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Soil Cleanup by In-Situ Aeration. XXI. Effects of Desorption Rates and Equilibria on Remediation Rates

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ABSTRACT

A model for soil vapor extraction (SVE) is developed which permits the use of nonlinear adsorption isotherms and takes desorption kinetics into account. The configuration modeled is a single vertical well. The model is used to exhibit the dependence of cleanup rate on the parameters of the nonlinear adsorption isotherm and on a rate constant k_f associated with adsorption. Cleanup curves similar to those found in modeling diffusion-limited SVE by the lumped diffusion parameter method are observed for small values of k_f. Slow cleanup rates can also result from isotherm parameter values. In particular, severe tailing in the terminal phase of remediation may result from an equilibrium isotherm which approaches the form $C^{\text{gas}} = K(C^{\text{sorbed}})^B$, where $B > 1$ as C^{sorbed} approaches zero. As with diffusion-limited SVE, short-term pilot-scale experiments may well not identify conditions which cause tailing during terminal phase cleanup. One can distinguish between poor SVE performance due to small rate constants and poor SVE performance due to the adsorption isotherm by soil gas volatile organic compound (VOC) concentration rebound curves. Rebound occurs if diffusion and/or desorp-

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tion rates are limiting. Rebound does not result if adsorption isotherm characteristics are limiting. Increases in the gas flow rate will not be helpful in the former case, while they will result in increased VOC removal rates in the latter.

INTRODUCTION

Soil vapor extraction (SVE) techniques are now well established for the removal of volatile organic compounds (VOCs) from contaminated sites. Some 83 Superfund sites were using or scheduled to use the technique as of October 1992, and it is in use on many other sites for removal of VOCs. EPA has published a number of reports on SVE (1–4), as well as the proceedings of a symposium on the subject (5). Hutzler and his coworkers (6, 7) and Wilson and Clarke (8) have reviewed the technique in detail. No attempt is made here to review the extensive literature on the subject.

The mathematical modeling of SVE provides physical insight into the factors affecting the process, as well as support for initial site-specific evaluation, interpretation of lab- and pilot-scale field data, design of pilot- and full-scale field SVE operations, and estimation of costs and cleanup times. Several groups in the United States have developed SVE models, including Marley and his coworkers at Vapex (9–15 and other papers); Johnson, Kemblowski, and their coworkers (16–20 and other papers); Cho (21); the Idaho National Engineering Laboratory (22, 23); and the Eckenfelder–Vanderbilt group (24–26, for example). SVE modeling work has also been carried out at the University of Málaga in Spain (27–30, for example).

The assumption of local equilibrium with respect to transport of VOC between the advecting soil gas and the stationary phase(s) containing VOC as an adequate approximation (31, 32) has been found invalid at a number of sites. At these, rapid decline in off-gas VOC concentrations after a brief initial phase of operation (a few days, sometimes only a few hours) followed by an extended period of tailing during the final phase of the cleanup indicates that local equilibrium is not being maintained—that diffusion and/or desorption kinetics are acting as a bottleneck which limits the release of VOC to the advecting gas. DiGiulio et al. (33) described possible pilot-scale field experiments to assess mass transport limitations, and Lyman and Noonan (3) commented that such limitations are common. DiGiulio (34) discussed in some detail the importance of mass transport limitations in SVE.

Some time ago we presented a lumped parameter method for including mass transport kinetics limitations in SVE models (27–30, 35) which could give removal rates much reduced below those obtained from models making the local equilibrium assumption. Unfortunately, however, this model could not yield with the same parameter set the rapid initial VOC removal rates and the quite slow rates toward the end of the remediation which are observed in the field. The lumped parameter approach to diffusion mass transport is evidently over-simplified and does not provide the broad spectrum of time constants necessary to describe what is happening.

This difficulty was discussed recently (36), and a model for SVE lab column operation was described which used a more realistic approach to diffusion transport. This was one of two distributed diffusion models explored which assume that VOC diffuses from water-saturated layers of finite thickness before it reaches the advecting soil gas and is removed. In one approach the NAPL is present as droplets distributed throughout the water-saturated low-permeability layers; in the other the nonaqueous phase liquid (NAPL) is present as a film within the water-saturated lamellae. The two approaches could be made to yield realistic and rather similar results on suitable selection of the parameters in the models.

In subsequent papers of this series (37, 38) we discussed the extension of the first approach (in which NAPL is present as distributed droplets distributed throughout the low-permeability lenticular domains) and the second approach (in which NAPL is present as a thin layer within the low-permeability lenticular domains from which it must diffuse to the advecting air) to SVE by means of a horizontal slotted pipe well. The models performed well, easily producing the high initial VOC removal rates, the rapid declines in off-gas VOC concentration, and the lengthy plateaus and tailing observed experimentally.

The physical picture with these models was not clear, however. For the first model it was not evident how droplets of NAPL could migrate to or be formed in the interiors of the low-permeability domains. For the second it was not evident how the postulated thin layer of NAPL was to be created deep within the low permeability structures in the first place. This left these models of the diffusion process lacking a credible, easily visualized physico-chemical basis. They had meaning in terms of the least dimension of the low-permeability structures from which diffusion was taking place, and they produced physically acceptable results, but the physical picture was rather contrived.

A subsequent model (39) avoided these difficulties by having the NAPL present as droplets only in the mobile (air-filled) porosity, and excluding it from the water-saturated low-permeability porous domains. It was assumed that VOC could migrate into these domains only by diffusion of dissolved VOC in the aqueous phase. It was assumed that initially (at the time of the spill or sudden leak) the VOC is present only as vapor and NAPL, both in the air-filled porosity, and that subsequently the VOC diffuses into the water-saturated domains. In remediation one therefore sees rapid removal of VOC initially as the NAPL droplets evaporate in the advecting gas stream, followed by a much slower rate of removal as VOC diffuses back out of the water-saturated domains.

There is another mechanism for kinetic control of SVE, however, which none of the above modeling work takes into account. This is the rate of desorption of adsorbed VOC. If desorption processes are slow, efforts to enhance dispersion/diffusion are likely to have rather limited benefits. Recently there have been a number of reports on the desorption kinetics of VOCs in soils (40–44) indicating that diffusion is by no means the only factor impeding the rates of SVE cleanups. In addition, SVE models have generally assumed some sort of linear isotherm. Often this is simply Henry's law; sometimes a partition factor is measured experimentally or estimated from the concentration of natural organic carbon in the soil. One expects that use of more realistic isotherms in the SVE models may lead to the appearance of tailing in SVE remediation somewhat similar to that resulting from the kinetics of diffusion and, presumably, of desorption as well.

Here we shall first explore some aspects of various adsorption isotherms which might be considered for use in a model for SVE. This is followed by discussion of the constraint imposed on the expression for the rate of desorption by the expression for the rate of adsorption and the adsorption isotherm. The development of a model for the SVE of an adsorbed contaminant is then presented. The calculation of the gas flow field used here is identical to that employed in a number of our earlier SVE models (39, for example), so only the results will be presented here. The approach to local adsorption/desorption equilibrium will be discussed in detail. A section on results presents plots of runs showing the dependence of SVE cleanup rates on the various parameters of the model. The paper closes with a section on conclusions.

ANALYSIS

The configuration of the single vertical SVE well analyzed here is shown in Fig. 1, along with much of the notation. The model for development

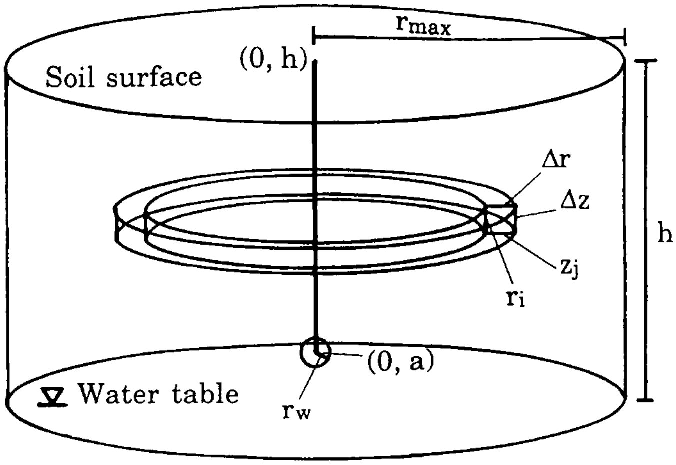

FIG. 1 The geometry of an SVE well and some of the notation used.

of an SVE model breaks down into three major parts; the analysis of the equilibrium and mass transport factors governing the release of the VOC being vapor stripped, the calculation of the soil gas flow field in the vicinity of the vacuum well, and the combining of the two to form the model.

A. Adsorption Isotherms and Rates of Adsorption and Desorption

We first turn to the relationship governing the equilibrium distribution of the semivolatile organic compound (SVOC) between the mobile vapor phase and the stationary adsorbed (perhaps condensed) phase(s), and to the rates of adsorption and desorption.

Adsorption Isotherms

The isotherms will be written here in a way analogous to Henry's law, in which the vapor phase SVOC concentration C^g (kg/m^3 of air) is expressed in terms of the stationary phase concentration C^g (kg/m^3 of soil). (Usually adsorption isotherms give C^s as a function of C^g; it turns out here to be convenient to invert the equation.) We shall explore a number of isotherms to determine which are physically reasonable for application in SVE and which must be eliminated or modified.

1. The Linear Isotherm. The simplest isotherm is the linear isotherm—an extension of Henry's law,

$$C^g = K_L C^s \tag{1}$$

This is widely used in modeling work because it is simple. Unfortunately, it cannot be even approximately correct at large values of C^s since these will yield values of C^g in excess of the value allowed by the equilibrium vapor pressure of the pure liquid SVOC, C^g_{sat}, given by

$$C^g_{\text{sat}} = \frac{(\text{MW})P^{\text{O}}_{\text{vap}}(T)}{RT} \tag{2}$$

where MW = molecular weight of the SVOC, kg/mol
$P^{\text{O}}_{\text{vap}}(T)$ = pure SVOC vapor pressure (atm) at temperature T
T = temperature, K
R = gas constant, 8.204×10^{-5} m^3 atm/mol·deg

One can patch the linear isotherm to avoid this difficulty by calculating C^g by Eq. (1) and then, if $C^g > C^g_{\text{sat}}$, setting $C^g = C^g_{\text{sat}}$.

2. The Freundlich Isotherm. The Freundlich isotherm, commonly written as

$$C^g = K_F(C^g)^{1/n} \tag{3}$$

is written in our form as

$$C^g = (1/K_F)^n(C^s)^n \tag{4}$$

This is widely used but suffers from the same problem at large values of C^s as does the linear isotherm, and so requires the introduction of a similar patch to avoid values of C^g larger than C^g_{sat}.

3. The Langmuir Isotherm. The Langmuir isotherm may be written as

$$C^s = C^s_{\text{max}} \frac{C^g}{C^g_{1/2} + C^g} \tag{5}$$

which is readily solved for C^g; one obtains

$$C^g = \frac{C^g_{1/2}C^s}{C^g_{\text{max}} - C^s} \tag{6}$$

In the applications of interest here, this isotherm suffers from the disadvantage that C^g approaches infinity as C^g approaches $C^s_{\max}$, which is physically impossible; C^g must never be larger than C^g_{sat}.

4. *The BET Isotherm.* The BET isotherm is given by

$$C^g = \frac{G_m c(C^g/C^g_{\text{sat}})}{[1 - (C^g/C^g_{\text{sat}})][1 + (c - 1)(C^g/C^g_{\text{sat}})]} \tag{7}$$

where G_m and c are constants characteristic of the SVOC, the adsorbent, and the temperature. Equation (7) can be solved for C^g/C^g_{sat}; the result is

$$\frac{C^g}{C^g_{\text{sat}}} = \frac{-(G_m c/C^s + 2 - c) + [(G_m c/C^s + 2 - c)^2 + 4(c - 1)]^{1/2}}{2(c - 1)} \tag{8}$$

As C^s approaches infinity, C^g/C^g_{sat} approaches unity, which is the desired behavior. The BET isotherm therefore shows acceptable behavior at high SVOC soil concentrations without modification. Some representative plots of C^g/C^g_{sat} versus C^s/G_m are given in Fig. 2.

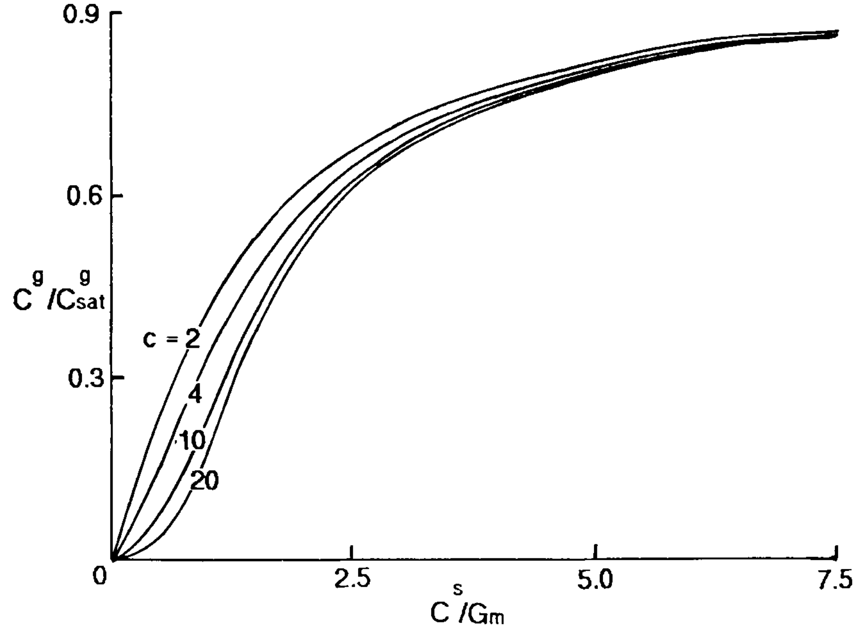

FIG. 2 Plots of C^g/C^g_{sat} (ordinate) versus C^s/G_m (abscissa) for the B-E-T isotherm. c = 2, 4, 10, and 20, as indicated.

5. Another Acceptable Isotherm. Another group of isotherms for which C^g approaches C^g_{sat} from below as C^s approaches infinity is given by the equation

$$C^g = \frac{C^g_{sat}(C^s/C')^B}{1 + (C^s/C')^B} \tag{9}$$

where C' and B are parameters depending on the SVOC, the adsorbent medium, and the temperature. At low values of C^s/C' this approaches the behavior of the Freundlich isotherm,

$$C^g = \frac{C^g_{sat}}{(C')^B}(C^s)^B \tag{10}$$

and as C^s/C' approaches infinity, C^g approaches C^g_{sat}, as desired. Some plots of C^g versus C^s are given for various values of the exponent B in Fig. 3.

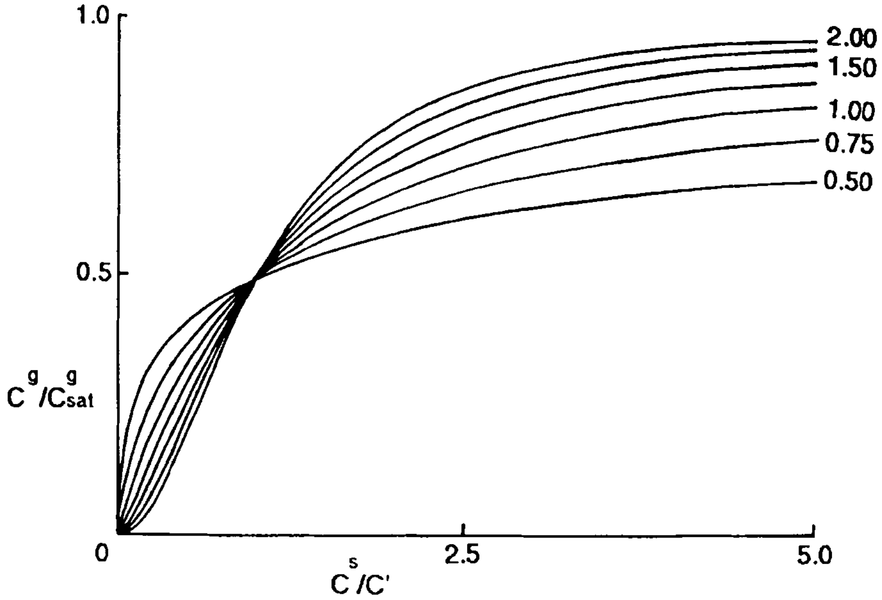

FIG. 3 Plots of C^g/C^g_{sat} (ordinate) versus C^s/C' (abscissa) for the isotherm specified by Eq. (9), a modified Freundlich isotherm. Values of the exponent B are 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.0, from bottom to top on the right.

Generally, then, we can write

$$C^g = F(C^s) \tag{11}$$

where F is a physically acceptable continuous isotherm function such as Eq. (8) or (9), or may be one of the other isotherm functions, modified, if necessary, to permit it to handle values of C^s sufficiently large that the simple function would generate values of C^g larger than C^g_{sat}.

Adsorption and Desorption Rates

We next turn to the rates of adsorption and desorption. The process being considered is

$$\text{SVOC}^g \underset{k_r}{\overset{k_f}{\Longleftrightarrow}} \text{SVOC}^s$$

For the forward reaction rate we write

$$R_{\text{forward}} = k_f C^g \tag{12}$$

and for the reverse reaction, similarly,

$$R_{\text{reverse}} = k_r C^s \tag{13}$$

where k_f and k_r may be functions of C^g, C^s, and possibly other variables. Then at equilibrium

$$R_{\text{forward}} = R_{\text{reverse}} \tag{14}$$

so

$$k_f C^g = k_r C^s \tag{15}$$

and

$$C^g = (k_r/k_f)C^s = F(C^s) \tag{16}$$

from Eq. (11). We therefore see that the functions k_r and k_f must be related by the equation

$$k_r = k_f F(C^s)/C^s \tag{17}$$

That is, for a given isotherm F, once we postulate a form for k_f, k_r is determined from thermodynamic considerations.

We wish to write expressions for the rates of adsorption and desorption of SVOC. To do this we next carry out a mass balance for SVOC in a volume element in which we consider only adsorption/desorption kinetics. Let

V = volume of the volume element, m^3
ν = gas-filled porosity of soil, dimensionless
m = mass of SVOC in the volume element, kg

Then

$$m = \Delta V(\nu C^g + C^s) \tag{18}$$

and

$$\left[\frac{\partial}{\partial t}(m/\Delta V)\right]_{\substack{\text{ads}\\\text{des}}} = 0 = \nu\left[\frac{\partial C^g}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} + \left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} \tag{19}$$

from which

$$\left[\frac{\partial C^g}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = -(1/\nu)\left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} \tag{20}$$

Now

$$\left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = k_f C^g - k_r C^s \tag{21}$$

which, with Eq. (17), yields

$$\left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = k_f[C^g - F(C^s)] = \frac{dC^s}{dt} \tag{22}$$

and, with Eq. (20),

$$\left[\frac{\partial C^g}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = -(k_f/\nu)[C^g - F(C^s)] \tag{23}$$

This is as far as purely formal arguments will permit us to go. At this point we must select on some basis the rate "constant" k_f for the adsorption reaction. As mentioned above, this may itself be a function of concentrations, etc. In our subsequent work we shall take it to be a constant, thereby making the assumption that the adsorption process is simply first order in the gaseous SVOC concentration. If more detailed information permits one to choose some other rate law, perhaps more complex, this presents no difficulties in the subsequent theoretical analysis.

B. Gas Flow Field

We assume a porous medium of constant, isotropic permeability, so may use the method of images from electrostatics (45) for calculating the soil gas pressures near the SVE well. We work in cylindrical coordinates r, z. The analysis is given in detail elsewhere (39), so we will merely summarize the results here. Let

h = thickness of porous medium (depth to water table), m
$r_{\max}$ = radius of domain of interest, m
r_w = radius of gravel packing of the well, m
P_w = wellhead gas pressure (<1 atm), atm
P_a = ambient pressure, atm
$P(r, z)$ = soil gas pressure at the point (r, z), atm
K_D = Darcy's constant, m^2/atm·s
a = distance of well above the water table, m
Q = molar gas flow rate to well, mol/s
q = standard volumetric gas flow rate to well, m^3/s
v_r = r-component of superficial velocity, m/s ($m^3/m^2\cdot s$)
v_z = z-component of superficial velocity, m/s ($m^3/m^2\cdot s$)
R = gas constant, 8.206×10^{-5} m^3 atm/mol·deg
T = temperature, degrees Kelvin

The pressure of an ideal gas in a porous medium satisfies the equation

$$\nabla^2 P^2 = 0 \tag{24}$$

with boundary conditions

$$\frac{\partial P^2(r, 0)}{\partial z} = 0 \tag{25}$$

at the water table, and

$$P^2(r, h) = P_a^2 = 1 \text{ atm}^2 \tag{26}$$

at the soil surface. Define a potential function $W(r, z)$ by

$$W(r, z) + P_a^2 = P^2(r, z) \tag{27}$$

so the problem becomes

$$\nabla^2 W = 0 \tag{28}$$

$$\frac{\partial W(r, 0)}{\partial z} = 0 \tag{29}$$

$$W(r, h) = 0 \tag{30}$$

There must also be a sink at (0, a) to represent the vacuum well.

We use the method of images (45) to construct W; it is given by

$$W = A \sum_{n=-\infty}^{\infty} \left[-\frac{1}{\{r^2 + [z - 4nh - a]^2\}^{1/2}} - \frac{1}{\{r^2 + [z - 4nh + a]^2\}^{1/2}} + \frac{1}{\{r^2 + [z - (4n-2)h - a]^2\}^{1/2}} + \frac{1}{\{r^2 + [z - (4n-2)h + a]^2\}^{1/2}} \right] \tag{31}$$

The constant A is evaluated by the requirement that at (0, $a + r_w$), $P = P_w$, the wellhead pressure. Here r_w is the radius of the well gravel packing. We find that

$$A = (P_w^2 - P_a^2)/S \tag{32}$$

where S is given by

$$S = \sum_{n=-\infty}^{\infty} \left[-\frac{1}{|r_w - 4nh|} - \frac{1}{|2a + r_w - 4nh|} + \frac{1}{|r_w - (4n-2)h|} + \frac{1}{|2a + r_w - (4n-2)h|} \right] \tag{33}$$

The Darcy's constant can be calculated in terms of observables from Eq. (34),

$$K_D = \frac{qS}{2\pi(P_w^2 - P_a^2)} \tag{34}$$

The superficial velocity of the gas is given by

$$v = -K_D \nabla P = -K_D \nabla W / [2(P_a^2 + W)^{1/2}] \tag{35}$$

where the components of ∇W are $\partial W/\partial r$ and $\partial W/\partial z$, and the velocity components are v_r and v_z. This completes the summary of the calculation of the soil gas velocity field.

C. Completion of the Model: Volume Elements and Surfaces of Volume Elements, Advective Mass Balance

See Fig. 1. The volume of the annular volume element is given by

$$\Delta V_{ij} = (2i - 1)\pi(\Delta r)^2\Delta z \tag{36}$$

The surfaces of this volume element are given by the following equations:

Inner $S^{\mathrm{I}}_{ij} = 2(i - 1)\pi\Delta r\Delta z$ (37)

Outer $S^{\mathrm{O}}_{ij} = 2i\pi\Delta r\Delta z$ (38)

Top and Bottom $S^{\mathrm{T}}_{ij} = S^{\mathrm{B}}_{ij} = (2i - 1)\pi(\Delta r)^2$ (39)

The advective mass balance for VOC in this volume element is then

$$\begin{aligned} \nu\Delta V_{ij}\left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\mathrm{adv}} &= S^{\mathrm{I}}_{ij}v^{\mathrm{I}}_{ij}[S(v^{\mathrm{I}})C^g_{i-1,j} + S(-v^{\mathrm{I}})C^g_{ij}] \\ &+ S^{\mathrm{O}}_{ij}v^{\mathrm{O}}_{ij}[-S(-v^{\mathrm{O}})C^g_{i+1,j} - S(v^{\mathrm{O}})C^g_{ij}] \\ &+ S^{\mathrm{B}}_{ij}v^{\mathrm{B}}_{ij}[S(v^{\mathrm{B}})C^g_{i,j-1} + S(-v^{\mathrm{B}})C^g_{ij}] \\ &+ S^{\mathrm{T}}_{ij}v^{\mathrm{T}}_{ij}[-S(-v^{\mathrm{T}})C^g_{i,j+1} - S(v^{\mathrm{T}})C^g_{ij}] \end{aligned} \tag{40}$$

where

$$v^{\mathrm{I}}_{ij} = v_r\left[(i - 1)\Delta r, \left(j - \frac{1}{2}\right)\Delta z\right] \tag{41}$$

$$v^{\mathrm{O}}_{ij} = v_r\left[i\Delta r, \left(j - \frac{1}{2}\right)\Delta z\right] \tag{42}$$

$$v^{\mathrm{B}}_{ij} = v_z\left[\left(i - \frac{1}{2}\right)\Delta r, (j - 1)\Delta z\right] \tag{43}$$

$$v^{\mathrm{T}}_{ij} = v_z\left[\left(i - \frac{1}{2}\right)\Delta r, j\Delta z\right] \tag{44}$$

and the function $S(v)$ is zero if $v \leq 0$ and one if $v > 0$. The rate of change of C^g_{ij} with time is then given by

$$\frac{dC^g_{ij}}{dt} = \left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\mathrm{adv}} + \left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\substack{\mathrm{ads}\\ \mathrm{des}}} \tag{45}$$

The differential equations which constitute the model are Eqs. (22), (23), (40), and (45).

It is possible to speed up the calculations substantially by making the steady-state approximation for C^g_{ij} in Eq. (45); one sets dC^g_{ij}/dt equal to zero in Eq. (45), solves the ijth algebraic equation which results for C^g_{ij}, and, in the computer coding, starts with the largest values of i and j and works downward to lower values. Discrepancies between the results obtained from the integration of the time-dependent equations and results from solution of the mixed algebraic and differential equations resulting from the steady-state treatment were about 0.1%.

The total residual mass of contaminant is calculated from Eq. (46),

$$M_{\text{tot}} = \sum_{i=1} \sum_{j=1} \Delta V_{ij}[\nu C^g_{ij} + C^s_{ij}] \tag{46}$$

and the VOC concentration in the off gas is given by

$$C_{\text{effl}} = C^g_{1,j\text{well}} \tag{47}$$

where $\Delta V_{1,j\text{well}}$ is the volume element containing the screened section of the well.

D. Initial Distribution of VOC among the Phases

We assume that the VOC at the site has had ample opportunity to equilibrate between the vapor and the adsorbed phases. A mass balance on a volume element containing contaminant gives

$$C_{\text{total}} = \nu C^g + C^s \tag{48}$$

This, with Eq. (11), gives

$$C^s = C_{\text{total}} - \nu F(C^s) \tag{49}$$

Since C^g is generally much smaller than C^s, Eq. (49) can be solved iteratively according to the scheme

$$C^s_{k+1} = C_{\text{total}} - \nu F(C^s_k) \tag{50}$$

where we set $C^s_1 = C_{\text{total}}$ on the right-hand side to initiate the iteration.

RESULTS

These models were implemented in TurboBASIC on an AlphaSystem 486-DX microcomputer running at 50 MHz. A simple Euler method was used for the integration. Typical runs with the steady-state model for SVE with a single vertical well required about 6–30 minutes, depending on how long a time period was simulated. All runs modeled used Eq. (9) for the adsorption isotherm. Default values of the parameters are given in Table 1. Results are presented as plots of $M_{\mathrm{tot}}(t)/M_{\mathrm{tot}}(0)$ versus time in days; Figs. 9 and 10 also include plots of $C_{\mathrm{effl}}(t)/C^{g}_{sat}$ to show soil gas concentration rebound after wells have been shut down.

Figure 4 shows the dependence of cleanup on the isotherm parameter C^{g}_{sat}, which is the saturation vapor concentration of the VOC. Values of C^{g}_{sat}, from the top down, are 25, 50, 100, and 200 mg/L. Run duration is 50 days. As expected, we see a dramatic increase in VOC removal rate as its vapor pressure (and therefore C^{g}_{sat}) increases. The value of k_f, 10^{-4} s^{-1}, is sufficiently large that kinetic limitations are not a significant factor in these runs.

The effect of the isotherm parameter C' on the cleanup rate is shown in Fig. 5. C' gives a measure of the adsorptive capacity of the soil; the

TABLE 1
Default Values of the Parameters Used in the SVE Model

Depth to water table	10 m
Depth of well	8.5 m
Soil density	1.7 g/cm^3
Soil permeability	0.1 m^2/atm·s
Soil porosity	0.3
Air flow rate	50 SCFM
C^{g}_{sat}	200 mg/L
C'	1000 mg/kg
Exponent B	1
Rate constant k_f	10^{-4} s^{-1}
Domain radius	15 m
I_r	15
J_z	10
Temperature	15°C
$N_{\max}$ in image potential series	40
Contaminant concentration	500 mg/kg
Radius of contaminated zone	10 m
Depth of contaminated zone: Figs. 4–8	8 m
Figs. 9 and 10	10 m
Initial total contaminant mass: Figs. 4–8	2136 kg
Figs. 9 and 10	2670 kg
Δt: Figs. 4–8	100 seconds
Figs. 9 and 10	10 seconds
Duration of run: Figs. 4–7	50 days
Figs. 8–10	10 days

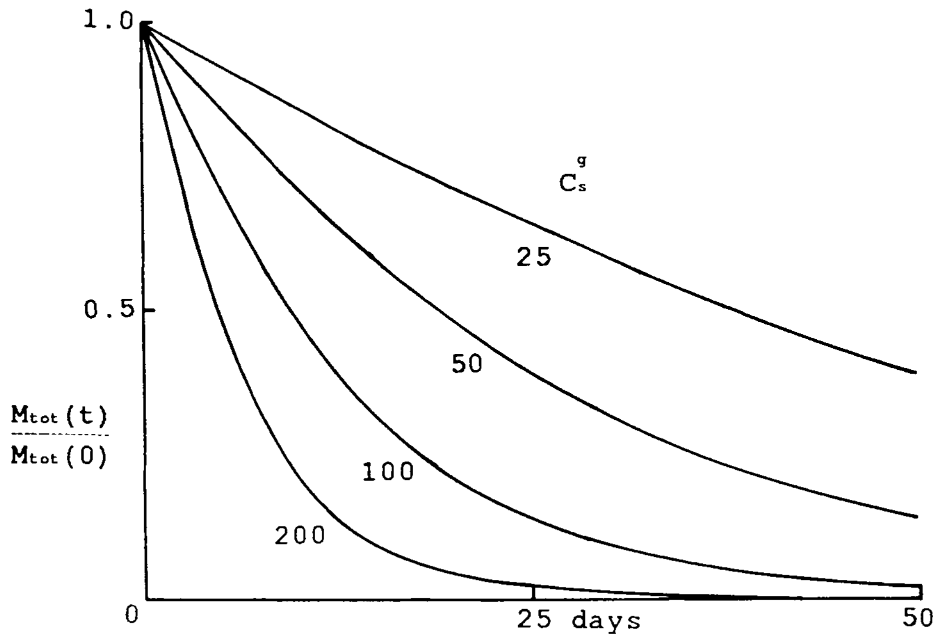

FIG. 4 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ versus time, days; effect of the isotherm parameter C^g_{sat}. C^g_{sat} = 25, 50, 100, and 200 mg/L from the top down. Other parameters as in Table 1.

larger C', the higher the concentration of adsorbed VOC must be to yield a given vapor concentration. We therefore expect C' to increase with increasing clay content and concentration of natural organic carbon in the soil, and to see VOC removal rates become smaller as C' increases. This is observed in the runs shown in Fig. 5, for which C' = 500, 1000, 2000, and 4000 mg/kg, from the bottom up.

Inspection of the isotherm plots in Fig. 3 shows that, as C^s decreases, C^g decreases more rapidly toward zero as B is increased. We therefore expect that VOC removal will become slower as B increases, as is observed in the runs shown in Fig. 6 as B is given values of 1, 1.25, 1.5, 1.75, and 2. Also, we see that the larger values of B result in very pronounced tailing. Tailing is normally associated with kinetic processes. The value of k_f used in these runs is sufficiently large that the desorption rate is not controlling; the tailing in this case is purely an equilibrium phenomenon associated with the nonlinearity of the adsorption isotherm

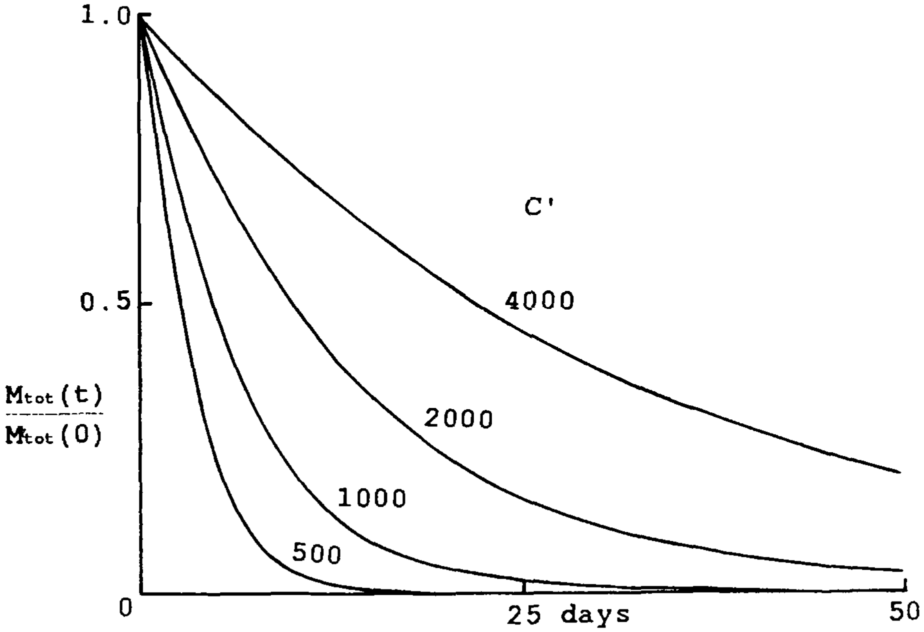

FIG. 5 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ versus time, days; effect of the isotherm parameter C'. $C' = 500$, 1000, 2000, and 4000 mg/kg, from the bottom up. Other parameters as in Table 1.

as C^s becomes small. With this type of tailing, isotherm tailing, one does not expect to find soil gas VOC concentration rebound after the well has been shut down. If B is larger than 1, the binding of the VOC molecules being removed becomes stronger as desorption approaches completion, so removal becomes more difficult. If one is using linear isotherm terminology, one would say that the air/soil partition coefficient decreases with decreasing VOC concentration.

The effects of gas flow rate are shown in Figs. 7 and 8. In Fig. 7 the value of k_f, the desorption rate constant, is 10^{-5} s^{-1}, one-tenth the value for k_f used in Fig. 8. The durations of these runs are 50 days. In Fig. 7 the effect of gas flow rate (25, 50, 100, and 200 SCFM) is relatively slight since the removal is desorption rate-limited. We see, for instance, that doubling the gas flow rate from 100 to 200 SCFM increases the cleanup rate negligibly.

In Fig. 8 the value of k_f has been increased to 10^{-4} s^{-1}, the durations

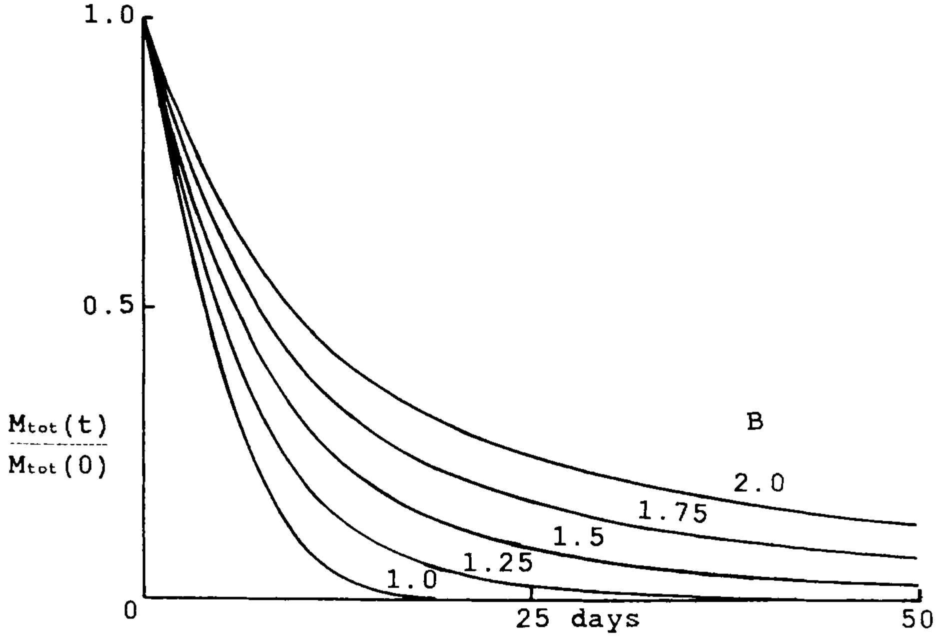

FIG. 6 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ versus time, days; effect of the isotherm exponent B. B = 1.0, 1.25, 1.5, 1.75, and 2.0, from the bottom up. Other parameters as in Table 1.

of the runs are 10 days, and again the gas flow rates are 25, 50, 100, and 200 SCFM. At this faster desorption rate the cleanup is now mainly advection-limited, and increasing the gas flow rate therefore results in substantial increases in cleanup rate, although cleanup rate is not proportional to gas flow rate as would be the case in a strictly local equilibrium model.

The measurement of soil gas VOC concentration rebound after gas flow at the SVE well has been stopped has been suggested earlier as a means of assessing the importance of kinetic limitations (33, 34, 46), and model calculations indicate that this is a good way of estimating the impact of

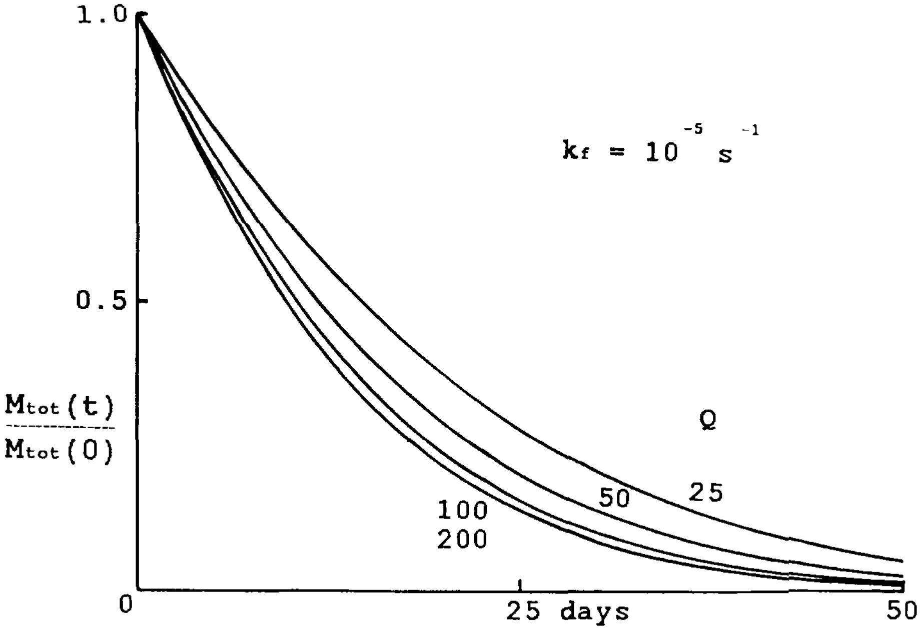

FIG. 7 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ versus time, days; effect of the gas flow rate Q. Q = 200, 100, 50, and 25 SCFM, from the bottom up; $k_f = 10^{-5}$ s^{-1}; other parameters as in Table 1.

diffusion kinetics on SVE (36, 39, 47). In connection with desorption equilibria and kinetics, one expects concentration rebound measurements to provide a means of distinguishing between tailing associated with equilibrium isotherm control (a large value of B, for example, as seen above) and tailing associated with kinetic control by the rate of desorption (i.e., a small value of k_f).

This is explored in the runs plotted in Figs. 9 and 10. In these runs the simulations were run for 10 days; 5 days of SVE followed by 5 days of equilibration for the observation of concentration rebound. In Fig. 9 the value of B used is 1, so at low total soil VOC concentrations the isotherm

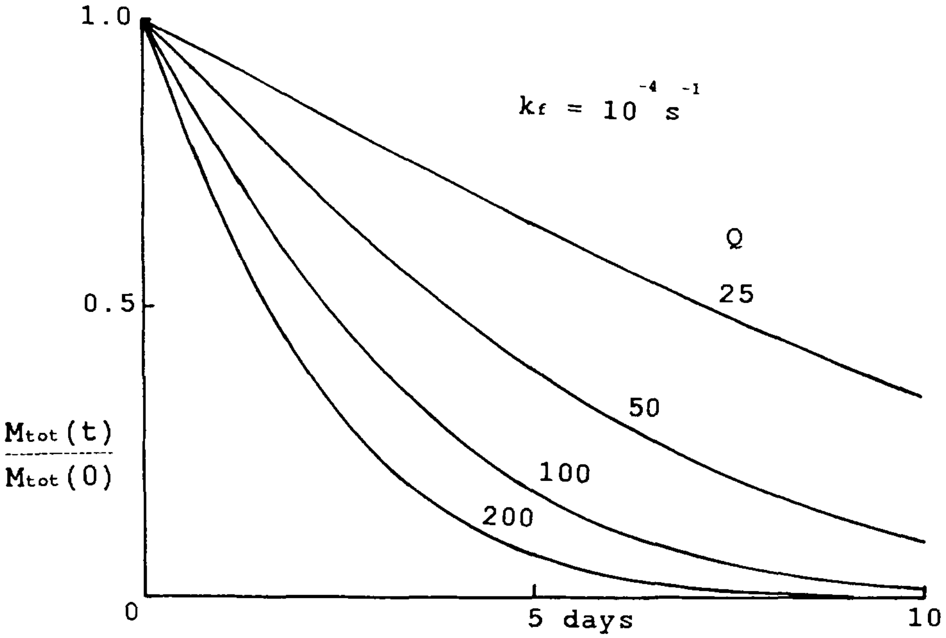

FIG. 8 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ versus time, days; effect of the gas flow rate Q. Q = 200, 100, 50, and 25 SCFM, from the bottom up; $k_f = 10^{-4}$ s^{-1}; duration of run = 10 days; other parameters as in Table 1.

is linear; in Fig. 10, $B = 2$, corresponding to a strongly nonlinear isotherm at low VOC concentrations. In both figures the values of k_f used were 10^{-3}, 10^{-4}, and 10^{-5} s^{-1}, covering the range from very fast to very slow desorption.

In Fig. 9 we see that concentration rebound is virtually negligible for $k_f = 10^{-3}$ s^{-1}, amounts to an increase of about 30% for $k_f = 10^{-4}$ s^{-1}, and results in an increase of about 500% for $k_f = 10^{-5}$ s^{-1}. The first two of these runs show rather rapid removal and little tailing; the last one exhibits a good deal of tailing. (See Fig. 7 for the behavior of a run identical to the last over a period of 50 days.)

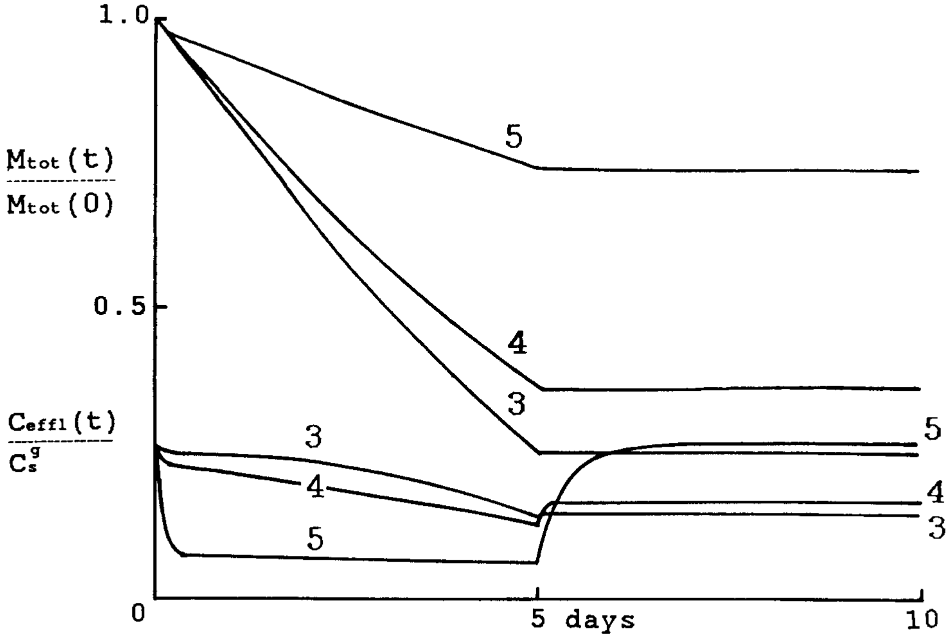

FIG. 9 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ and of reduced off-gas VOC concentration $C_{effl}(t)/C_{sat}^g$ versus time, days; effect of k_f on soil gas VOC concentration rebound after shutdown. $k_f = 10^{-3}$ (3), 10^{-4} (4), and 10^{-5} s^{-1} (5) as indicated; $B = 1$; other parameters as in Table 1.

In Fig. 10 we also see that concentration rebound is virtually negligible for $k_f = 10^{-3}$ s^{-1}, yields an increase of about 30% for $k_f = 10^{-4}$ s^{-1}, and results in an increase of about 500% for $k_f = 10^{-5}$ s^{-1}. Here $B = 2$, so the strongly nonlinear isotherm causes severe tailing in all of the runs. Evidently, however, one can distinguish between tailing resulting from slow desorption rates (which also result in soil gas VOC concentration rebound) and tailing resulting from a nonlinear adsorption isotherm (which does not show rebound). Cleanup can be substantially accelerated by increasing the gas flow rate if the tailing is due to a nonlinear adsorption isotherm. On the other hand, cleanup will be only slightly accelerated by

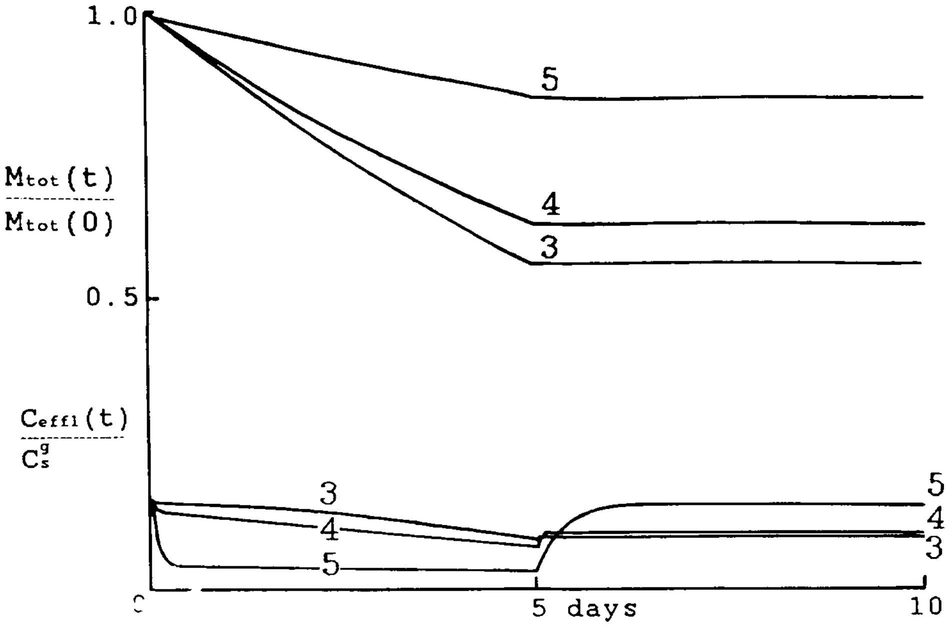

FIG. 10 Plots of reduced residual contaminant mass $M_{tot}(t)/M_{tot}(0)$ and of reduced off-gas VOC concentration $C_{effl}(t)/C^g_{sat}$ versus time, days; effect of k_f on soil gas VOC concentration rebound after shutdown, $k_f = 10^{-3}$ (3), 10^{-4} (4), and 10^{-5} s^{-1} (5) as indicated; $B = 2$; other parameters as in Table I.

increasing the gas flow rate if the tailing is due to a slow desorption reaction rate. Thus, distinguishing between the two cases is a matter of some practical interest in selecting operating conditions for an SVE system.

CONCLUSIONS

A mathematical model for SVE has been developed which permits the exploration of the impact of nonlinear adsorption isotherms and of the rate of VOC adsorption by the soil on the rate of cleanup by SVE. This model has been used to exhibit the dependence of cleanup rate on the parameters of the nonlinear adsorption isotherm and on a rate constant k_f associated with the adsorption process. The results lead to the following conclusions.

- Cleanup curves of a sort quite similar to those found in modeling diffusion-limited SVE by the lumped diffusion parameter method are observed for small values of k_f.
- Reduced cleanup rates can also be the result of the values of the isotherm parameters. In particular, severe tailing in the terminal phase of the remediation may be the result of an equilibrium isotherm which approaches the form $C^g = K(C^s)^B$, where $B > 1$ as C^s approaches zero.
- As with diffusion-limited SVE, it is quite probable that short-term pilot-scale experiments will not identify conditions which will result in significant tailing during the terminal phase of a cleanup by SVE.
- One can distinguish between poor SVE performance due to small adsorption/desorption rate constants and poor SVE performance due to the characteristics of the adsorption isotherm by measurements of soil gas VOC concentration rebound curves after gas flow to a well has ceased. Rebound will result if diffusion and/or desorption rates are limiting. Rebound will not result if the characteristics of the adsorption isotherm are limiting. Increases in the gas flow rate will not be advantageous in the former case, while they will result in increased VOC removal rates in the latter situation.

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