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Soil Clean Up by *in-situ* Aeration. VII. High-Speed Modeling of Diffusion Kinetics

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Soil Clean Up by *in-situ* Aeration. VII. High-Speed Modeling of Diffusion Kinetics

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Abstract

A mathematical model for soil vacuum extraction is developed which allows the modeling of vapor stripping from media of highly heterogeneous permeability, in which one may not be able to make the assumption of local equilibrium between the stationary phase(s) and the moving vapor phase with respect to volatile organic compound (VOC) transport. A lumped parameter approximation is used to deal with the kinetics of diffusion (and/or desorption) of the VOC from the interiors of lumps of clay or porous bedrock out into the advecting soil gas. This model, which makes the steady-state approximation for the VOC vapor concentrations, typically uses less than one-twentieth the computer time of an earlier nonsteady-state model and gives results which are in excellent agreement with that model. This model also yields results which are in agreement with a local equilibrium model if the rate constant for diffusion/desorption is large. The effects of impermeable caps and passive vent wells decrease as the rate of diffusion/desorption is decreased.

INTRODUCTION

Soil vacuum extraction (SVE, soil venting, soil vapor stripping, soil vacuuming) has become a widely accepted technique for the removal of volatile organic compounds (VOCs) from the vadose zone at hazardous waste sites, spills, leaking underground storage tanks, etc. Hutzler, Murphy, and Gierke (*1*) comprehensively reviewed SVE; their article includes a list of representative pilot and field scale operations. Sink (*2*) recently published a list of 29 SVE operations in a report on the treatment of off-gases from SVE for VOC removal. DiGiulio et al. (*3*) made several recommendations regarding the design of field tests for assessing SVE feasibility. These authors note the importance of diffusion kinetics, and describe a rather simple field test for assessing the impact of such kinetic limitations on SVE. Fall et al. (*4*), Hutzler, McKenzie, and Gierke (*5*), and Sterrett (*6*) reported observing kinetic (diffusion and/or desorption) limitation experimentally in lab or field studies, although other workers found local equilibrium models adequate at some sites (Refs. *7* and *8*, for example).

Most mathematical models of SVE make the local equilibrium assumption that the mobile vapor phase and the stationary condensed phase(s) in immediate contact with it are at equilibrium with respect to VOC transport (Refs. *7–12*, for example). Exceptions include a one-dimensional lab column model developed by Hutzler, McKenzie, and Gierke (*5*), and lab column and two-dimensional vapor stripping well models by Wilson (*13*). Our two-dimensional model makes use of a lumped parameter approximation to handle diffusion kinetics and can be run on a microcomputer. Although the results of the model appear quite reasonable, it suffers from a major disadvantage in that one must use very small values of the time increment when doing the numerical integrations required by the model. When the model is used on a 20-MHz PC-AT clone microcomputer with a math coprocesser, times required for physically realistic simulations are typically 60 h or more per run. This severely limits the usefulness of the model for the practical simulation of SVE operations which are diffusion controlled. We felt that it was imperative to develop a model for vapor stripping well operation which would include diffusion kinetics and which would run on a microcomputer at least 10 times faster than our first diffusion-controlled model. This would permit the ready inclusion of diffusion/desorption kinetics in modeling work where this was needed. In the present paper we develop models for vapor stripping in laboratory columns and by means of field vapor extraction wells which include diffusion/desorption limited kinetics and which utilize a steady-state approximation similar to that used in chemical kinetics to simplify the rate equations arising in that field. See Laidler's text for a discussion of this approximation (*14*).

ANALYSIS

In the following models we shall make the steady-state approximation for the vapor-phase VOC concentrations. That is, we assume that the vapor-phase concentrations are sufficiently small that the mass of contaminant VOC in the vapor phase is an almost negligible fraction of the total mass of VOC present in the system. If this is the case, then the net rates of change with time of the vapor-phase VOC concentrations with time will be extremely small in comparison to their rates of change by diffusion (replenishment) and their rates of change by advection (removal). The steady-state approximation consists in setting these very small net rates of change of VOC concentrations in the vapor phase equal to zero. This type of approximation is very commonly used to simplify the analysis of the kinetic mechanisms of chemical reactions; one sets the net rates of change of highly active intermediate species present at extremely low concentrations (atoms, free radicals, etc.) equal to zero. In chemical kinetics the approximation is quite well established and very good; our use of it in this new context will obviously require justification by comparison with the results of calculations in which it is not made.

One-Dimensional (Laboratory Column) Model

The model we take for SVE in a laboratory column is diagrammed in Fig. 1. Let

A = cross-sectional area of column
ν = soil air-filled porosity
w = soil volumetric moisture content
$v_{i+1/2}$ = linear gas velocity between the ith and $(i + 1)$th compartments into which the column is mathematically partitioned
c_i^v = vapor phase VOC concentration in the ith compartment
c_i^s = stationary phase(s) VOC concentration in the ith compartment

Other terms are defined in Fig. 1. We use SI units throughout.

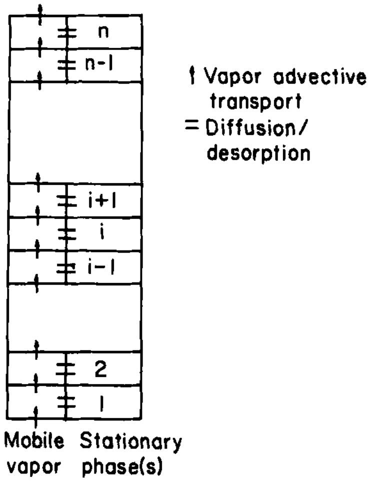

FIG. 1. Model for soil vapor stripping in a laboratory column; mathematical partitioning.

As with our previous diffusion-controlled model, we use a lumped parameter method for approximating diffusion and desorption kinetics; estimation of the rate parameter for diffusion was discussed earlier (*13*). The lumped parameter approach assumes that diffusion into and out of the blocks of low-permeability porous medium is governed by

$$\frac{dc_i^s}{dt} = \lambda \left[\frac{c_i^v}{K_{\mathrm{H}}} - c_i^s \right] \tag{1}$$

Included here is the assumption that partitioning of VOC between the vapor and stationary phases is linear—that the system obeys Henry's law, with an effective Henry's constant which typically is substantially smaller than the Henry's constant for the VOC in aqueous solutions.

If we focus only on diffusion transport between the stationary and vapor phases in the ith compartment (a conservative process), we have

$$\nu A \Delta x \left(\frac{dc_i^v}{dt} \right)_{\mathrm{diff}} + wA\Delta x \frac{dc_i^s}{dt} = 0 \tag{2}$$

where Δx is the length increment in the column. So

$$\nu A \Delta x \left(\frac{dc_i^v}{dt} \right)_{\mathrm{diff}} = -\lambda w A \Delta x \left(\frac{c_i^v}{K_{\mathrm{H}}} - c_i^s \right) \tag{3}$$

A mass balance on the vapor phase in the ith compartment gives

$$\nu A \Delta x \left(\frac{dc_i^v}{dt} \right) = \underbrace{v_{i-1/2} \nu A c_{i-1}^v - v_{i+1/2} \nu A c_i^v}_{\text{(advection)}} - \underbrace{wA\Delta x \lambda \left(\frac{c_i^v}{K_{\mathrm{H}}} - c_i^s \right)}_{\text{(diffusion)}} \tag{4}$$

$$= 0 \text{ (from steady-state approximation for the vapor phase concentrations)}$$

Solving Eqs. (4) for c_i^v then yields

$$c_i^v = \frac{w\lambda}{\nu} c_i^s \bigg/ \left(\frac{v_{1/2}}{\Delta x} + \frac{w\lambda}{\nu K_{\mathrm{H}}} \right), \qquad i = 1 \tag{5}$$

and

$$c_i^v = \left(\frac{v_{i-1/2}}{\Delta x} c_{i-1}^v + \frac{w\lambda}{\nu} c_i^s \right) \bigg/ \left(\frac{v_{i+1/2}}{\Delta x} + \frac{w\lambda}{\nu K_{\mathrm{H}}} \right), \qquad i = 2, 3, \ldots$$

Equations (1) are then integrated forward in time, with the c_i^v being calculated at every step from Eqs. (5). This integration can either be done by a standard predictor-corrector method (*15*), or one can rearrange Eqs. (1) to

$$\frac{dc_i^s}{dt} + \lambda c_i^s = \frac{\lambda c_i^v}{K_H} \tag{6}$$

One then assumes that c_i^v remains essentially constant during the time increment in the integration, Δt. Integration then yields

$$c_i^s(\Delta t) = c_i^s(0) \exp(-\lambda \Delta t) + c_i^v(0)[1 - \exp(-\lambda \Delta t)]/K_H \tag{7}$$

At this point we are in position to carry out the calculation. We need an expression for the gas velocity within the column; this is given by (*8*)

$$v_x = \frac{K_D(P_{in}^2 - P_{out}^2)}{2L}\left(P_{in}^2 - \frac{P_{in}^2 - P_{out}^2}{L} - x\right)^{-1/2} \tag{8}$$

where P_{in} is the column inlet pressure (atm), P_{out} is the column outlet pressure (atm), and K_D is the soil permeability.

The next step is the initialization of the $c_i^s(0)$—the initial VOC concentrations in the pore liquid. These are given by

$$c_i^s(0) = 10^{-3}\rho \underline{c}/w \tag{9}$$

where ρ = soil density (g/cm^3)
$\underline{c}$ = VOC concentration, mg VOC/kg of soil
w = volumetric moisture content of the soil, dimensionless

The $c_i^v(0)$ are then calculated from Eqs. (5). This is followed by calculation of the $c_i^s(\Delta t)$ by predictor-corrector integration of Eqs. (1) or by Eqs. (7). These values are then used in Eqs. (5) to calculate the $c_i^v(\Delta t)$. One then repeats these last two steps to carry out the integration of the system over the duration of the run.

Our use of the steady-state approximation from chemical kinetics in this different context requires some scrutiny. We therefore compare the results of this approach with those of a local equilibrium analysis of the same system; the two should be in close agreement in the limit as $\lambda \rightarrow \infty$. A local equilibrium analysis gives

$$c_i^v = K_H c_i^s \tag{10}$$

and

$$m_i = Av\Delta x c_i^v + Aw\Delta x c_i^s \tag{11}$$

so that

$$m_i = A\Delta x[\nu K_{\mathrm{H}} + w]c_i^s \tag{12}$$

A mass balance on the *i*th volume element gives

$$dm_i/dt = A\nu[v_{i-1/2}c_{i-1}^v - v_{i+1/2}c_i^v] \tag{13}$$

Substitution of Eqs. (10) and (12) in Eqs. (13) yields

$$\frac{dc_i^s}{dt} = \frac{\nu K_{\mathrm{H}}}{\nu K_{\mathrm{H}} + w}\,\frac{v_{i-1/2}c_{i-1}^s - v_{i+1/2}c_i^s}{\Delta x} \tag{14}$$

for the local equilibrium approach.

We next examine the steady-state approach in the limit as λ→∞. Our starting point is Eqs. (1) and (5),

$$\frac{dc_i^s}{dt} = \lambda\left(\frac{c_i^v}{K_{\mathrm{H}}} - c_i^s\right) \tag{1'}$$

and

$$c_i^v = \left(\frac{v_{i-1/2}}{\Delta x}c_{i-1}^v + \frac{w\lambda}{\nu}c_i^s\right) \Big/ \left(\frac{v_{i+1/2}}{\Delta x} + \frac{w\lambda}{\nu K_{\mathrm{H}}}\right), \qquad i = 2, 3, \ldots \tag{5'}$$

Divide Eqs. (5′) by K_{H} and subtract c_i^s to obtain

$$\left(\frac{c_i^v}{K_{\mathrm{H}}} - c_i^s\right) = \frac{1}{\Delta x}\left(\frac{(v_{i-1/2}c_{i-1}^v/K_{\mathrm{H}}) - (v_{i+1/2}c_i^s)}{(v_{i+1/2}/\Delta x) + (w\lambda/\nu K_{\mathrm{H}})}\right) \tag{15}$$

For λ→∞ we can neglect the first term in the denominator, so

$$\left(\frac{c_i^v}{K_{\mathrm{H}}} - c_i^s\right) = \frac{\nu K_{\mathrm{H}}}{w\lambda\Delta x}(v_{i-1/2}c_{i-1}^v/K_{\mathrm{H}} - v_{i+1/2}c_i^s) \tag{16}$$

Substituting Eqs. (16) and (10) into Eqs. (1) yields

$$\frac{dc_i^s}{dt} = \frac{\nu K_{\mathrm{H}}}{w\Delta x}(v_{i-1/2}c_{i-1}^s - v_{i+1/2}c_i^s) \tag{17}$$

Comparison of Eqs. (17) with Eqs. (14) from the local equilibrium approach shows that their right-hand sides differ by a factor of $1 + \nu K_{\mathrm{H}}/w$. Typically,

ν is roughly 0.3, w is about 0.2, and K_H is less than or equal to 0.005 (dimensionless), so our factor is smaller than 1.0075. It therefore appears that the steady-state approximation can be expected to lead to errors in clean-up time estimation of less than 1%.

Two-Dimensional Analysis of a Field Vapor Stripping Well

We use the overrelaxation procedure employed in earlier papers (*12*, *13*) to calculate the soil gas velocity field in the vicinity of a vapor extraction well. This permits us to include stratification, anisotropy, and other inhomogeneities in the permeability function, impermeable caps, and passive wells if desired. In this paper we therefore need concern ourselves only with the movement of the contaminant VOC in the presence of a given soil gas velocity field. Cylindrical symmetry is assumed, and the system (illustrated in Fig. 2) is therefore described by the two cylindrical coordinates r and z. Insofar as possible, the notation of the previous section is used; modifications in notation are as follows.

c_{ij}^v = VOC vapor concentration in the ijth ring-shaped volume element
c_{ij}^s = stationary (condensed phase) VOC concentration in ijth volume element
Δr, Δz = length increments in the r and z directions, as indicated
$V_{ij} = \pi(2i + 1)\Delta z \Delta r^2$ = volume of ijth volume element

We assume as before that diffusion and/or desorption processes are first order, so

$$\frac{dc_{ij}^s}{dt} = \lambda(c_{ij}^v/K_H - c_{ij}^s) \tag{18}$$

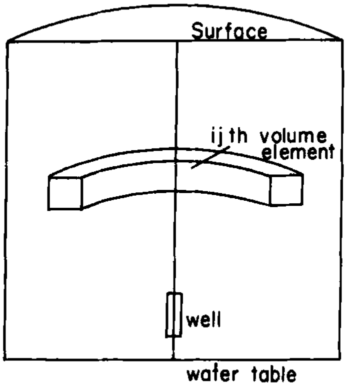

FIG. 2. Model for soil vapor stripping by means of a vacuum extraction well; mathematical partitioning of the domain of interest.

If we focus only on diffusion transport between the stationary and the vapor phases in the ijth volume element, we have

$$\nu V_{ij}\left(\frac{\partial c^{v}_{ij}}{\partial t}\right)_{\text{diff}} + wV_{ij}\frac{dc^{s}_{ij}}{dt} = 0 \tag{19}$$

since this process conserves VOC within the volume element.

Advective transport is considered next. The upper and lower surface areas of V_{ij} are given by $\pi(2i + 1)\Delta r^2$. The outer cylindrical surface to V_{ij} is $2\pi(i + 1)\Delta r\Delta z$, and the inner cylindrical surface to this volume element is $2\pi i\Delta r\Delta z$. From Eqs. (18) and (19) we see that

$$\nu V_{ij}\left(\frac{\partial c^{v}_{ij}}{dt}\right)_{\text{diff}} = -wV_{ij}\lambda(c^{v}_{ij}/K_{\mathrm{H}} - c^{s}_{ij}) \tag{20}$$

A mass balance on the vapor phase in the ijth volume element gives

$$\begin{aligned}\pi(2i + 1)\Delta z\Delta r^2\frac{dc^{v}_{ij}}{dt} &= -v^{\mathrm{R}}_{ij}S(-v^{\mathrm{R}}_{ij})2\pi(i + 1)\Delta r\Delta zc^{v}_{i+1,j}\\ &- v^{\mathrm{U}}_{ij}S(-v^{\mathrm{U}}_{ij})\pi(2i + 1)\Delta r^2c^{v}_{i,j+1} + v^{\mathrm{L}}_{ij}S(v^{\mathrm{L}}_{ij})2\pi i\Delta r\Delta zc^{v}_{i-1,j}\\ &+ v^{\mathrm{B}}_{ij}S(v^{\mathrm{B}}_{ij})\pi(2i + 1)\Delta r^2c^{v}_{i,j-1} + [v^{\mathrm{L}}_{ij}S(-v^{\mathrm{L}}_{ij})2\pi i\Delta r\Delta z\\ &- v^{\mathrm{R}}_{ij}S(v^{\mathrm{R}}_{ij})2\pi(i + 1)\Delta r\Delta z - v^{\mathrm{U}}_{ij}S(v^{\mathrm{U}}_{ij})\pi(2i + 1)\Delta r^2\\ &+ v^{\mathrm{B}}_{ij}S(-v^{\mathrm{B}}_{ij})\pi(2i + 1)\Delta r^2]c^{v}_{ij} - w\pi(2i + 1)\Delta z\Delta r^2\lambda(c^{v}_{ij}/K_{\mathrm{H}} - c^{s}_{ij})\nu^{-1}\end{aligned} \tag{21}$$

The notation for the velocities is indicated in Fig. 3. The function $S(v)$ is a unit step, vanishing for $v < 0$ and equal to 1 for $v > 0$.

The quantity dc^{v}_{ij}/dt is then set equal to zero from the steady-state approximation, and Eqs. (21) are solved for c^{v}_{ij}; this yields the following set of linear algebraic equations for these quantities.

$$c^{v}_{ij} = \frac{\begin{aligned}&-v^{\mathrm{R}}_{ij}S(-v^{\mathrm{R}}_{ij})2\pi(i + 1)\Delta r\Delta zc^{v}_{i+1,j} - v^{\mathrm{U}}_{ij}S(-v^{\mathrm{U}}_{ij})\pi(2i + 1)\Delta r^2c^{v}_{i,j+1}\\ &\quad + v^{\mathrm{L}}_{ij}S(v^{\mathrm{L}}_{ij})2\pi i\Delta r\Delta zc^{v}_{i-1,j} + v^{\mathrm{B}}_{ij}S(v^{\mathrm{B}}_{ij})\pi(2i + 1)\Delta r^2c^{v}_{i,j-1}\\ &\quad + w\pi(2i + 1)\Delta z\Delta r^2\lambda c^{s}_{ij}\nu^{-1}\end{aligned}}{\begin{aligned}&-v^{\mathrm{L}}_{ij}S(-v^{\mathrm{L}}_{ij})2\pi i\Delta r\Delta z + v^{\mathrm{R}}_{ij}S(v^{\mathrm{R}}_{ij})2\pi(i + 1)\Delta r\Delta z\\ &\quad + v^{\mathrm{U}}_{ij}S(v^{\mathrm{U}}_{ij})\pi(2i + 1)\Delta r^2 + v^{\mathrm{B}}_{ij}S(-v^{\mathrm{B}}_{ij})\pi(2i + 1)\Delta r^2\\ &\quad + w\pi(2i + 1)\Delta z\Delta r^2\lambda/K_{\mathrm{H}}\nu\end{aligned}} \tag{22}$$

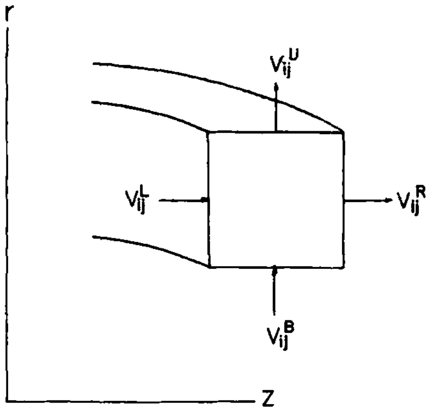

FIG. 3. Notation for the soil gas velocities at the four surfaces of one of the ring-shaped volume elements used in modeling a vacuum extraction well.

Recall that

$$dc_{ij}^s/dt = \lambda(c_{ij}^v/K_H - c_{ij}^s) \tag{18'}$$

This set of equations can be integrated forward in time by a predictor-corrector method or by assuming that the c_{ij}^v can be regarded as essentially constant during the differential time increment used in the numerical integration. The first method uses the following algorithm.

starter:

$$c_{ij}^s(\Delta t)^* = c_{ij}^s(0) + \Delta t \frac{dc_{ij}^s(0)}{dt} \tag{23}$$

predictor:

$$c_{ij}^s(t + \Delta t)^* = c_{ij}^s(t - \Delta t) + 2\Delta t \frac{dc_{ij}^s(t)}{dt} \tag{24}$$

corrector:

$$c_{ij}^s(t + \Delta t) = c_{ij}^s(t) + \frac{\Delta t}{2} \frac{dc_{ij}^s(t)}{dt} + \frac{dc_{ij}^s(t + \Delta t)^*}{dt} \tag{25}$$

The second method yields, as before,

$$c_{ij}^s(t + \Delta t) = c_{ij}^s(t) \exp(-\lambda \Delta t) + c_{ij}^v(t)[1 - \exp(-\lambda \Delta t)]/K_H \tag{26}$$

The computational procedure is then as follows.

First, one inputs the system parameters (dimensions, isotherm parameter, porosity, moisture content, etc.) and the gas velocities from the program used in our earlier local equilibrium models. One then initializes the $c^s_{ij}(0)$ values exactly as in the column model discussed in the last section.

One then iterates Eqs. (22) holding the $c^s_{ij}(0)$ at their initial values until the $c^v_{ij}(0)$ have converged. (Actually, this turns out not to be necessary unless one is interested in the initial transient behavior of the system, which is rarely of concern.)

One then calculates the $c^s_{ij}(\Delta t)$ from Eqs. (23) and (25) or Eq. (26). This is followed by calculation of the $c^v_{ij}(\Delta t)$ by means of a couple of iterations of Eqs. (22). Note that terms will be missing from these equations along the boundaries and the axis of the cylindrical domain of interest.

One is now in position to continue the integration forward in time of this system of differential and algebraic equations. The mass of contaminant still remaining in the domain of interest at time t is readily calculated from the values of the $c^s_{ij}(t)$, and plots showing the distribution of contaminant in the domain of interest can be made as desired. These have been discussed in detail in our earlier work.

RESULTS

Computer programs were written in TurboBASIC to implement the diffusion-limited models of vapor stripping in laboratory columns and by means of vapor extraction wells. The laboratory column model, which runs very rapidly, was used extensively for testing approximations and algorithms. It is unlikely to be particularly useful, however, since the very process of collecting soil samples and packing them into lab columns disrupts the soil inhomogeneities which are a major cause of diffusion-limited soil vapor extraction. In this section we therefore focus our attention on results obtained with the two-dimensional cylindrically symmetrical model for soil vapor extraction in the field with a single vacuum well. The runs were made on MMG286 microcomputers with math coprocessors and running at 12 or 20 mHz. A typical run required between 2 and 3 h. This compares very favorably with the run times of 2–4 days required for similar runs (carried to similar levels of clean up) made with our earlier diffusion-limited model (*13*), and is not significantly longer than the computation times required to run similar systems for similar times with our local equilibrium model.

The standard parameter set used is given in Table 1. These parameters were used in all the runs except as noted on the figures or in the captions to the figures.

A set of runs was made to explore the validity of the steady-state approximation used in this model for diffusion-controlled soil vacuum ex-

TABLE 1
Standard Parameter Set for Simulations of a Soil Vapor Stripping Well

Parameter	Value
Radius of domain of influence	10 m
Depth of water table	8 m
Depth of well	6 m
Radius of impermeable cap	0 m
Gravel-packed radius of well	0.12 m
Wellhead pressure	0.866 atm
Temperature	12°C
Gas-filled porosity	0.2
Water-filled porosity	0.2
Pneumatic permeability, K_z	0.6206 $m^2/atm{\cdot}s$
Pneumatic permeability, K_r	0.6206 $m^2/atm{\cdot}s$
Effective Henry's constant	0.01 (dimensionless)
Initial contaminant concentration	10 mg/kg
Soil density	1.7 g/cm^3
Molar gas flow rate	1.102 mol/s
Volumetric gas flow rate	0.02579 m^3/s

traction and to see the effect of varying the rate constant λ for diffusion from the porous domains of low permeability. The parameters for these runs are given in Table 1; only the diffusion rate constant was varied. A calculation was made using our local equilibrium model for comparison purposes. Three calculations were made for each of the values of λ shown in Fig. 4. These were 1) a calculation using our "exact" model (i.e., without the steady-state approximation); 2) a calculation in which the predictor-corrector method was used for the numerical integration; and 3) a calculation in which the integrated form of the differential equations was used for the numerical integration. All three models which included diffusion gave results which are virtually identical; plots at the scale of Fig. 4 would be completely indistinguishable. These numerical results are in agreement with our analysis above of the lab column model in which it was found that one could expect excellent agreement between the steady-state diffusion-limited model with a large diffusion rate constant and the local equilibrium model. The steady-state model which uses the integrated form of the differential equations was slightly faster than the steady-state model which uses the predictor-corrector method. Both of these were a minimum of 6 times faster than the "exact" diffusion-limited model. It was found that the value of $\lambda\Delta t$ must be 0.01 or less if reliable results are to be obtained with the steady-state models; Δt was set equal to 100 s for the runs with $\lambda = 10^{-4}\ s^{-1}$.

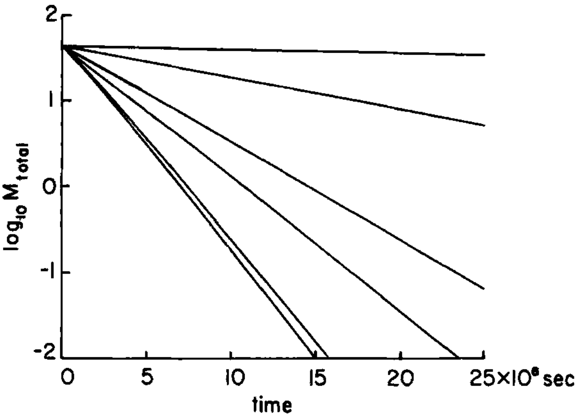

FIG. 4. Plots of $\log_{10}$ total contaminant mass versus time; effect of diffusion rate constant λ. From the top down, values of λ are 10^{-8}, 10^{-7}, 5×10^{-7}, 10^{-6}, 10^{-5}, and 10^{-4} s^{-1}. The plot with $\lambda = 10^{-4}$ s^{-1} is indistinguishable at this scale from a plot with $\lambda = \infty$ (the local equilibrium model). Other system parameters are given in Table 1. No passive wells or impermeable caps are present.

It was observed that for this system and at this gas flow rate the local equilibrium results were indistinguishable from those obtained when $\lambda = 10^{-4}$ s^{-1}. As λ decreases below 10^{-5} s^{-1}, however, the rate of VOC removal becomes progressively slower.

Another set of runs was made in which the effective Henry's constant K_H was reduced from 10^{-2} to a value of 10^{-3}; these are shown in Fig. 5.

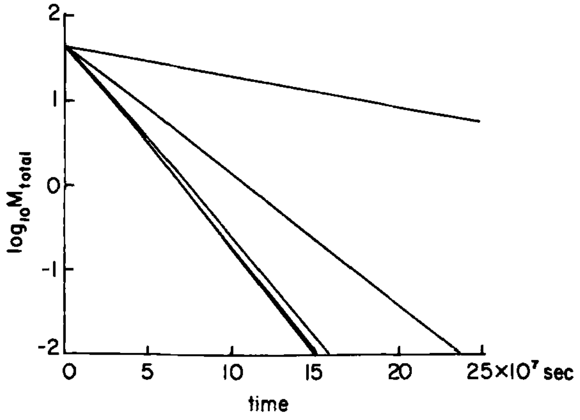

FIG. 5. Plots of $\log_{10} M_{total}$ versus time; effect of diffusion rate constant λ. K_H for these runs has been reduced to 0.001. From the top down, values of λ are 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5} s^{-1}, and ∞ (local equilibrium).

(Note the change in scale of the time axis between Figs. 4 and 5.) It was found that, if all of the system parameters except λ and K_H are held constant and that K_H is varied proportional to λ, then the clean-up time is proportional to λ^{-1}. A comparison of Figs. 4 and 5 also shows that the damaging effects of a small effective Henry's constant are not limited to local equilibrium and near-local equilibrium calculations.

In our earlier work on diffusion-limited SVE (*13*, *16*), rather limited numbers of runs were presented and a number of interesting points were left unexplored because of the punishing time requirements of computations with the exact model. The steady-state model eliminates this problem, and we here investigate these matters.

In Figs. 6 and 7 the effects of overlying impermeable caps are investigated for a range of values of the diffusion rate constant. Figure 6 compares runs having no cap with runs having a cap of radius 6 m. We see that a cap results in the greatest percentage reduction in clean-up time (to, say, the 99.9% level) if the diffusion rate constant is large; for slow diffusion rates the cap has a negligible effect. Figure 7 compares runs made with caps of 4 and 8 m radius for systems having a range of diffusion rate constants. The larger caps give shorter clean-up times, but, as in Fig. 6, the differences decrease as the diffusion rate constant becomes smaller. These results are as one would expect intuitively, since the effect of a cap is to increase the efficiency of the gas flow pattern by increasing gas flow rates in the relatively stagnant portions of the domain near the periphery of the cylinder; however, the efficiency of the gas flow pattern in advection becomes less and less important as diffusion rates become more and more limiting.

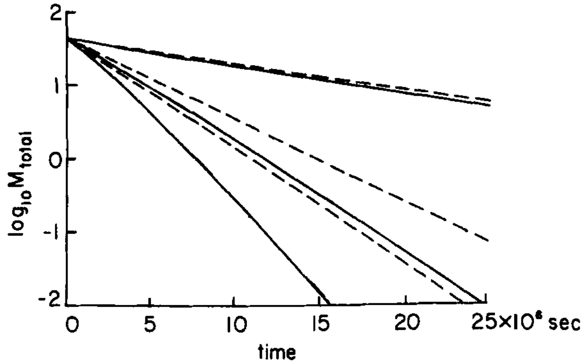

FIG. 6. Plots of $\log_{10} M_{total}$ versus time; effect of an impermeable cap of 6 m radius. Runs made without a cap are indicated with dashed lines. From the top down, values of λ are 10^{-7}, 5×10^{-7}, 10^{-6} s^{-1}, and ∞ (local equilibrium).

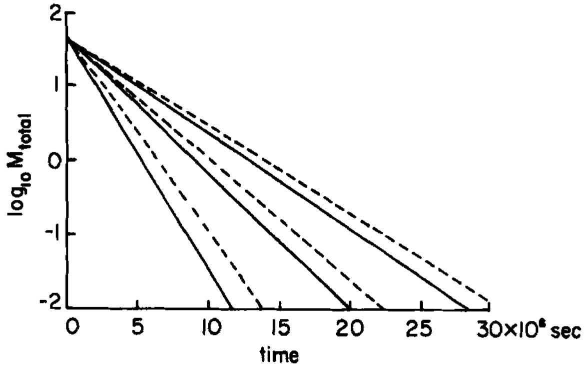

FIG. 7. Plots of $\log_{10} M_{total}$ versus time; effects of impermeable caps of 4 m radius (dashed lines) and 8 m radius (solid lines). Values of λ are 5×10^{-7}, 10^{-6} s^{-1}, and ∞ (local equilibrium) from the top down.

The effects of the presence of a set of passive vent wells located around the periphery of the domain of interest and screened along their entire length are shown in Figs. 8 and 9. No impermeable cap is present in these runs. For this particular geometry, the passive wells result in relatively little changes in removal efficiencies; with the local equilibrium run and the run with the largest diffusion rate constant (10^{-5} s^{-1}), the presence of

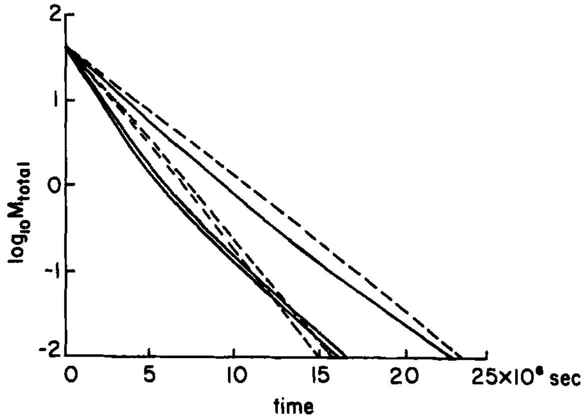

FIG. 8. Plots of $\log_{10} M_{total}$ versus time; effects of passive wells screened along their entire length and located around the periphery of the domain. Runs made with passive wells present (solid lines) and absent (dashed lines) have values of λ of 10^{-6}, 10^{-5} s^{-1}, and ∞ from the top down.

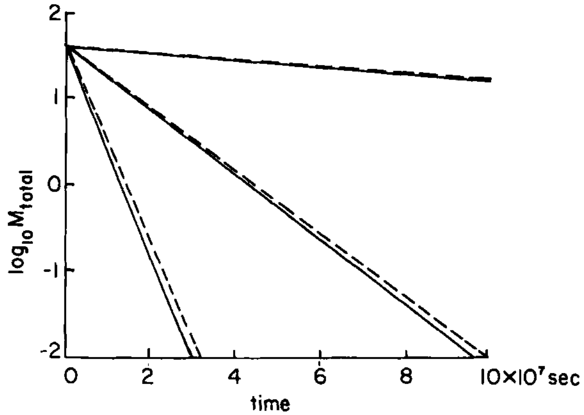

FIG. 9. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells. Runs with passive wells present (solid lines) and absent (dashed lines) have values of λ of 10^{-8}, 10^{-7}, and 5×10^{-7} s^{-1} from the top down.

passive wells may actually reduce efficiency toward the end of the run. As the diffusion rate constant becomes very small, the effect of the passive wells on clean-up time is seen to decrease on a percentage basis, as one would expect.

The situation is rather different if these passive wells are combined with overlying impermeable caps. In Fig. 10, runs were made with or without impermeable caps of radius 10 m and passive vent wells screened along their entire lengths. The combination of caps and passive wells results in

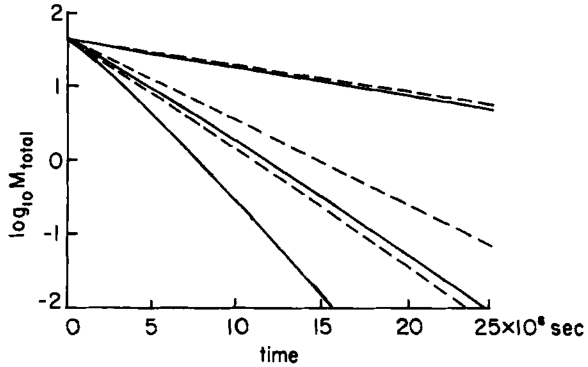

FIG. 10. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells combined with a 10-m impermeable cap. Runs with passive wells and caps present are indicated with solid lines; runs without wells and caps are shown with dashed lines. Values of λ are 10^{-7}, 5×10^{-7}, and 10^{-6} s^{-1} from the top down.

significant increases in removal rates for diffusion rate constants of 5×10^{-7} s^{-1} and larger. As before, as diffusion becomes slower it overpowers the effects of anything one can do to the gas flow pattern.

In Fig. 11, runs were made with and without caps and passive wells screened along their entire lengths; the radius of the impermeable cap was 8 m. In this configuration the passive wells are highly beneficial, more than doubling the rate of removal for the local equilibrium model and resulting in very substantial increases in removal rates for diffusion rate constants greater than 5×10^{-7} s^{-1}. If one is under some pressure to meet a rather short deadline for clean up of a site (a not uncommon situation), these results suggest that money spent on a configuration involving both caps and passive wells might be well spent.

The effects of gas flow rate are shown in Figs. 12 and 13. In Fig. 12 we see that clean-up rates for the local equilibrium model are directly proportional to the soil gas flow rate, exactly as one would anticipate. As diffusion processes become more limiting, however, the payoff achieved by increasing the gas flow rate becomes less and less. In Fig. 13 it is apparent that doubling the gas flow rate from 2.75 to 5.5 mol/s results in only a 20% increase in clean-up rate if the diffusion rate constant is 10^{-6} s^{-1}. If this parameter is 10^{-7} s^{-1}, increasing the gas flow rate from 2.75 to 5.5 mol/s results in a negligible increase in removal rate. One concludes that diffusion limitations should be explored in some depth during the pilot phase of an SVE feasibility study. DiGiulio et al. (*3*) recently published a very good experimental procedure for doing this, which should probably become routine practice.

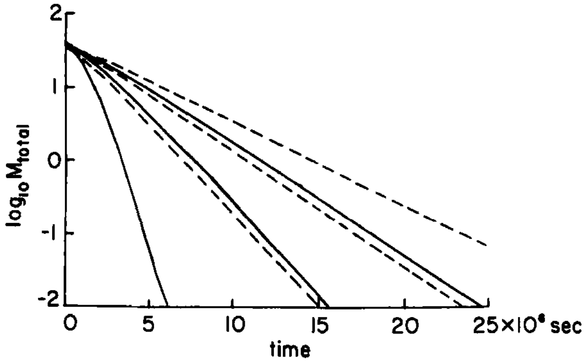

FIG. 11. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells combined with an 8-m impermeable cap. Runs with passive wells and caps present are shown with solid lines; runs without wells and caps are shown with dashed lines. Values of λ are 5×10^{-7}, 10^{-6} s^{-1}, and ∞ (local equilibrium) from the top down.

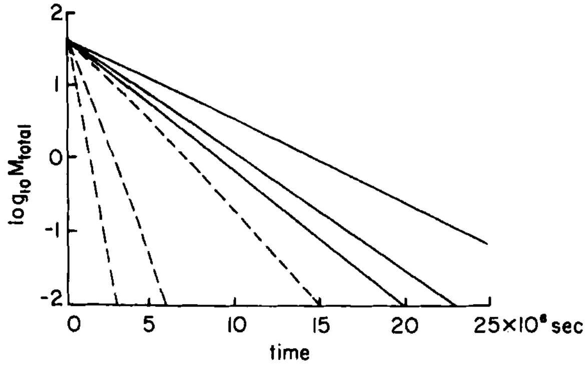

FIG. 12. Plots of $\log_{10} M_{total}$ versus time; effects of gas flow rate. No passive wells or caps are present. Runs made with the local equilibrium assumption are shown with dashed lines. Runs having $\lambda = 5 \times 10^{-7}$ s^{-1} are shown with solid lines. Gas flow rates in each of the two sets of runs are 1.05, 2.75, and 5.5 mol/s from the top down.

CONCLUSIONS

An improved mathematical model for soil vapor extraction with a vacuum well has been developed which permits one to take into account diffusion and/or desorption kinetics by means of a lumped parameter method. The effects of the diffusion rate constant, effective Henry's constant, gas flow rate, impermeable caps, and passive wells have been examined by means of this model. The model, which uses a steady-state approximation, yields results which are indistinguishable from the results of an earlier, more exact model; the present model requires 1/6th to

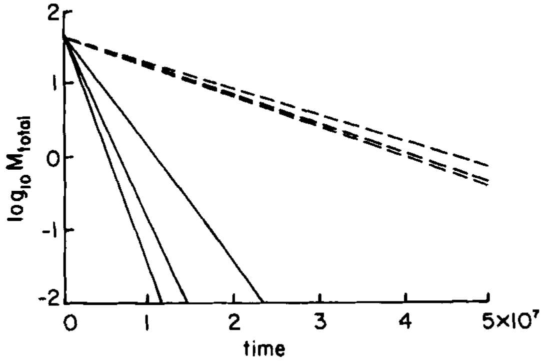

FIG. 13. Plots of $\log_{10} M_{total}$ versus time; effects of gas flow rate. No passive wells or caps are present. Runs made with $\lambda = 10^{-7}$ s^{-1} are shown with dashed lines; runs made with $\lambda = 10^{-6}$ s^{-1} are shown with solid lines. Gas flow rates are 1.05, 2.75, and 5.5 mol/s from the top down in each set.

1/25th the computer time of the earlier method, so it can readily be used for design calculations requiring a large number of simulations. The model runs on readily available microcomputers.

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