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Removal of Semivolatiles from Soils by Steam Stripping. IV. Effects of Adsorption/Desorption Kinetics

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ABSTRACT

A mathematical model is developed for in-situ steam stripping of semivolatile organic compounds (SVOCs) in which the adsorption isotherm of the SVOCs on the soil is nonlinear and in which desorption kinetics may be rate limiting. Severe tailing, similar to that found with diffusion-limited steam stripping, is readily produced by the model, even under situations in which adsorption–desorption kinetics are rapid. The results also indicate that field experiments alone are not likely to be able to distinguish between limitations imposed on the rate of steam-stripping remediation by diffusion kinetics and those imposed by desorption kinetics.

INTRODUCTION

The removal of biologically refractory semivolatile organic compounds (SVOCs) from contaminated soils by ambient temperature techniques such as soil vapor extraction or air sparging is not feasible because of the low vapor pressures of these compounds. It appears that steam stripping may provide a technology better adapted to addressing these nonbiodegradable SVOCs in situ.

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Steam stripping was reviewed relatively recently (1), and this review has been updated in our past papers on the subject (2–4). In the present paper we explore the effects of the kinetics of contaminant adsorption and desorption on the rate of cleanup by steam stripping. References of particular interest in connection with modeling work are the detailed and elegant treatment of Falta et al. (5, 6) and the papers published by Lord and his coworkers at Drexel University (7–13). Of these last, Ref. 9 includes the development of a local equilibrium model for steam stripping.

Our purpose here is to develop an in-situ steam-stripping model which includes adsorption/desorption kinetics to determine if it is feasible to distinguish by field experiments between the effects of diffusion kinetics (explored in Ref. 3) and the effects of adsorption/desorption kinetics. This is possibly a matter of some practical importance since lab-scale studies in steam-stripping columns could be used to characterize adsorption/desorption behavior. However, such studies would not be suitable for investigating diffusion kinetics effects in in-situ steam stripping since the soil structures largely responsible for the diffusion effects (lenses and other heterogeneities) would be disrupted in the processes of sample collection and column packing. Diffusion kinetics effects in in-situ steam stripping can only be studied in the field.

ANALYSIS

We shall assume that the initial transient period during which the soil is being heated up to 100°C by the injected steam contributes little to the removal of the SVOCs, so that we may regard our system as isothermal and the steam flow as being in a steady state. [Initial transient periods were explored for a one-dimensional column model in an earlier paper (4).] The problem then breaks down into three components. First is the calculation of the gas flow field, which can be done either by relaxation methods or by the method of images from electrostatics. The second component is the analysis of the local behavior of the SVOC—its adsorption isotherm and the rates of its adsorption and desorption. The third component is the merging of the first two to form the steam-stripping model.

The Gas Flow Field

We shall use gas flow fields calculated by the method of images (14); the calculations have been described in detail previously (2, 3), so the results will only be summarized here. Use of the method of images is restricted to porous media which are of constant, isotropic permeability.

The geometry of the system and some of the notation are indicated in Fig. 1.

In steady-state flow, an ideal gas can be assumed to obey

$$\nabla \cdot (K_D \nabla P^2) = 0 \tag{1}$$

where P = gas pressure, atm
K_D = Darcy's constant, m^2/atm·s

In a homogeneous isotropic medium, Eq. (1) reduces to

$$\nabla^2 (P^2) = 0 \tag{2}$$

The boundary conditions for the system are

$$P(r, h) = P_0, \qquad 0 < r < \infty, \qquad P_0 = 1 \text{ atm} \tag{3}$$

$$\frac{\partial P(r, 0)}{\partial z} = 0, \qquad 0 < r < \infty \tag{4}$$

Also, there must be a gas source at $(0, a)$.

As shown earlier, the distribution of charges shown in Fig. 2 provides a potential function which provides a source (the steam injection well) and which satisfies the boundary conditions in the region of interest. Thus, the method of images gives as the solution to this problem the following function.

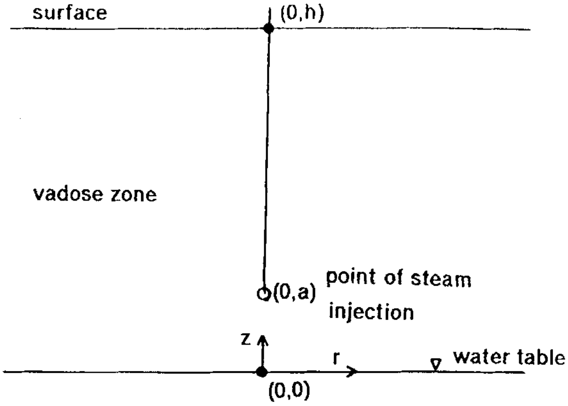

FIG. 1 Geometrical setup and notation for the calculation of the gas pressure distribution in the vicinity of a steam or hot air injection well.

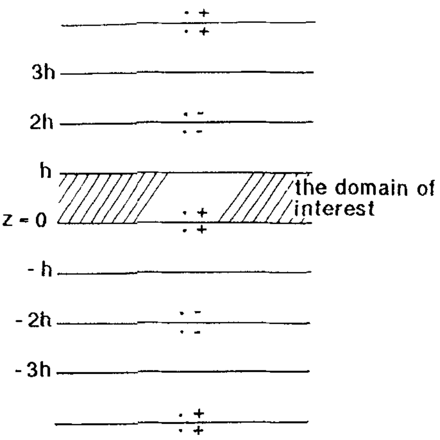

FIG. 2 Distribution of gas sources and sinks used in constructing the function W for calculating the gas velocity field in the vicinity of a steam or hot air injection well.

$$P^2 = W = P_0^2 + A \sum_{n=-\infty}^{\infty} \left[\frac{1}{\{r^2 + [z - 4nh - a]^2\}^{1/2}} + \frac{1}{\{r^2 + [z - 4nh + a]^2\}^{1/2}} - \frac{1}{\{r^2 + [z - (4n - 2)h - a]^2\}^{1/2}} - \frac{1}{\{r^2 + [z - (4n - 2)h + a]^2\}^{1/2}} \right] \tag{5}$$

where

$$A = \frac{P_w^2 - P_0^2}{S} \tag{6}$$

and

$$S(r_w, a, h) = \sum_{n=-\infty}^{\infty} \left[\frac{1}{\{r_w^2 + [-4nh]^2\}^{1/2}} + \frac{1}{\{r_w^2 + [2a - 4nh]^2\}^{1/2}} - \frac{1}{\{r_w^2 + [-(4n - 2)h]^2\}^{1/2}} - \frac{1}{\{r_w^2 + [2a - (4n - 2)h]^2\}^{1/2}} \right] \tag{7}$$

Darcy's constant K_D is related to observables by the relationship

$$K_D = \frac{q}{2\pi} \frac{S(r_w, a, h)}{P_w^2 - P_0^2} \tag{8}$$

In these equations

P_w = wellhead pressure, atm
r_w = radius of gravel packing of well, m
q = steam flow rate, m^3/s, = RTQ
Q = molar steam flow rate, mol/s
R = gas constant, 8.204×10^{-5} atm·m^3/mol·deg
T = temperature, K

The superficial gas velocities are then given by

$$v_r = -\frac{K_D}{2W^{1/2}} \frac{\partial W}{\partial r} \tag{9}$$

$$v_z = -\frac{K_D}{2W^{1/2}} \frac{\partial W}{\partial z} \tag{10}$$

This completes the calculation of the velocity field for the steam flow in the vicinity of the injection well.

Adsorption Isotherms and Rates of Adsorption and Desorption

We next turn to the relationship governing the equilibrium distribution of the 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^s (kg/m^3 of soil). We shall explore a number of isotherms to determine which are physically reasonable for application in steam stripping and which must be eliminated or modified.

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

$$C^g = K_L C^s \tag{11}$$

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

$$C^g_{\text{sat}} = \frac{(\text{MW})P^0_{\text{vap}}(T)}{RT} \tag{12}$$

where MW = molecular weight of the SVOC, kg/mol
$P^0_{\text{vap}}(T)$ = 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. (11) and then, if $C^g > C^g_{\text{sat}}$, setting $C^g = C^g_{\text{sat}}$.

The Freundlich Isotherm. The Freundlich isotherm, commonly written as

$$C^s = K_F(C^g)^{1/n} \tag{13}$$

is written in our form as

$$C^g = (1/K_F)^n(C^s)^n \tag{14}$$

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}.

The Langmuir Isotherm. The Langmuir isotherm may be written as

$$C^s = C^s_{\text{max}} \frac{C^g}{C^g_{1/2} + C^g} \tag{15}$$

which is readily solved for C^g; one obtains

$$C^g = \frac{C^g_{1/2}C^s}{C^s_{\text{max}} - C^s} \tag{16}$$

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

The BET Isotherm. The BET isotherm is given by

$$C^s = \frac{G_m c(C^g/C^g_{\text{sat}})}{[1 - (C^g/C^g_{\text{sat}})][1 + (c - 1)(C^g/C^g_{\text{sat}})]} \tag{17}$$

where G_m and c are constants characteristic of the SVOC, the adsorbent, and the temperature. Equation (17) can be solved for C^g/C^g_{sat}; the result is

$$\frac{C^g}{C^g_{\text{sat}}} = \frac{-(G_m c/C^s + 2 - c) + [(G_m c/C^s + 2 - c)^2 + 4(c - 1)]^{1/2}}{2(c - 1)} \tag{18}$$

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. 3.

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

$$C^g = \frac{C^g_{\text{sat}}(C^s/C')^B}{1 + (C^s/C')^B} \tag{19}$$

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,

$$C^g = \frac{C^g_{\text{sat}}}{(C')^B}(C^s)^B \tag{20}$$

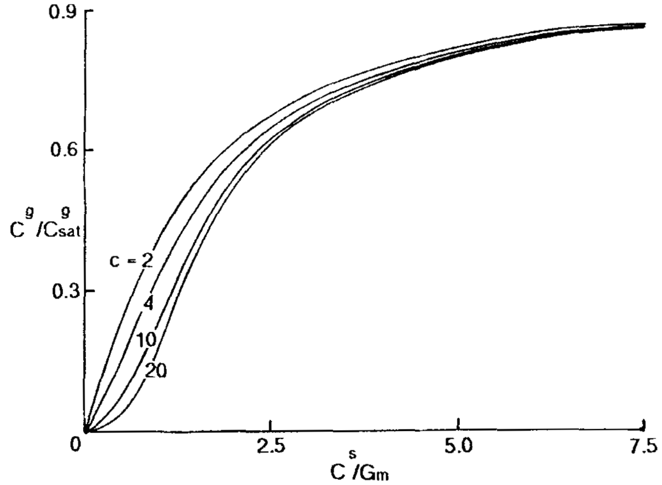

FIG. 3 Plots of the BET isotherm. The abscissa is C^g/C^g_{sat}; the ordinate, C^s/G_m. Values of c are 2, 4, 10, and 20.

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. 4.

Generally, then, we can write

$$C^g = F(C^s) \tag{21}$$

where F is a physically acceptable continuous isotherm function such as Eqs. (18) or (19), 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

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

For the forward reaction rate we write

$$R_{\text{forward}} = k_f C^g \tag{22}$$

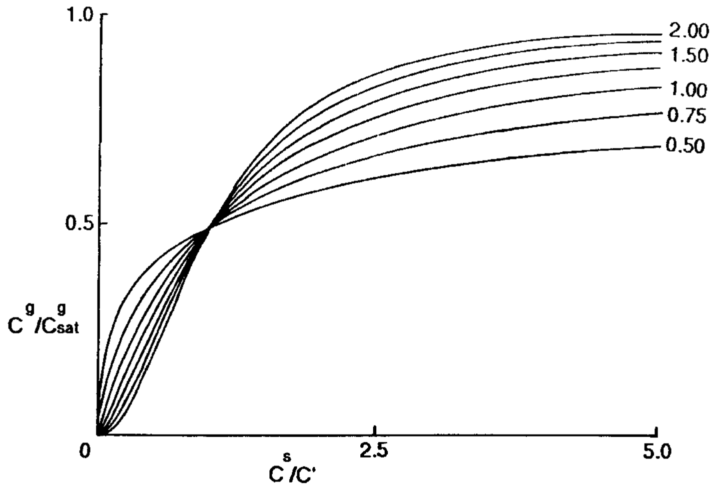

FIG. 4 Plots of the modified Freundlich isotherm. The ordinate is C^g/C^g_{sat}; the abscissa, C^s/C'. Values of the exponent B are 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00, from bottom to top on the right.

and for the reverse reaction, similarly,

$$R_{\text{reverse}} = k_r C^s \tag{23}$$

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

Then at equilibrium

$$R_{\text{forward}} = R_{\text{reverse}} \tag{24}$$

so

$$k_f C^g = k_r C^s \tag{25}$$

and

$$C^g = (k_r/k_f)C^s = F(C^s) \tag{26}$$

from Eq. (21). We therefore see that the functions k_r and k_f must be related by the equation

$$k_r = k_f F(C^s)/C^s \tag{27}$$

That is, 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

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

Then

$$m = \Delta V(\nu C^g + C^s) \tag{28}$$

and

$$\left[\frac{\partial}{\partial t}(m/\Delta V)\right]_{\substack{\text{ads}\\\text{des}}} = 0 = \nu\left[\frac{\partial C^g}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} + \left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} \tag{29}$$

from which

$$\left[\frac{\partial C^g}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = -(1/\nu)\left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} \tag{30}$$

Now

$$\left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = k_f C^g - k_r C^s \tag{31}$$

which, with Eq. (27), yields

$$\left[\frac{\partial C^s}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = k_f[C^g - F(C^s)] \tag{32}$$

and, with Eq. (30),

$$\left[\frac{\partial C^g}{\partial t}\right]_{\substack{\text{ads}\\\text{des}}} = -(k_f/\nu)[C^g - F(C^s)] \tag{33}$$

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.

Construction of the Model

We are now in position to merge the vapor flow dynamics and the adsorption/desorption kinetics to construct the differential equations which constitute the steam-stripping model.

Partition the soil domain around the steam injection well into a set of ring-shaped volume elements coaxial to the steam injection well, of vertical thickness Δz and horizontal thickness Δr. Then let the inner radius of the ith ring be given by

$$r_i = (i - 1)\Delta r \tag{34}$$

Also, let

$$z_j = (j - 1)\Delta z \tag{35}$$

The size of this volume element is given by

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

and the surfaces of the volume ΔV_{ij} are

$$A_{ij}^{\mathrm{I}} = 2\pi r_i \Delta z \qquad \text{(Inner surface)} \tag{37}$$

$$A_{ij}^{\mathrm{O}} = 2\pi r_{i+1} \Delta z \qquad \text{(Outer surface)} \tag{38}$$

$$A_{ij}^{\mathrm{T}} = A_{ij}^{\mathrm{B}} = \pi(r_{i+1}^2 - r_i^2) \qquad \text{(Top and Bottom surfaces)} \tag{39}$$

Let the superficial velocity components ($\mathrm{m^3/m^2 \cdot s}$) at these surfaces to the volume element be given by

$$v_{ij}^{\mathrm{I}} = v_r[(i-1)\Delta r, (j - \tfrac{1}{2})\Delta z] \tag{40}$$

$$v_{ij}^{\mathrm{O}} = v_r[i\Delta r, (j - \tfrac{1}{2})\Delta z] \tag{41}$$

$$v_{ij}^{\mathrm{T}} = v_z[(i - \tfrac{1}{2})\Delta r, j\Delta z] \tag{42}$$

$$v_{ij}^{\mathrm{B}} = v_z[(i - \tfrac{1}{2})\Delta r, (j-1)\Delta z] \tag{43}$$

where v_r and v_z are defined by Eqs. (9) and (10). Also, define the function

$$\begin{aligned} S(v) &= 0, \qquad v < 0 \\ &= 1, \qquad v > 0 \end{aligned} \tag{44}$$

A mass balance for advective transport of SVOC in ΔV_{ij} leads to

$$\begin{aligned} \left[\frac{\partial C_{ij}^{g}}{\partial t}\right]_{\mathrm{adv}} = (1/\nu\Delta V_{ij})\{ & v_{ij}^{\mathrm{I}} A_{ij}^{\mathrm{I}}[S(v^{\mathrm{I}})C_{i-1,j}^{g} + S(-v^{\mathrm{I}})C_{ij}^{g}] \\ & + v_{ij}^{\mathrm{O}} A_{ij}^{\mathrm{O}}[-S(-v^{\mathrm{O}})C_{i+1,j}^{g} - S(v^{\mathrm{O}})C_{ij}^{g}] \\ & + v_{ij}^{\mathrm{B}} A_{ij}^{\mathrm{B}}[S(v^{\mathrm{B}})C_{i,j-1}^{g} + S(-v^{\mathrm{B}})C_{ij}^{g}] \\ & + v_{ij}^{\mathrm{T}} A_{ij}^{\mathrm{T}}[-S(-v^{\mathrm{T}})C_{i,j+1}^{g} - S(v^{\mathrm{T}})C_{ij}^{g}]\} \end{aligned} \tag{45}$$

From Eqs. (32) and (33) we can write

$$\frac{dC_{ij}^{s}}{dt} = \left[\frac{\partial C_{ij}^{s}}{\partial t}\right]_{\substack{\mathrm{ads}\\ \mathrm{des}}} = k_f[C_{ij}^{g} - F(C_{ij}^{s})] \tag{46}$$

and

$$\left[\frac{\partial C_{ij}^{g}}{\partial t}\right]_{\substack{\mathrm{ads}\\ \mathrm{des}}} = -(k_f/\nu)[C_{ij}^{g} - F(C_{ij}^{s})] \tag{47}$$

Then, lastly,

$$\frac{dC_{ij}^{g}}{dt} = \left[\frac{\partial C_{ij}^{g}}{\partial t}\right]_{\mathrm{advection}} + \left[\frac{\partial C_{ij}^{g}}{\partial t}\right]_{\substack{\mathrm{ads}\\ \mathrm{des}}} \tag{48}$$

The modeling equations are then Eqs. (45)–(48).

We close the analytical section with assignment of the initial conditions and the calculation of the total residual mass of SVOC.

Let us specify a cylindrical domain around the well and coaxial to it which is contaminated at a constant total concentration, C_{tot} (kg/m^3 of soil). Then

$$C_{tot} = \nu C_0^g + C_0^s \tag{49}$$

Let us further assume that the vapor and adsorbed phases have come to equilibrium with respect to SVOC transport, so the Eq. (49) can be rewritten as

$$C_{tot} = \nu F(C_0^s) + C_0^s \tag{50}$$

Equation (50) is generally not solvable for C_0^s algebraically. Usually, however, $\nu F(C_0^s) \ll C_0^s$, so one can solve Eq. (50) easily by iteration according to the following scheme.

$$x_1 = C_{tot} \tag{51}$$

$$x_{i+1} = C_{tot} - \nu F(x_i), \qquad i = 2, 3, \ldots \tag{52}$$

and continue until convergence takes place (generally just a few iterations). Then

$$C_0^s = x_{final} \tag{53}$$

and

$$C_0^g = F(C_0^s) \tag{54}$$

Finally, the residual mass of contaminant at any time t during the course of the run is given by

$$M_{tot}(t) = \sum_{i=1}^{n_r} \sum_{j=1}^{n_z} \Delta V_{ij}[\nu C_{ij}^g + C_{ij}^s] \tag{55}$$

RESULTS

The model was implemented in TurboBASIC and run on an Alphasystem personal computer using an 80486 microprocessor running at 50 MHz. A typical 10-day run required about 15 minutes. In all the runs presented here, k_f was taken to be a constant, so that the adsorption reaction is assumed to be simply first order in the vapor-phase concentration of the SVOC. Default parameters for the runs are given in Table 1. Note that the plots of $M_{tot}(t)/M_{tot}(0)$ begin only after the soil mass has been heated up to 100°C; the initial heating period is not modeled. The isotherm represented by Eq. (19) was used in the calculations.

TABLE 1
Default Model Parameter Values Used for the Runs Plotted in Figs. 5, 6, and 7

Depth to water table	10 m
Depth of well	8 m
Soil density	1.7 g/cm^3
Soil permeability	0.10 m^2/atm·s
Initial soil moisture content	0.3
C^{g}_{sat}	250 mg/L
Isotherm parameter C'	1000 mg/kg
Isotherm exponent B, Fig. 5	1.0
Rate constant k_f, Fig. 6	1.0×10^{-3} s^{-1}
k_f, Fig. 7	2.5×10^{-5} s^{-1}
Domain radius	15 m
Steam flow rate	5.0 kg/h
Temperature	100 °C
Radius of contaminated zone	8 m
Depth of contaminated zone	4 m
Initial contaminant concentration	2000 mg/kg
Initial contaminant mass	2734.44 kg
Δt	25 seconds

The effect of k_f on the rate of cleanup is seen in Fig. 5. Values of k_f are 10^{-2}, 10^{-3} (nearly superimposed), 2×10^{-4}, 10^{-4}, 5×10^{-5}, and 2.5×10^{-5} s^{-1}. The exponent B in these runs is 1.0. For the larger values of k_f the rate of SVOC removal is essentially independent of k_f, and the process is, as expected, equilibrium controlled. Cleanup is essentially complete in about 10 days. As k_f decreases, the rate of desorption also decreases, and we find very markedly decreased cleanup rates. In contrast to our earlier results on diffusion-limited steam stripping, however, for these runs controlled by the SVOC desorption rate there is no initial period of rapid cleanup which is then followed by a long period of tailing as SVOC must diffuse out of the porous medium and into the advecting vapor phase. If the process is severely limited by desorption kinetics, Fig. 5 suggests that even initially the rate of removal of SVOC will be slow, in contrast to what one finds when diffusion kinetics are limiting. This initially gave us some cause for hope that one could readily distinguish the effects of desorption kinetics from the effects of diffusion kinetics.

It turned out, however, that this type of behavior of the cleanup curves could readily be changed simply by changing the value of the exponent B. In Fig. 6 we see plots of $M_{\mathrm{tot}}(t)/M_{\mathrm{tot}}(0)$ versus time for values of B ranging from 0.25 to 2.00. The value of k_f in these runs is 10^{-2} s^{-1}, so the rates of adsorption and desorption are quite fast. We see, however,

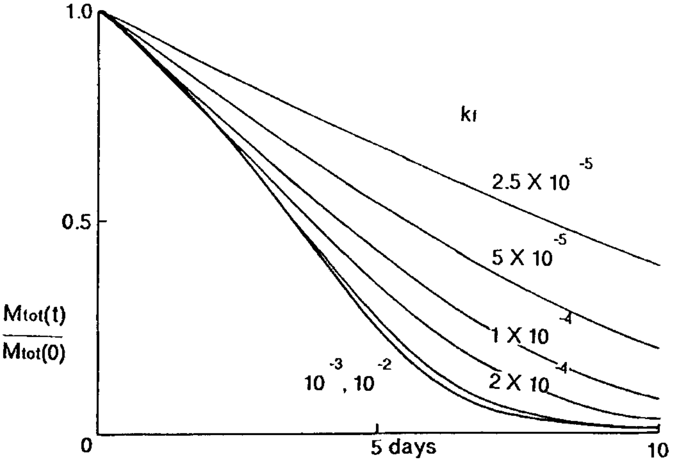

FIG. 5 Plots of $M_{\mathrm{total}}(t)/M_{\mathrm{total}}(0)$ versus time; effect of the rate constant for adsorption k_f. $k_f = 2.5, 5, 10, 20, 100$, and $1000 \times 10^{-5}\ \mathrm{s}^{-1}$, from top to bottom; $B = 1$. Other parameters as in Table 1.

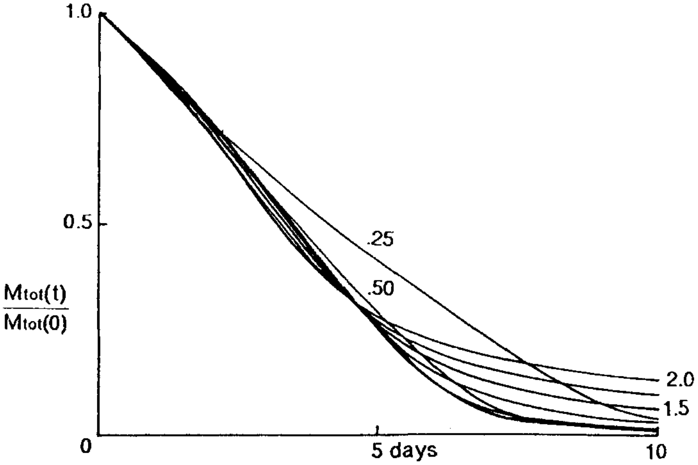

FIG. 6 Plots of $M_{\mathrm{total}}(t)/M_{\mathrm{total}}(0)$ versus time; effect of the value of the exponent B under equilibrium-controlled conditions. $B = 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75$, and 2.00 as indicated; $k_f = 10^{-3}\ \mathrm{s}^{-1}$. Other parameters as in Table 1.

that, even with this equilibrium-controlled desorption, tailing along toward the end of the cleanup is quite marked for values of B between 1.50 and 2.00. This tailing in fact mimics rather well the sort of tailing one can readily produce by means of steam-stripping models including only diffusion kinetics limitation.

Before one dismisses these results as pertaining to a contrived and probably unrealistic isotherm, one should remind oneself that at low SVOC concentrations this isotherm is virtually identical to the widely used Freundlich isotherm, and at high SVOC concentrations this isotherm gives a vapor-phase SVOC concentration equal to that which one calculates from the equilibrium vapor pressure of the pure SVOC. Use of relatively large (i.e., >1) values of B corresponds to the situation in which the adsorption sites are heterogeneous and the last SVOC to be removed from the soil is bound more strongly than that which is removed initially, certainly a reasonable surmise.

Figure 7 portrays runs for which the rate constant k_f is quite small ($2.5 \times 10^{-5}\ \mathrm{s}^{-1}$); in these runs B = 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00. The duration of these runs is 50 days (that of the runs shown in Figs. 5 and 6 is 10), and the tailing which was observed for $B > 1$ in Fig. 6 is seen here as well. As before, the shapes of the curves during the first few days of cleanup give no idea as to the extent of the tailing which occurs in the terminal phase of the remediation.

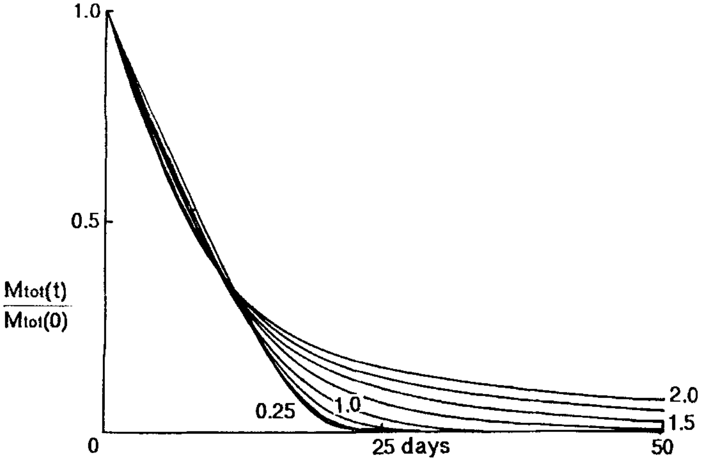

FIG. 7 Plots of $M_{\mathrm{total}}(t)/M_{\mathrm{total}}(0)$ versus time; effect of the value of the exponent B under desorption kinetics-limited conditions. B = 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 as indicated; $k_f = 2.5 \times 10^{-5}\ \mathrm{s}^{-1}$. Other parameters as in Table 1.

In Figs. 8 and 9 we explore the effect on cleanup rate of the extent to which the contaminant has penetrated down into the soil. This depends to a surprising degree on the initial contaminant concentration and on the value of B, the exponent in the adsorption isotherm. The three runs depicted in Fig. 8 were made with the model parameter values given in Table 2. B is equal to unity, and the initial contaminant concentrations are larger than the value of C'. The value of k_f, the adsorption rate constant, is 0.001 s^{-1}, large enough so that we expect the system to be essentially equilibrium-controlled. Cleanup is relatively rapid in all cases, being nearly complete in about 10 days. As expected, the greater the extent to which the contaminant has spread vertically (and to which the initial contaminant concentration has decreased), the slower is the cleanup, but the effect here is not large.

The three runs shown in Fig. 9 were made with the parameter values listed in Table 3. The value of k_f is again taken to be 0.001 s^{-1}, B is equal to 2, and the initial contaminant concentrations are substantially less than the value of C'. The effects of the changes in B and the initial contaminant concentration are disastrous in terms of the cleanup rate; even in the most favorable case cleanup is not complete after 50 days. We also see that the cleanup rate decreases spectacularly and tailing becomes more severe

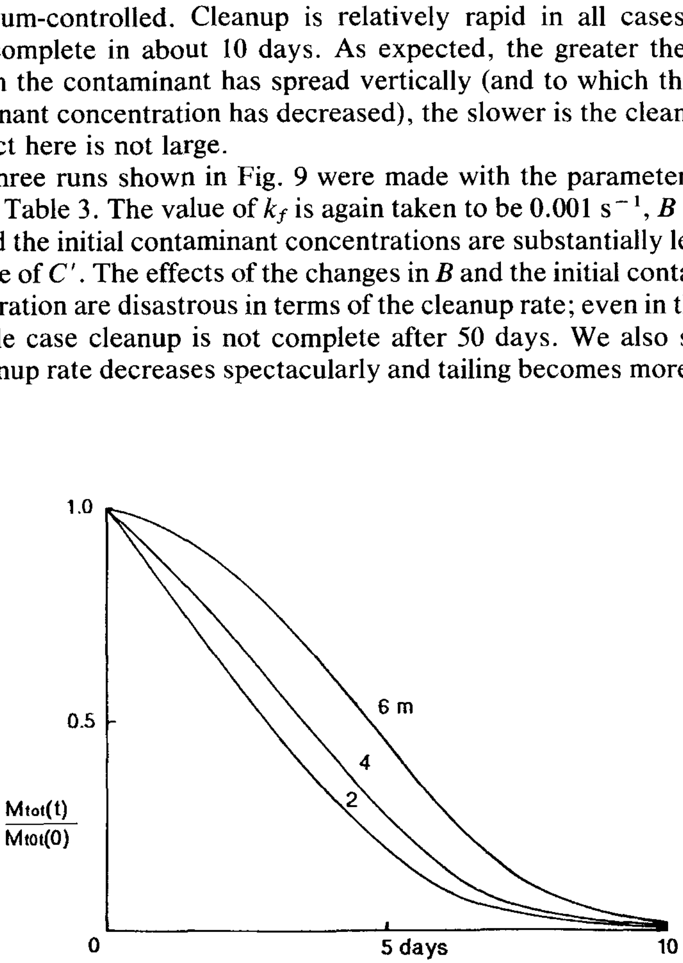

FIG. 8 Plots of $M_{total}(t)/M_{total}(0)$ versus time; effect of the extent of vertical spreading of the contaminant. Depth to which contaminant has spread = 6, 4, and 2 m from the top down. B = 1; initial contaminant concentrations = 1333.33, 2000, and 4000 mg/kg from the top down. Other parameters as in Table 2.

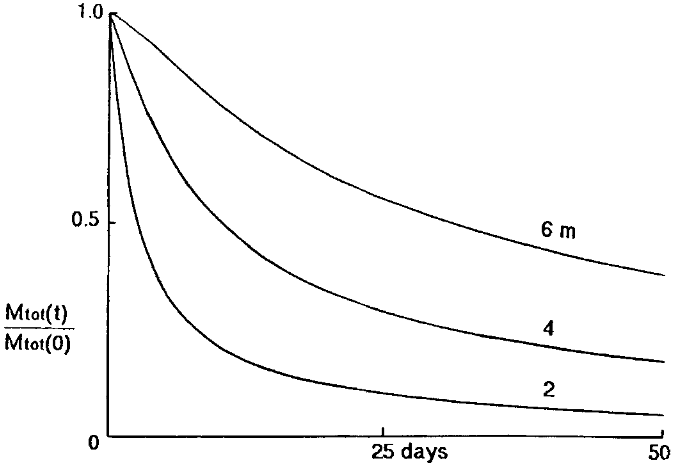

FIG. 9 Plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time; effect of the extent of vertical spreading of the contaminant. Depth to which contaminant has spread = 6, 4, and 2 m from the top down. $B = 2$; initial contaminant concentrations = 133.333, 200, and 400 mg/kg from the top down. Other parameters as in Table 3.

as the contaminant spreads vertically (and the initial contaminant concentration decreases), in contrast to the results shown in Fig. 8.

The reason for the great discrepancy between the results shown in Fig. 8 and those shown in Fig. 9 is found in the magnitude of the quantity $(C^s/C')^B$, to which the vapor concentration C^s is essentially proportional when $(C^s/C')^B$ is substantially less than unity. In Fig. 8 $(C^s/C')^B$ is relatively large throughout the bulk of the runs, yielding relatively large values of C^g which result in rapid cleanup rate. In Fig. 9 $(C^s/C')^B$ is < 1 even in the initial phases of the cleanups, and the exponent $B = 2$ causes it to decrease quite rapidly toward zero as C^s decreases. The different behav-

TABLE 2
Model Parameter Values Used for the Runs Plotted in Fig. 8

Exponent B	1.0
Rate constant k_f	1.0×10^{-3}
Depth of contaminated zone	2, 4, 6 m
Initial contaminant concentration	4000, 2000, 1333.33 mg/kg
Initial contaminant mass	2734.44 kg
Other parameters as in Table 1	

TABLE 3
Model Parameter Values Used for the Runs Plotted in Fig. 9

Exponent B	2.0
Rate constant k_f	1.0×10^{-3}
Radius of contaminated zone	8 m
Depth of contaminated zone	2, 4, 6 m
Initial contaminant concentration	400, 200, 133.333 mg/kg
Initial contaminant mass	2734.44 kg
Other parameters as in Table 1	

iors of the two sets of runs are therefore as one would expect. Interestingly, the extreme tailing seen in Fig. 9 is not the result of slow kinetics here, but of a progressively more unfavorable equilibrium between adsorbed and gaseous contaminant as the total contaminant concentration decreases. This is essentially equivalent to a linear isotherm "constant" which decreases during the course of the remediation.

CONCLUSIONS

Use of a simple extension of the Freundlich isotherm in a steady-state mathematical model for the steam stripping of semivolatiles from contaminated soils leads us to the following conclusions.

- It will be difficult, if not impossible, to differentiate by field studies alone between kinetics limitations due to diffusion processes and kinetics limitations due to desorption processes. A combination of field and laboratory studies could probably accomplish this, but may not be worth the effort.
- It is possible to generate simulations showing severe tailing toward the end of the cleanup resulting from the form of the adsorption isotherm even when adsorption and desorption rates are rapid. For this type of tailing one should not see soil gas SVOC concentration rebound when the gas flow is stopped, in contrast to what is expected when adsorption/desorption kinetics are slow.
- Attempts to predict cleanup times from pilot studies carried out for short periods of time are likely to result in predictions which are excessively optimistic, as was found to be the case when diffusion kinetics are limiting.
- Attempts to predict cleanup times from lab-column studies carried out to near-complete cleanup should be successful if adsorption/desorption kinetics are limiting, but, as mentioned earlier (3), are not suitable for

investigating the impact of diffusion kinetics limitations on remediation rates in the field.

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