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Soil Clean Up by *in-situ* Aeration. XV. Effects of Variable Air Flow Rates in Diffusion-Limited Operation

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ABSTRACT

A model for soil vapor extraction (SVE) is developed which includes the effects of mass transport kinetics of VOC between nonaqueous phase liquid (NAPL) droplets and the aqueous phase, and between the aqueous and vapor phases. The model permits time-dependent gas flow rates in the vapor extraction well. The model is employed to demonstrate the effectiveness of certain types of pilot-scale SVE experiments in determining the rate of mass transport processes. It is also used to explore several time-dependent air flow schedules for SVE well operation. The results indicate that the use of suitably selected air flow schedules in SVE can result in greatly reduced volumes of air to be treated for VOC removal with relatively little increase in the time required to meet remediation standards.

INTRODUCTION

The use of soil vapor extraction (SVE, soil venting, soil vapor stripping, *in-situ* vapor stripping, soil vacuum extraction, etc.) is now routine in site remediations involving vadose zone contamination with volatile organic compounds (VOCs). The U.S. EPA has recently published a guide (1) and a handbook (2) discussing the technique, both of which include an extensive list of references. Hutzler and his coworkers have published a detailed review (3), and this was subsequently updated in a paper from our group (4). The literature on soil vapor extraction is now quite extensive.

The nature of the technique is such that assessment of its feasibility and the design of a SVE system in any particular application are rather site-specific. These depend on the site geology (depth to water table, pneumatic permeability of vadose zone soils, presence of overlying impermeable structures such as floors or parking lots, heterogeneity of soil, presence of natural or other nonvolatile organics) and on contaminant properties (vapor pressure, water solubility, partition coefficient on organic carbon, and Henry's constant, all at ambient soil temperature). This has led to considerable interest in the mathematical modeling of SVE for feasibility studies, data interpretation, and system design. Johnson, Kemblowski, Colthart, and their associates have published extensively on this (5–7). Hoag, Marley, Cliff, and their associates at Vapex (8–10) were among the first to use mathematical modeling techniques in SVE. Cho has carried out a quite detailed study in which modeling work was supported by extensive experimental verification (11). Our group has published a number of papers on the mathematical modeling of SVE under a variety of conditions (Refs. 12–14 and other papers in this series).

One of the more significant of the site-specific aspects of SVE is the extent to which the kinetics of diffusion and/or desorption may limit the rate at which VOCs can be removed. If one has a site with a highly homogeneous sandy soil containing very little natural organic material and relatively little moisture, one may expect to find that diffusion/desorption rates present no problem and that a local equilibrium treatment of the process is quite adequate. On the other hand, if the porous medium has a highly heterogeneous permeability, if it contains significant amounts of clay or humic organic material, or if it contains substantial amounts of water, the kinetics of diffusion and/or desorption may prove to be serious bottlenecks in the removal of VOCs by SVE. DiGuilio et al. (15) discussed this problem in some detail, and described experiments which could be done during pilot studies to ascertain the extent to which these mass transport kinetics problems may slow down the remediation. Gomez-Lahoz et al. (16) explored some aspects of the economic advantages to be obtained by pulsed operation of SVE systems within the framework of a one-dimensional model.

Here we present a mathematical model for soil vapor extraction which includes two possible kinetic bottlenecks and which allows one to vary arbitrarily the air flow rate through the vacuum well. The kinetic bottlenecks included are 1) the rate of aqueous solution of droplets of nonaqueous phase liquid (NAPL) distributed within the porous medium, and 2) the rate of mass transport of dissolved VOC into the moving gaseous phase. The pilot-scale experiments proposed by DiGiulio et al. (15) are then simulated with the model and found to provide valuable information about the rates of these kinetically limited processes. Lastly, several gas flow operating schedules for an SVE well are simulated with the objective of substantially reducing the total volume of soil gas which must be treated without substantially increasing the time required to achieve the target level of remediation.

THEORETICAL

We model here the operation of a single soil vapor extraction well screened at the bottom and drilled in a homogeneous, isotropic medium. The VOC contaminant is assumed to be initially present as NAPL, as dissolved VOC in the soil moisture, and as vapor in the soil gas. Mass transport of VOC between the NAPL phase and the aqueous phase is handled by means of a technique described earlier for modeling the solution of DNAPL droplets in groundwater in pump and treat operations (17) and in sparging (18). Mass transport of VOC between the aqueous phase and the moving vapor phase is handled by means of a lumped parameter method used previously in SVE modeling (Ref. 19, for example).

In order to model the advective motion of the gas-phase VOC, one must specify the flow field of the soil gas in the vicinity of the vapor extraction well. If one considers gas flow rates which are changing sufficiently slowly with time that one may assume that they have reached steady state, the soil gas pressure obeys Eq. (1):

$$\nabla \cdot \mathbf{K} \nabla P^2 = 0 \tag{1}$$

where $\mathbf{K}$ = pneumatic permeability tensor of the soil, $\mathrm{m^2/atm \cdot s}$
P = soil gas pressure, atm

If we further assume that the permeability is constant in space and isotropic, Eq. (1) simplifies to Laplace's equation in P^2:

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

The geometry and notation of the cylindrically symmetric system are indicated in Fig. 1. The boundary conditions for the solution are as follows.

1. At the bottom of the domain of interest:

$$\frac{\partial P^2(r, 0)}{\partial z} = 0 \tag{3}$$

[The water table, which is the lower boundary ($z = 0$), is impermeable to air, so the normal component of the pressure gradient must vanish there.]

2. At the top of the domain of interest:

$$P^2(r, h) = 1 \text{ atm}^2 \tag{4}$$

(The soil gas pressure at the surface of the soil, where $z = h$, is 1 atm.)

3. There must be a sink of magnitude Q_a mol/s at the point $(0, a)$, to represent the molar flow of gas to the vacuum well. This problem is readily solved by the method of images from electrostatics (see Ref. 12, for example); one obtains

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

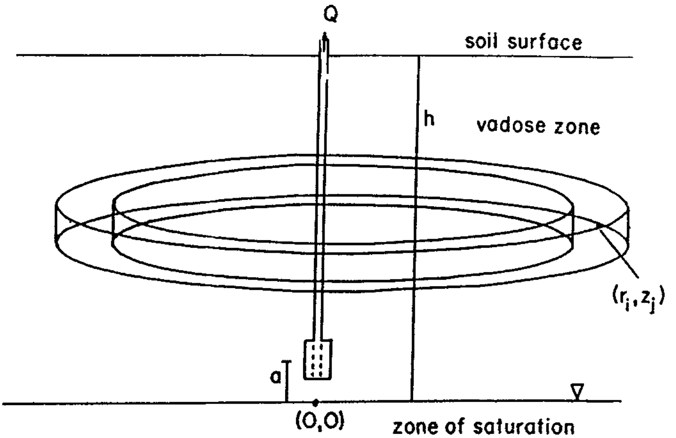

FIG. 1 Geometry and notation used in describing a SVE well.

Then

$$P(r, z) = [W + 1 \text{ atm}^2]^{1/2} \tag{6}$$

Darcy's law gives us the relationship between soil gas pressure gradient and superficial gas velocity v; this is

$$v = -K\nabla P \tag{7}$$

The superficial velocity components of the soil gas in the vicinity of the well are thus given by

$$v_r = -\frac{K}{2P}\frac{\partial W}{\partial r} \tag{8}$$

and

$$v_z = -\frac{K}{2P}\frac{\partial W}{\partial z} \tag{9}$$

The derivatives are given by

$$\begin{aligned}\frac{\partial W}{\partial r} = -\frac{RTQ_{ar}}{2\pi K}\sum_{n=-\infty}^{\infty}\Bigg[&-\frac{1}{\{r^2+[z-4nh-a]^2\}^{3/2}} \\ &-\frac{1}{\{r^2+[z-4nh+a]^2\}^{3/2}}+\frac{1}{\{r^2+[z-(4n-2)h-a]^2\}^{3/2}} \\ &+\frac{1}{\{r^2+[z-(4n-2)h+a]^2\}^{1/2}}\Bigg]\end{aligned} \tag{10}$$

and

$$\begin{aligned}\frac{\partial W}{\partial z} = -\frac{RTQ_a}{2\pi K}\sum_{n=-\infty}^{\infty}\Bigg[&-\frac{[z-4nh-a]}{\{r^2+[z-4nh-a]^2\}^{3/2}} \\ &-\frac{[z-4nh+a]}{\{r^2+[z-4nh+a]^2\}^{3/2}}+\frac{[z-(4n-2)h-a]}{\{r^2+[z-(4n-2)h-a]^2\}^{3/2}} \\ &+\frac{[z-(4n-2)h+a]}{\{r^2+[z-(4n-2)h+a]^2\}^{1/2}}\Bigg]\end{aligned} \tag{11}$$

Note that while W and its derivatives are directly proportional to Q_a, the variables P, v_r, and v_z are not. If we denote by primes (′) values of W, $\partial W/\partial r$, and $\partial W/\partial z$ calculated with $Q_a = 1$ mol/s, we can then express the soil gas pressure and gas velocities at other values of Q_a by Eqs. (12), (13), and (14):

$$P(r, z, Q_a) = [1\ \text{atm}^2 + Q_a W'(r, z)]^{1/2} \tag{12}$$

$$v_r(r, z, Q_a) = -\frac{K Q_a \partial W'/\partial r}{2[1\ \text{atm}^2 + Q_a W'(r, z)]^{1/2}} \tag{13}$$

$$v_z(r, z, Q_a) = -\frac{K Q_a \partial W'/\partial z}{2[1\ \text{atm}^2 + Q_a W'(r, z)]^{1/2}} \tag{14}$$

This permits us to evaluate W' and its derivatives at the necessary mesh points initially, and then to use the much simpler Eqs. (13) and (14) to calculate the gas velocities as functions of $Q_a(t)$ during the course of the simulation.

The second phase of the calculation is to use the gas flow field generated above in carrying out mass balances on the three phases in which the VOC is present (NAPL, aqueous, gaseous) in the ijth ring-shaped volume element, illustrated in Fig. 1. Let

$$r_i = (i - 1/2)\Delta r \tag{15}$$

$$z_j = (j - 1/2)\Delta z \tag{16}$$

Then

$$\Delta V_{ij} = (2i - 1)\pi(\Delta r)^2 \Delta z \tag{17}$$

The inner surface of the volume element is given by

$$S_{ij}^{\mathrm{I}} = 2\pi(i - 1)\Delta r \Delta z \tag{18}$$

The outer surface is

$$S_{ij}^{\mathrm{O}} = 2\pi i \Delta r \Delta z \tag{19}$$

The top (S_{ij}^{T}) and bottom (S_{ij}^{B}) surfaces are

$$S_{ij}^{\mathrm{T}} = S_{ij}^{\mathrm{B}} = (2i - 1)\pi(\Delta r)^2 \tag{20}$$

Define

m_{ij} = total mass of VOC in ΔV_{ij}, kg
C_{ij} = concentration of NAPL in ΔV_{ij}, kg/m^3
c_{ij}^w = concentration of aqueous (and possibly sorbed) VOC, kg/m^3 of aqueous phase
c_{ij}^g = vapor concentration of VOC, kg/m^3 of vapor phase

K_H = effective Henry's constant of VOC, c_{ij}^g/c_{ij}^w at equilibrium, dimensionless
ω = water-filled soil porosity, dimensionless
σ = air-filled soil porosity, dimensionless

The total mass of VOC in the *ij*th volume element is given by

$$m_{ij} = \Delta V_{ij}(C_{ij} + \omega c_{ij}^w + \sigma c_{ij}^g) \tag{21}$$

The soil gas superficial velocities at the four surfaces of the volume element are given by

$$v_{ij}^{\mathrm{I}} = v_r[(i-1)\Delta r,\quad (j-1/2)\Delta z] \qquad \text{(inner)} \tag{22}$$

$$v_{ij}^{\mathrm{O}} = v_r[i\Delta r,\quad (j-1/2)\Delta z] \qquad \text{(outer)} \tag{23}$$

$$v_{ij}^{\mathrm{B}} = v_z[(i-1/2)\Delta r,\quad (j-1)\Delta z] \qquad \text{(bottom)} \tag{24}$$

$$v_{ij}^{\mathrm{T}} = v_z[(i-1/2)\Delta r, j\Delta z] \qquad \text{(top)} \tag{25}$$

Define

$$\begin{aligned} S(v) &= 1, \quad v > 0 \\ &= 0, \quad v \leq 0 \end{aligned} \tag{26}$$

Then a mass balance on total VOC in the *ij*th volume element yields

$$\begin{aligned} \frac{dm_{ij}}{dt} = {} & S_{ij}^{\mathrm{I}} v_{ij}^{\mathrm{I}} \cdot [S(v^{\mathrm{I}}) \cdot c_{i-1,j}^g + S(-v^{\mathrm{I}}) \cdot c_{ij}^g] \\ & - S_{ij}^{\mathrm{O}} v_{ij}^{\mathrm{O}} \cdot [S(-v^{\mathrm{O}}) \cdot c_{i+1,j}^g + S(v^{\mathrm{O}}) \cdot c_{ij}^g] \\ & + S_{ij}^{\mathrm{B}} v_{ij}^{\mathrm{B}} \cdot [S(v^{\mathrm{B}}) \cdot c_{i,j-1}^g + S(-v^{\mathrm{B}}) \cdot c_{ij}^g] \\ & - S_{ij}^{\mathrm{T}} v_{ij}^{\mathrm{T}} \cdot [S(-v^{\mathrm{T}}) \cdot c_{i,j+1}^g + S(v^{\mathrm{T}}) \cdot c_{ij}^g] \end{aligned} \tag{27}$$

For the rate of solution of NAPL we use an expression developed previously for the rate of solution of DNAPL droplets in pump and treat and in sparging (17, 18); this is

$$\frac{dC_{ij}}{dt} = -\frac{3C_0^{2/3} D (c_s - c_{ij}^w) C_{ij}^{1/3}}{\rho \alpha_0^2} \tag{28}$$

where C_0 = initial NAPL concentration, kg/m^3
D = VOC diffusivity in the aqueous phase in the porous medium, m^2/s
c_s = solubility of VOC in soil water, kg/m^3 of aqueous phase
ρ = density of NAPL, kg/m^3
α_0 = initial NAPL droplet radius, m

From our assumed linear isotherm (i.e., an effective Henry's law), we have

$$c_{ij}^{g}(\text{equilibrium}) = K_{\mathrm{H}} c_{ij}^{w} \tag{29}$$

We use a lumped parameter approximation for mass transport (mt) of VOC between the aqueous and vapor phases,

$$\begin{aligned} \left(\frac{\partial c_{ij}^{g}}{\partial t}\right)_{\mathrm{mt}} &= \lambda[c_{ij}^{g}(\text{equil}) - c_{ij}^{g}] \\ &= \lambda[K_{\mathrm{H}} c_{ij}^{w} - c_{ij}^{g}] \end{aligned} \tag{30}$$

Now

$$\omega \frac{dc_{ij}^{w}}{dt} = -\frac{dC_{ij}}{dt} - \sigma \left(\frac{\partial c_{ij}^{g}}{\partial t}\right)_{\mathrm{mt}} \tag{31}$$

so

$$\frac{dc_{ij}^{w}}{dt} = -\frac{1}{\omega}\frac{dC_{ij}}{dt} - \frac{\sigma\lambda}{\omega}(K_{\mathrm{H}} c_{ij}^{w} - c_{ij}^{g}) \tag{32}$$

Differentiating Eq. (21) with respect to time yields

$$\frac{dm_{ij}}{dt} = \Delta V_{ij}\left[\frac{dC_{ij}}{dt} + \omega\frac{dc_{ij}^{w}}{dt} + \sigma\frac{dc_{ij}^{g}}{dt}\right] \tag{33}$$

Solving Eq. (33) for dc_{ij}^{g}/dt and utilizing Eq. (32) then yields

$$\frac{dc_{ij}^{g}}{dt} = \frac{1}{\sigma \Delta V_{ij}}\frac{dm_{ij}}{dt} + \lambda(K_{\mathrm{H}} c_{ij}^{w} - c_{ij}^{g}) \tag{34}$$

The differential equations constituting the model are Eqs. (27), (28), (32), and (34). Equation (27) may be used merely to handle the advection terms; the m_{ij} can be calculated from Eq. (21) if desired. The total mass of residual contaminant in the system is calculated from

$$M_{\text{total}} = \sum_{i=1}^{N_r}\sum_{j=1}^{N_z} m_{ij}(t) = \sum_{i=1}^{N_r}\sum_{j=1}^{N_z} \Delta V_{ij}[C_{ij} + \omega c_{ij}^{w} + \sigma c_{ij}^{g}] \tag{35}$$

The rate of removal of contaminant is readily calculated by

$$\frac{dM_{\text{total}}}{dt} = -\frac{M_{\text{total}}(t + \Delta t) - M_{\text{total}}(t)}{\Delta t} \tag{36}$$

If the gas flow rate in the system is not zero, the concentration of VOC in the exhausted soil gas is calculated by noting that the volumetric flow rate of the evacuated air (corrected to 1 atm) is given by

$$Q_{\text{vol}} = Q_a RT \tag{37}$$

where $R = 8.206 \times 10^{-5}$ m^3 atm/mol·deg and T is the absolute temperature. Then the effluent VOC concentration is given by

$$c_{\text{effl}} = \frac{dM_{\text{total}}}{dt} \bigg/ Q_{\text{vol}} \tag{38}$$

If the well is turned off, one can still follow the concentration of VOC in the vicinity of the well by examining the values of c^g_{ij} in the immediate vicinity of the well. In the present study, values of c^g_{ij} in the volume elements immediately above and immediately outside of the volume element containing the well were examined. These concentrations were found to be virtually identical. Following these values of the c^g_{ij} permits one to investigate the rate of "rebound" of the VOC concentration. This is useful in estimating the magnitude of the diffusion rate(s) of the system.

It is possible to develop a rough method for approximating the mass transport kinetics constant by comparing the equilibrium VOC gas-phase concentration with the VOC gas-phase concentration at steady-state. We assume a well-stirred one-compartment model having a volume V. At steady-state operation the rate of removal of VOC from the system by advection is equal to the rate of release of VOC from condensed phases in the system; use of a lumped parameter approach then gives

$$Qc^g_{ss} = k'V(c^g_{\text{equil}} - c^g_{ss}) \tag{39}$$

which yields

$$k' = \frac{Qc^g_{ss}}{V(c^g_{\text{equil}} - c^g_{ss})} \tag{40}$$

A reasonable value for V is that of a paraboloid of height h' and radius at the top of r', where r' is the effective radius of influence of the well (roughly equal to its depth) and h' is the depth to which the well is drilled; this gives $V = (\pi/2)h'r'^2$.

An alternative, perhaps better, approach to a rough estimate of the mass transport kinetics constant involves the use of a plug-flow model in the steady-state approximation. We assume one-dimensional gas flow through a volume V. At any point in the volume the rate of removal of VOC by advection is equal to the rate of its replenishment from the condensed phase(s). This gives

$$Q\frac{dc^g_{ss}}{dV} = k''[c^g_{\text{equil}} - c^g_{ss}] \tag{41}$$

where k'' is the rate constant for mass transport. Separation of variables and integration then yields

$$\log_e \frac{c^g_{\text{equil}}}{c^g_{\text{equil}} - c^g_{ss}} = k''V/Q \tag{42}$$

from which we obtain

$$k'' = (Q/V)\log_e \frac{c^g_{\text{equil}}}{c^g_{\text{equil}} - c^g_{ss}} \tag{43}$$

We choose V to be the paraboloidal volume mentioned above.

In the limit in which mass transport between the aqueous and the vapor phases is rapid compared to that between the NAPL and the aqueous phases, one can calculate an expression for the rate constant for the rebound rate of the VOC vapor concentration after the well has been shut off. This is done as follows. Once the gas flow in the well is stopped, the aqueous, vapor, and NAPL concentrations at any point in the system are related by

$$\omega\frac{dc^w}{dt} + \sigma\frac{dc^g}{dt} = -\frac{dC}{dt} \tag{44}$$

where the subscripts, not needed here, have been dropped. The limit mentioned above yields

$$c^w = c^g/K_H \tag{45}$$

which, on substitution into Eq. (44), yields

$$(\omega/K_H + \sigma)\frac{dc^g}{dt} = -\frac{dC}{dt} \tag{46}$$

An expression for dC/dt is obtained from Eq. (28); substitution of this into Eq. (46) and rearrangement then gives

$$\frac{dc^g}{dt} = \frac{3C_0^{2/3}DC^{1/3}}{(\omega + K_H\sigma)\rho\alpha_0^2}(K_Hc_s - c^g) \tag{47}$$

or

$$dc^g/dt = \beta K_Hc_s - \beta c^g \tag{48}$$

Integration of this equation then yields

$$c^g(t) = K_H c_s - [K_H c_s - c^g(0)] \exp(-\beta t) \tag{49}$$

where

$$\beta = \frac{3C_0^{2/3} D C^{1/3}}{(\omega + K_H \sigma)\rho \alpha_0^2} \tag{50}$$

is the rate constant for the rebound of the soil gas VOC concentration toward equilibrium once the SVE well has been turned off. This gives us an equation relating the observable rebound rate constant to the solution kinetics parameters which govern the rate of remediation of the domain. Note that Eq. (50) predicts that these rebound rate constants will decrease during the course of the clean up, since $C^{1/3}$ must decrease as the remediation proceeds.

This approach can be extended to the situation in which the rates of mass transfer between the NAPL and aqueous phases and the aqueous and gaseous phases are comparable, although one pays a price in terms of more complex formulas. We proceed as follows. After the well has been turned off so that there is no advection, we have

$$\omega \frac{dc^w}{dt} + \sigma \frac{dc^g}{dt} = -\frac{dC}{dt} \tag{51}$$

$$\frac{dc^g}{dt} = \lambda(K_H c^w - c^g) \tag{52}$$

and

$$\frac{dC}{dt} = -\frac{3DC_0^{2/3} C^{1/3}}{\rho \alpha_0^2}(c_s - c^w) \tag{53}$$

Let us approximate that $C^{1/3}$ remains constant during the rebound process, and define

$$\gamma = \frac{3DC_0^{2/3} C^{1/3}}{\rho \alpha_0^2} \tag{54}$$

$$G = c^g - K_H c_s \tag{55}$$

and

$$H = c^w - c_s \tag{56}$$

Then substitution of Eqs. (53)–(56) into Eqs. (51) and (52) and rearrangement yields

$$\frac{dH}{dt} = -\left[\frac{\gamma}{\omega} + \frac{\sigma \lambda K_H}{\omega}\right] H + \frac{\sigma \lambda}{\omega} G \tag{57}$$

and

$$dG/dt = \lambda K_H H - \lambda G \tag{58}$$

Let

$$A = \left(\frac{\gamma}{\omega} + \frac{\sigma\lambda}{\omega} K_H\right) \tag{59}$$

$$B = \sigma\lambda/\omega \tag{60}$$

$$C = \lambda K_H \tag{61}$$

$$D = \lambda \tag{62}$$

The time constants associated with Eqs. (57) and (58) are then the values of Λ satisfying the equation

$$\begin{vmatrix} -A + \Lambda & B \\ C & -D + \Lambda \end{vmatrix} = 0 \tag{63}$$

or

$$\Lambda^2 - (A + D)\Lambda + (AD - BC) = 0 \tag{64}$$

Of these, the smaller of the two will determine the length of time required for rebound of the VOC vapor concentration.

An alternative method suggested by R. D. Mutch, of Eckenfelder, Inc., (20) for exploring the limits imposed by diffusion and desorption kinetics during pilot studies is to rapidly inject a slug of clean air into the vapor extraction well and then to follow the subsequent increase in VOC concentration in this newly injected air. To model this we use the same basic approach as described above. The equations which describe the changes in the distribution of VOC between phases (NAPL, aqueous-adsorbed, vapor) are

$$\frac{dC}{dt} = -\frac{3C_0^{2/3}D(c_s - c^w)C^{1/3}}{\rho\alpha_0^2} \tag{65}$$

for the NAPL concentration,

$$\frac{dc^w}{dt} = \frac{3C_0^{2/3}D(c_s - c^w)C^{1/3}}{\omega\rho\alpha_0^2} - \frac{\sigma\lambda}{\omega}(K_H c^w - c^g) \tag{66}$$

for the aqueous-adsorbed VOC concentration, and

$$\frac{dc^g}{dt} = \lambda(K_H c^w - c^g) \tag{67}$$

for the vapor-phase VOC concentration. Note that, since there is no gas flow during the test after the initial rapid injection of the slug of clean air, there are no advection terms in Eq. (67). Note also that the total concentration of VOC in the domain being tested remains constant during the rebound process, so that

$$C_{\text{total}} = C + \omega c^{w} + \sigma c^{g} = \text{constant} \tag{68}$$

The desired initial values of c^w and C are selected, c^g is initialized to zero, and Eqs. (65)–(67) are integrated forward in time to model the test. The concentration of VOC in the vapor phase, c^g, is then plotted as a function of time for various values of the model parameters to give insight into their effects on VOC vapor concentration rebound.

RESULTS

A program implementing the variable airflow SVE model was written in TurboBASIC and run on MS-DOS microcomputers (80386-SX and 80386-DX microprocessors) equipped with math coprocessors and having clock speeds of 16 and 33 MHz, respectively. Run times ranged from about 15 minutes to as long as 4 hours.

There are two points of particular interest. The first is the extent to which one can gain useful information about kinetics limitations by examining the rebound of the soil gas VOC concentration in the vicinity of a well stripping an isolated domain after the well has been shut down, an experimental technique proposed earlier by DiGiulio et al. (15). Secondary points are the extent to which rate constants estimated from rebound rates agree with rate constants estimated from Eq. (40) or (43) and with rate constants calculated from Eqs. (50) and (64). The second major point is the extent to which one can reduce the volume of water-saturated soil gas from which VOCs must be removed without seriously increasing the time required for remediation.

Default parameters for the runs to be described are given in Table 1. The VOC parameters were selected to correspond to those of trichloroethylene (TCE). In Fig. 2 we see the course of remediation as measured by plotting M_{total} against time. For this run the NAPL droplet diameter is 0.1 cm, so the rate of solution is relatively rapid and the remediation is complete in about 18 days. Examination of Eq. (28) leads one to Eq. (69) as an absolute lower bound for the 100% clean-up time for the case in which solution kinetics are limiting:

$$t(100\%) = \frac{\rho \alpha_0^2}{2Dc_s} \tag{69}$$

TABLE 1
Default Parameters for the SVE Modeling Runs Presented

Radius of domain of interest	5 m
Thickness of vadose zone	5 m
Height of well above the bottom of the vadose zone	0.1 m
N_r, N_z	5, 5
Air-filled porosity	0.3
Water-filled porosity	0.1
Pneumatic permeability	1.0 m^2/atm·s
Density of soil	1.7 g/cm^3
Identity of the VOC	Trichloroethylene, TCE
Water solubility of VOC	1100 mg/L
Effective Henry's constant of VOC, dimensionless	0.2
Density of NAPL VOC	1.46 g/cm^3
Diffusivity of VOC in the aqueous phase	2×10^{-10} m^2/s
Time constant λ for aqueous VOC/vapor transport	1×10^{-4} s^{-1}
Initial NAPL concentration in the soil	2000 mg/kg
Initial NAPL droplet diameter, $2\alpha_0$	0.1 cm
Radius of zone of contamination	5 m
Depth of zone of contamination	5 m
Molar gas flow rate	1.0 mol/s, 50.95 ft^3/min
Ambient temperature	20°C
Initial total contaminant mass	1404 kg
Δt	100 seconds

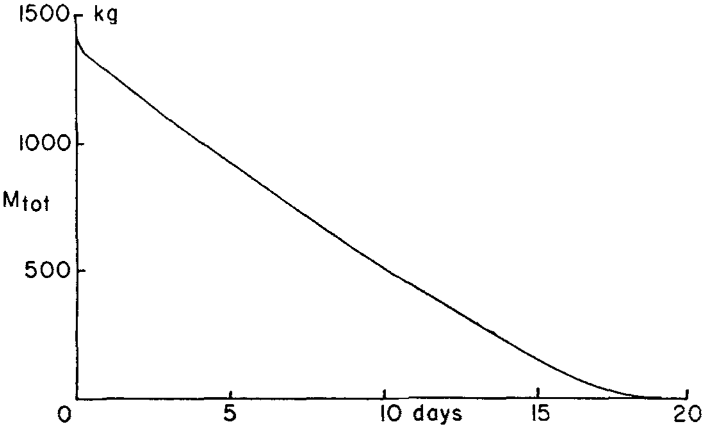

FIG. 2 Plot of mass of residual contaminant versus time. $2\alpha_0 = 0.1$ cm. Default parameters as in Table 1.

Substitution of numerical values into Eq. (69) gives a lower bound for the clean-up time of 9.6 days, so the system is not severely diffusion-limited.

In Fig. 3 the soil gas effluent VOC concentrations (measured as $c^g_{2,j\mathrm{well}}$) are plotted against time (on the same time scale as used in Fig. 2) for runs in which the gas flow was turned off after 1, 5, or 15 days. In these runs the diameter of the NAPL droplets is 0.1 cm, so solution of the droplets is comparatively rapid. The rate of rebound of the soil gas VOC concentration toward its equilibrium value (0.22 kg/m^3) decreases somewhat with increasing duration of the evacuation phase, and the rebound is fairly rapid. After 15 days of treatment the rate of rebound is about 49% of the recovery rate after 1 day of treatment. The rate constants k for rebound were calculated by determining the half-life of the recovery to the equilibrium concentration (0.22 kg/m^3) and then setting $k = 0.693/t_{1/2}$. This procedure gave results virtually identical to those obtained by least-squares fits of the data and is much less laborious. Rate constants k' and k'' were estimated from Eqs. (40) and (43), making the assumption that the volume V has the dimensions given in Table 1 ($h' = 4.9$ m, $r' = h'$), giving it a value of 184.8 m^3. Values of k, k', and k'' are given in Table 2. The rather drastically simplified single-compartment or plug-flow calculations leading to Eqs. (40) and (43) both appear to estimate values for the rate constant for VOC concentration recovery which are roughly within 30% of the values obtained from the recovery curves themselves.

In all the runs presented here, the principal bottleneck is the rate of solution of NAPL from the droplets. Figure 4 shows plots of c^g_{effl} versus

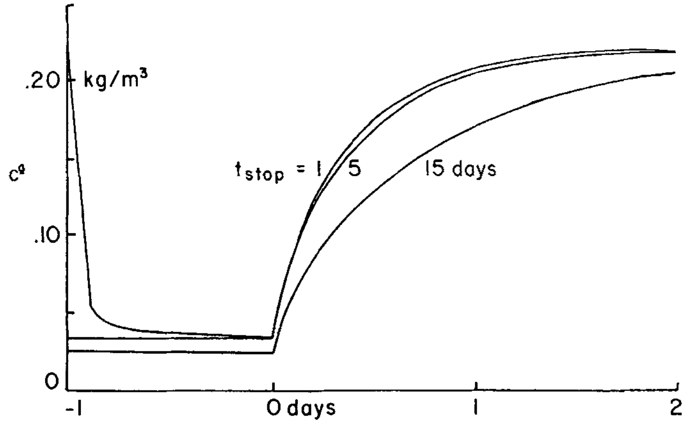

FIG. 3 Plots of c^g_{effl} versus time since shutdown, $t_{\mathrm{stop}} = 1,5$, and 15 days. $2\alpha_0 = 0.1$ cm. Default parameters as in Table 1.

TABLE 2
Values of k, k', and k'' Calculated for the Runs Shown in Fig. 3

Stop time (days)	k (s^{-1})	k' (s^{-1})	k'' (s^{-1})
1	3.54×10^{-5}	2.46×10^{-5}	2.25×10^{-5}
5	3.25×10^{-5}	2.34×10^{-5}	2.15×10^{-5}
15	1.72×10^{-5}	1.57×10^{-5}	1.48×10^{-5}

time for droplets of initial effective diameter $2\alpha_0 = 0.1$, 0.2, and 0.3 cm. In these three runs the gas flow was stopped after 5 days and the rebound of the soil gas VOC concentration was plotted for an additional 7 days. Default parameters are given in Table 1. As expected, the increase in NAPL droplet diameter results in a severe decrease in the rate of recovery of VOC concentration. Values of k, k', and k'' calculated for these runs are given in Table 3. Again, the values of k' and k'' are roughly within 30% of those of k.

In the runs to be considered next, the value of $2\alpha_0$ used is 0.3 cm, so these runs are severely solution-kinetics limited. Other parameters are as in Table 1. Figure 5 shows a plot of M_{total} versus time for a run having a constant air-flow rate of 1 mol/s (51 ft^3/min). The time required for clean up is slightly over 90 days. The lower bound estimate given by Eq. (69) is 86.4 days, confirming the severe diffusion kinetics limitation of the system.

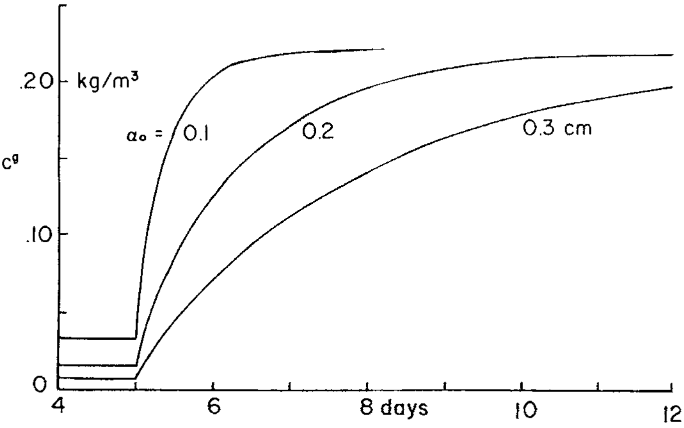

FIG. 4 Plots of c^g_{fm} versus time since shutdown, t_{stop} = 5 days. $2\alpha_0$ = 0.1, 0.2, and 0.3 cm. Default parameters as in Table 1.

TABLE 3
Values of k, k', and k'' Calculated for the Runs Shown in Fig. 4

$2\alpha_0$ (cm)	k (s^{-1})	k' (s^{-1})	k'' (s^{-1})
0.1	3.25×10^{-5}	2.34×10^{-5}	2.15×10^{-5}
0.2	8.81×10^{-6}	9.27×10^{-6}	8.95×10^{-6}
0.3	3.87×10^{-6}	4.68×10^{-6}	4.60×10^{-6}

Additional runs were made with these parameters in which the well was stopped and c^g_{effl} was monitored to ascertain its recovery pattern at various times during the progress of the clean up. These results are shown in Fig. 6. The gas flow was stopped after 5, 20, and 70 days of SVE, as indicated on the figure. Here one does see a marked decrease in rate of recovery toward the end of the clean up. Evidently one is not likely to obtain data indicating the full severity of mass transport limitations from runs carried out for a relatively short period of time. However, the effects do not appear to be extreme, as indicated by the relatively modest curvature seen in the plot of M_{total} in Fig. 5 and suggested by the weak dependence of Eq. (50) on C. The values of k, k', and k'' calculated from the runs shown in Fig. 6 are given in Table 4. As before, we find that k' and k'' are roughly comparable to the rate constant for the recovery of the VOC concentration in the soil gas. It is evident that Eq. (50) gives a very reasonable estimate for the value of the VOC rebound rate constant.

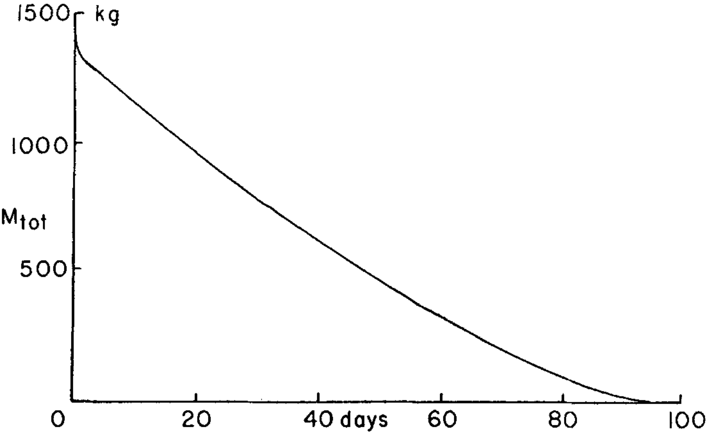

FIG. 5 Plot of residual VOC mass versus time, $2\alpha_0$ = 0.3 cm. Default parameters as in Table 1.

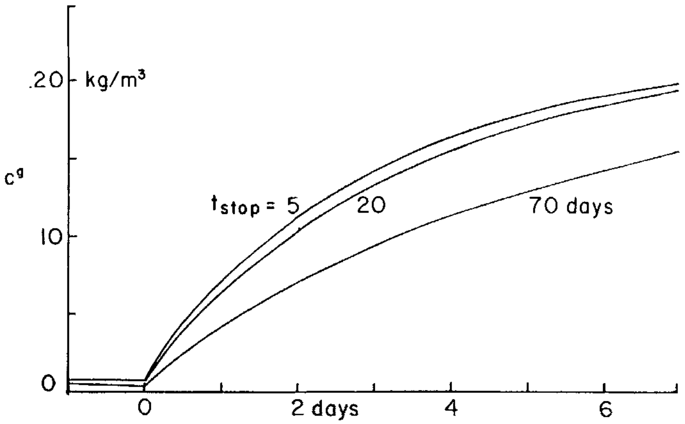

FIG. 6 Plots of $c^g_{\rm em}$ versus time since shutdown, $t_{\rm stop}$ = 5, 20, and 70 days. $2\alpha_0 = 0.3$ cm. Default parameters as in Table 1.

Equation (64) was also used to calculate the rate constant associated with the soil gas VOC concentration rebound for this system. Table 5 shows the dependence of the smaller of the two roots of Eq. (64) on the extent to which the clean up has progressed. The initial NAPL concentration was 2000 mg/kg (3.4 kg/m^3), and values of the rate constant are given down to a NAPL concentration of 0.01 kg/m^3. In agreement with Eq. (50) and with the numerical results, the rate constant is found to decrease during the progress of the clean up, but the effect is not large until almost the very end.

The great impact of mass transport kinetics limitations on the remediation is evident when one calculates the volume of air required to move 1404 kg of VOC (the initial mass present) if the gas is saturated ($c^g_{\rm sat} = K_{\rm H}c_s = 0.2 \times 1.1$ kg/m^3 = 0.22 kg/m^3); this is 6383 m^3. The volume of air actually used in the run shown in Fig. 5 to achieve clean up is about 191,000 m^3, a volume about 30 times greater than this theoretical mini-

TABLE 4

Values of k, k', and k'' Calculated for the Runs Shown in Fig. 6

Stop time (days)	k (s^{-1})	k' (s^{-1})	k'' (s^{-1})	β (s^{-1})
(0)	—	—	—	3.88×10^{-6}
5	3.87×10^{-6}	4.68×10^{-6}	4.60×10^{-6}	
20	3.52×10^{-6}	4.31×10^{-6}	4.24×10^{-6}	
70	2.02×10^{-6}	2.61×10^{-6}	2.58×10^{-6}	

TABLE 5
Dependence of Soil Gas VOC Concentration Rebound Rate Constant on the Progress of Clean Up. $2\alpha_0 = 0.3$ cm. Other Parameters as in Table 1

C (kg/m^3)	Λ_- (s^{-1})
3.4	3.82×10^{-6}
3.0	3.67×10^{-6}
2.6	3.50×10^{-6}
2.2	3.31×10^{-6}
1.8	3.10×10^{-6}
1.4	2.86×10^{-6}
1.0	2.56×10^{-6}
0.8	2.37×10^{-6}
0.6	2.16×10^{-6}
0.4	1.89×10^{-6}
0.2	1.50×10^{-6}
0.15	1.36×10^{-6}
0.10	1.19×10^{-6}
0.05	0.947×10^{-6}
0.02	0.699×10^{-6}
0.01	0.555×10^{-6}

mum. Evidently in a run of this sort one is treating an enormous volume of gas which is highly dilute in VOC, an expensive proposition. We therefore turn to our second major objective, the exploration of means by which one might possibly reduce the very large volumes of gas which are likely to be handled at sites which are kinetically controlled.

The runs shown in Figs. 7, 8, and 9 test the feasibility of three approaches. Default parameters are as in Table 1 except that $2\alpha_0 = 0.3$ cm in all these runs. Diffusion limitation is severe, as was the case in Fig. 5. Recall that the 100% clean-up time [t(100%)] for the run plotted in Fig. 5 is 95 days, that the gas-flow rate in that run is 51 ft^3/min, and that the total volume of gas used is 191,000 m^3.

In Fig. 7 the same parameters are used as in Fig. 5, except that the concentration of the effluent soil gas, c^g_{effl}, was continuously monitored, and whenever it got below $0.2c^g_{\text{sat}}$, the current value of the molar gas-flow rate of the well was multiplied by 0.9. During the first day of the run the molar gas-flow rate dropped rapidly to about one-fifth of its initial value of 1.0 mol/s (51 ft^3/min), then slowly drifted down to about 4% of its initial value by the time clean up was 98% complete. The time required for clean up was 116 days, and the total volume of air drawn from the well was 29,600 m^3, about 15.5% of that required in the run pictured in Fig. 5.

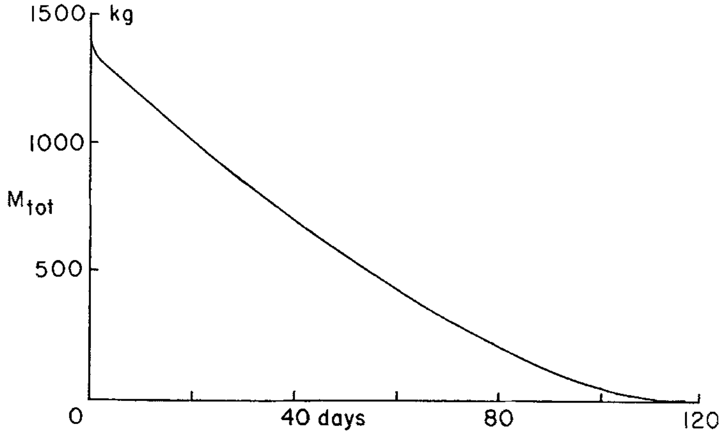

FIG. 7 Plot of residual VOC mass versus time, $2\alpha_0 = 0.3$ cm. Default parameters as in Table 1. The air flow rate $Q(t)$, initially 1 mol/s, is multiplied by 0.9 whenever c^g_{effl} is less than $0.2c^g_{\text{sat}}$.

In Fig. 8 we see the results of a run in which the molar air-flow rate was 0.4 mol/s (25 ft^3/min) but for which the air flow was switched off completely when the value of c^g_{effl} went below $0.2c^g_{\text{sat}}$. When c^g_{effl} recovered to a value above $0.4c^g_{\text{sat}}$, the air flow was switched back on. This cycle was continued throughout the run. The clean-up time was 130 days,

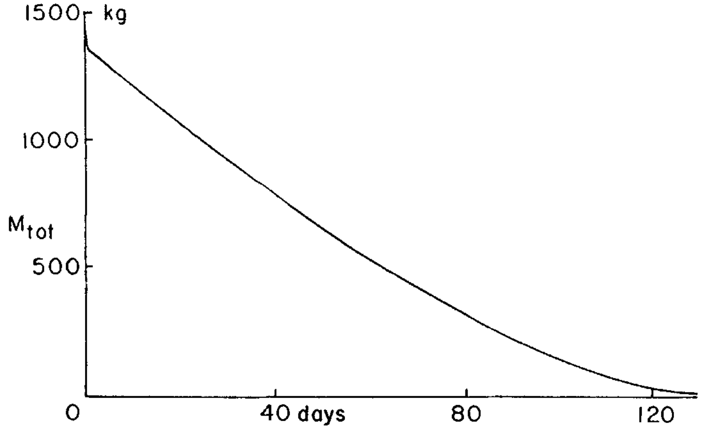

FIG. 8 Plot of residual VOC mass versus time, $2\alpha_0 = 0.3$ cm. Default parameters as in Table 1. $Q(t) = 0.4$ mol/s, but is switched to 0 whenever c^g_{effl} is less than $0.2c^g_{\text{sat}}$.

and the volume of gas drawn from the well was 22,100 m^3, 11.6% of that required in the run pictured in Fig. 5.

Figure 9 shows results for a run in which the molar air-flow rate was 0.1 mol/s (5.1 ft^3/min). This air flow was switched on and off using the same criteria as were used for the run shown in Fig. 8, but the air-flow rate was low enough that no switching occurred until the run was nearly complete. The clean-up time was 125 days, and the volume of gas drawn from the well was 21,400 m^3, 11.2% of that required in the run shown in Fig. 5.

We now turn to the results obtained modeling the clean air slug injection test suggested by Mutch. The computer program modeling this test was written in BASICA and run with the BASICA interpreter; a run required just a few seconds. Default parameters for these runs are given in Table 1, except that $2\alpha_0 = 0.2$ cm and $dt = 112.5$ seconds.

In Fig. 10 plots of c^g/c^g_{sat} versus time are shown for various values of the effective NAPL droplet diameter. Here c^g_{sat} is the saturation vapor concentration of the VOC, given by $K_H c_s$. The initial very rapid rise in vapor-phase VOC concentration is associated with mass transport from the aqueous phase to the vapor phase; the rate constant for this process in these runs was relatively large, 10^{-4} s^{-1}. Long after this process has come to a steady-state, the mass transport of VOC from the NAPL phase through the aqueous phase to the vapor phase continues. The rate of mass transport of VOC from the NAPL phase decreases with decreasing

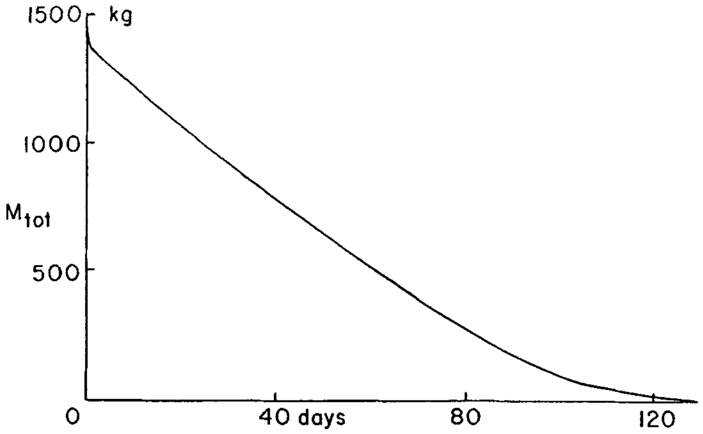

FIG. 9 Plot of residual VOC mass versus time, $2\alpha_0 = 0.3$ cm. Default parameters as in Table 1. $Q(t) = 0.1$ mol/s, but is switched to 0 whenever c^g_{effl} is less than $0.2c^g_{\text{sat}}$.

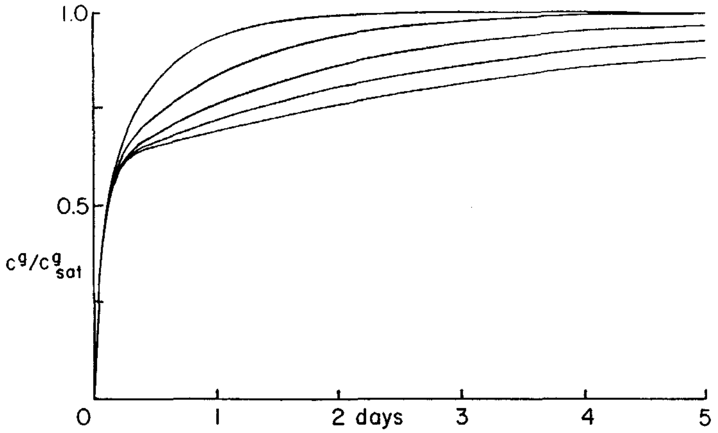

FIG. 10 Plot of c^g/c^g_{sat} versus time, air injection slug test. Effect of NAPL effective droplet diameter. $2\alpha_0$ = 0.1, 0.15, 0.2, 0.25, and 0.3 cm from the top down. Other parameters as in Table 1.

surface-to-volume ratio of the NAPL, so the rate constant for solution of the larger NAPL droplets is much slower than it is for the smaller droplets.

The effect of the initial aqueous-phase VOC concentration on the rate of rebound of the VOC vapor concentration is seen in Fig. 11. The smaller the initial value of c^w, the smaller is the rapid initial rise in c^g and the

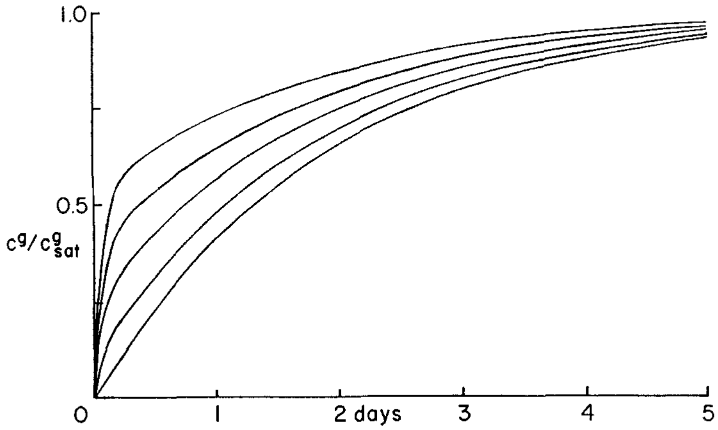

FIG. 11 Plot of c^g/c^g_{sat} versus time, air injection slug test. Effect of initial aqueous phase VOC concentration. Initially, c^w = 50, 250, 500, 750, and 1000 mg/L from the bottom up. Other parameters as in Table 1.

more clearly are the much slower solution kinetics of the NAPL droplets displayed. These results suggest that one might wish to inject clean air for an extended period (perhaps several hours) in order to reduce c^w as much as possible before shutting off the air flow and following the kinetics of the VOC vapor concentration rebound. These results, like those in Fig. 10, also indicate the importance of making sufficiently many measurements over a sufficiently long period of time so that the slow kinetic process(es) can be characterized. If one expects that "the" rate constant for mass transport is that associated with the very rapid initial rise of the rebound curve, one may be in for a very unpleasant surprise.

The effect of λ, the lumped parameter used to characterize the mass transport between the aqueous and vapor phases, is seen in Fig. 12. For sufficiently small values of λ the curves appear to be characterized by a single rate constant, and the "dogleg" seen for larger values of λ disappears. This relatively sharp break in the VOC vapor-phase rebound curves is seen only when the rate of mass transport from the aqueous to the gaseous phase is markedly faster than the rate of mass transport from the NAPL to the aqueous phase.

The effect of the relative magnitudes of the air-filled porosity σ and the water-filled porosity ω is seen in Fig. 13. Here the rate constant for mass transport of VOC between the aqueous and the vapor phases is relatively large (10^{-4} s^{-1}), so the curves show the characteristic dogleg appearance. The larger the water-filled porosity (and the smaller the air-filled porosity),

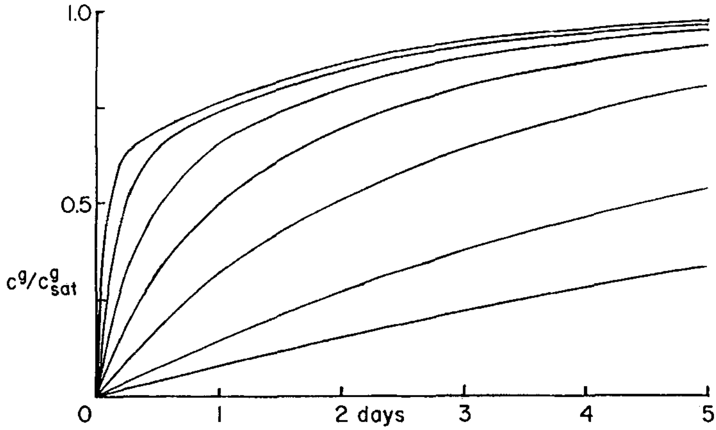

FIG. 12 Plot of c^g/c^g_{sat} versus time, air injection slug test. Effect of the rate constant for VOC mass transport between the aqueous and vapor phases, λ. $\lambda = 1 \times 10^{-4}$, 5×10^{-5}, 2×10^{-5}, 1×10^{-5}, 5×10^{-6}, 2×10^{-6}, and 1×10^{-6} s^{-1} from the top down. Other parameters as in Table 1.

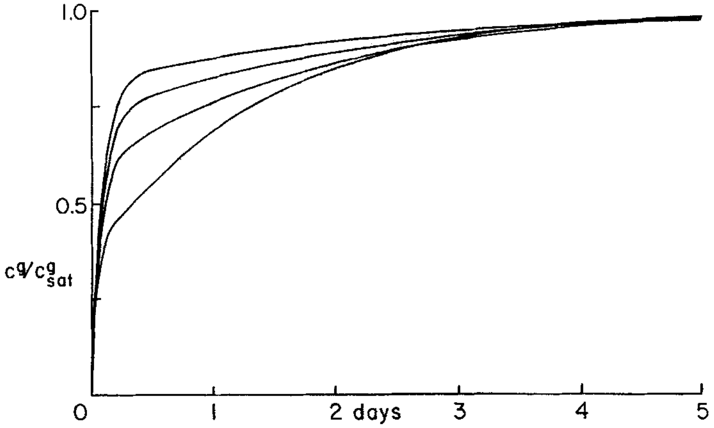

FIG. 13 Plot of c^g/c^g_{sat} versus time, air injection slug test. Effect of increasing the water-filled porosity ω (and decreasing the air-filled porosity σ). $\omega + \sigma = 0.4$. Water-filled porosity = 0.2, 0.15, 0.1, and 0.05 from the top down. Air-filled porosity = 0.2, 0.25, 0.3, and 0.35 from the top down. Other parameters as in Table 1.

the higher the initial rapid rebound of the curve and the poorer the characterization of the NAPL-aqueous phase mass transfer process. Evidently one would be well advised to try to carry out those tests on soils which were as well drained as possible, and certainly not shortly after periods of very wet weather.

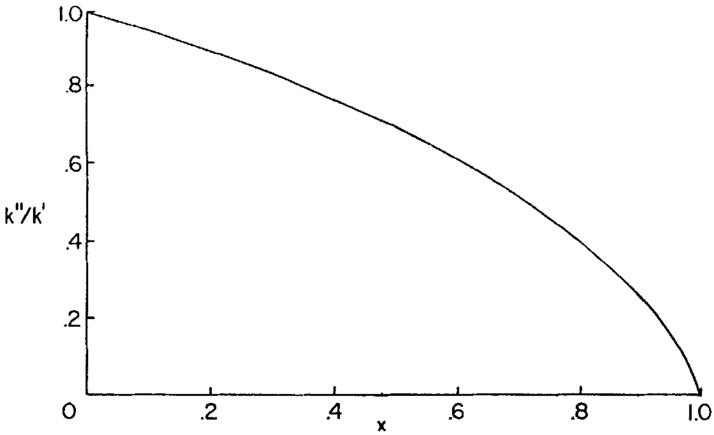

FIG. 14 Plot of k''/k' versus $x = c^g_{ss}/c^g_{equil}$. The function plotted is $-[(1 - x)/x] \cdot \log_e(1 - x)$.

The relationship between the two methods for roughly estimating mass transfer kinetics rate constants (Eqs. 40 and 43) is indicated in Fig. 14, in which the ratio k''/k' is plotted against $c_{ss}^{g}/c_{\text{equil}}^{g}$. This ratio is given by $-[(1 - x)/x] \log_e(1 - x)$, where $x = c_{ss}^{g}/c_{\text{equil}}^{g}$. We see that the values of k'' are always less than those of k', with k'' approaching k' as $c_{ss}^{g}/c_{\text{equil}}^{g}$ approaches zero. We find no such simple inequality between the values of k' and k'', on the one hand, and k on the other.

CONCLUSIONS

Estimates of the extent to which mass transport (diffusion/solution/desorption) kinetics may be limiting in soil vapor extraction can be made by examining the time dependence of soil gas VOC concentration for a period after the well has been shut down, and also by comparing the steady-state soil gas VOC concentration during pumping of the well with the equilibrium soil gas VOC concentration reached after a well has been shut down. In certain cases the rate constants calculated by these means are related to diffusion parameters in the model by a simple algebraic equation. Diffusion/solution/desorption kinetics can also be studied by the rapid injection of a slug of clean air, after which one follows the time dependence of the VOC vapor concentration rebound.

If a site is mass transport limited, significant amounts of money can be wasted by pumping the SVE wells at excessive flow rates, in that a large volume of gas is being pumped and also a large volume of water-saturated gas is being treated for VOC removal before discharge. Reductions in the volume of gas by a factor of one-fifth or less may be possible by working at a suitably selected constant low gas-flow rate by continuously adjusting the gas-flow rate to maintain at least a certain minimum VOC concentration in the exhausted soil gas, or by cycling the air flow on and off to maintain at least a certain minimum VOC concentration in the exhausted soil gas. The increases in clean-up times which result from such air-flow rate limitation are rather minor, and the savings quite substantial.

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