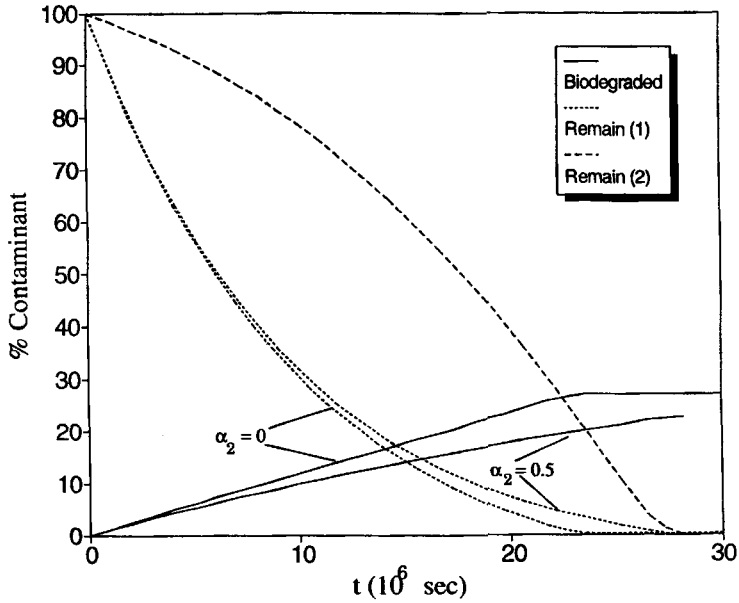

FIG. 8 Contaminant removal by stripping and biodegradation versus time, for $\alpha_2 = 0$ and $\alpha_2 = 0.5$. ($C_2^s = 75$ mg/L; $K_{C2} = 0.075$ mg/L; $\lambda_{C1} = 10^{-7}\ s^{-1}$; $\lambda_O = 2 \times 10^{-6}\ s^{-1}$). See Table 2 for parameter values.

to be expected such as were mentioned above for runs with larger values of the mass transfer rate parameters.

CONCLUSIONS

A mathematical model for bioassisted soil vapor extraction has been modified to include a second, nonvolatile substrate in addition to the contaminant. The effects of competitive inhibition through adsorption of the second substrate on the active enzymatic sites of the microorganisms and through its competition with the first substrate for oxygen have been examined under conditions of both rapid and slow mass transport of oxygen and of the volatile substrate. The model gives results which are qualitatively reasonable, but the parameters must be assigned on the basis of laboratory studies. Still, the model provides a way to develop insight into the nature of the interactions involved in the quite complex and intimately linked processes occurring in bioassisted soil vapor extraction.

When one is doing feasibility studies for the remediation of the vadose zone contaminated by a mixture of biodegradable VOCs, or a single target

VOC in the presence of other biodegradable substances naturally occurring in the soil, bioventing should be one of the first technologies to be checked, because this technique has the advantages of soil vapor stripping together with others arising from the biological processes. These biological processes are promoted by the large amounts of oxygen drawn into the soil, but to have effective remediation one must be sure that this oxygen is made available to the microorganisms where it is most needed.

If mass transport of oxygen to the microorganisms in the contaminated area is rather slow, the biological processes will be limited by the amount of oxygen available, and there is no need of very realistic values for the other parameters. If these mass transport limitations are likely to occur for oxygen, they will also probably be limiting SVE efficiency, so important contributions of the biodegradation processes to remediation are to be expected if the oxygen, in short supply to the microorganisms, is not utilized exclusively for the oxidation of other substrates present. On the other hand, if the mass transport of oxygen between the gaseous and aqueous phase is not controlling, rather complicated biological interactions may arise (simply because of the complexity of the system), but important reductions in the cleanup times are likely to be obtained compared to the SVE technique alone, especially if nearly complete removal is needed.

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