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Soil Cleanup by In-Situ Aeration. XVII. Field-Scale Model with Distributed Diffusion

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ABSTRACT

A mathematical model for soil vapor extraction (SVE) is developed which models mass transport of volatile organic compounds (VOCs) through aqueous boundary layers by means of a distributed diffusion approach. The well configuration modeled is that of a buried horizontal slotted pipe. The model yields high off-gas VOC concentrations initially, followed by a rapid drop-off to a relatively long plateau, followed in turn by a terminal region of tailing, the length of which is highly variable and is determined by the range of the distribution of values of the aqueous diffusion layers. The results suggest that it will be difficult, if not impossible, to develop models which permit the accurate prediction of SVE cleanup times from data taken in short-term pilot-scale experiments during which only 5–25% of the VOC present in the domain of influence of the well is removed.

INTRODUCTION

Soil vapor extraction (SVE) is now a well-established technology for the remediation of hazardous waste sites contaminated with volatile organic compounds (VOCs). Some 83 Superfund sites were using or scheduled to use the technique as of October 1992, and it is being used on a large

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number of other sites involving VOCs. EPA has published a number of reports describing the technique and discussing its strengths and weaknesses (1–4). The agency has also published the proceedings of a symposium on the subject (5). Hutzler and his coworkers have provided excellent reviews (6, 7), and Wilson and Clarke discussed the technique in some detail in a recent book (8).

Mathematical modeling techniques for SVE are useful for initial site-specific evaluation, interpretation of lab and pilot-scale field data, design of pilot and full-scale field SVE facilities, and estimation of costs and cleanup times. A number of workers have developed SVE models, including the Vapex group (9–15 and other papers); Johnson, Kemblowski, and their collaborators (16–20 and other papers); Cho (21); the group at the Idaho National Engineering Laboratory (22, 23); and the Eckenfelder-Vanderbilt group (24–26, for example).

Initially it was hoped that the assumption of local equilibrium with respect to VOC transport between the advecting vapor phase and the stationary phase(s) containing VOC would be valid (27), and indeed at some sites this seems to be the case (28, for example). There have been other sites, however, at which rapid declines in off-gas VOC concentrations after the initial phase of operation and prolonged tailing of off-gas VOC concentrations during the terminal phase make it painfully clear that local equilibrium is not being maintained and that the kinetics of diffusion and/or desorption are limiting the rate of mass transport to the vapor phase. DiGiulio et al. (29) proposed pilot-scale field experiments to assess the extent to which mass transport limitations are occurring, and Lyman and Noonan (3) indicate that these are common.

We have developed a relatively simple lumped parameter method for including mass transport limitations in SVE models. This method gave removal rates which were greatly reduced below those resulting from similar systems in which local equilibrium was assumed (30–33). This model, however, could not yield simultaneously the rapid initial removal rates and the quite slow removal rates toward the end of the remediation which are observed experimentally.

This difficulty was discussed in a recent paper (34), and a lab column model was presented which employs a more realistic approach to diffusion transport. This was actually one of two models explored. These distributed diffusion models assume that VOC diffuses from layers of soil water of finite thickness before it reaches the advecting soil gas and is removed. In one approach, the NAPL is present as droplets distributed throughout the water-saturated low-porosity layers; in the other, the NAPL is present as a film within the water-saturated lamellae. The two approaches could be made to yield rather similar results on a suitable selection of the parameters in the models. The second model requires less than half the computer time required by the first. It also permits use of steady-state approximations which speed the computations still further, if desired.

In the present work we discuss the extension of the second approach (in which NAPL is present as a thin layer within the low-permeability lenticular domains from which it must diffuse to the advecting air) to SVE by means of a horizontal slotted pipe well. A section presenting the analysis is followed by some representative results showing the dependence of cleanup time on some of the model parameters. Ideally, one would hope that mathematical modeling would permit one to make reasonably accurate estimates of site cleanup times on the basis of pilot-scale data obtained from experiments of relatively short duration. As will be seen later in this paper, this hope is probably forlorn; pilot-scale experiments in which the great bulk of the VOC is removed from the domain of influence of the well are apparently needed to make an accurate assessment of the time required to remediate a site.

ANALYSIS

The configuration of the horizontal slotted pipe SVE well is shown in Fig. 1, along with much of the notation. The model for diffusion transport, together with notation, is shown in Fig. 2. The development of an SVE model breaks down into three major parts: the calculation of the soil gas flow field in the vicinity of the vacuum well, the analysis of the equilibria

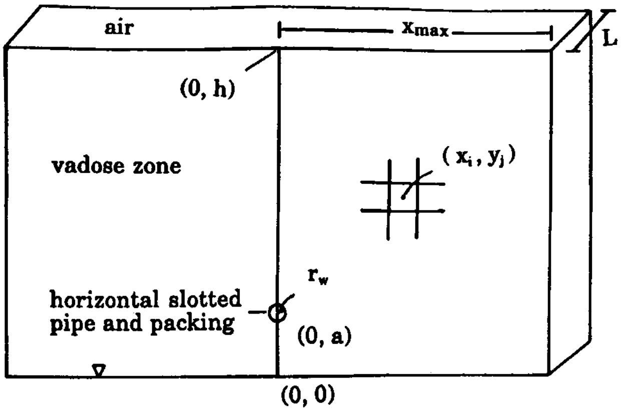

FIG. 1 Soil vapor extraction with a horizontal slotted pipe. Large-scale geometry and notation.

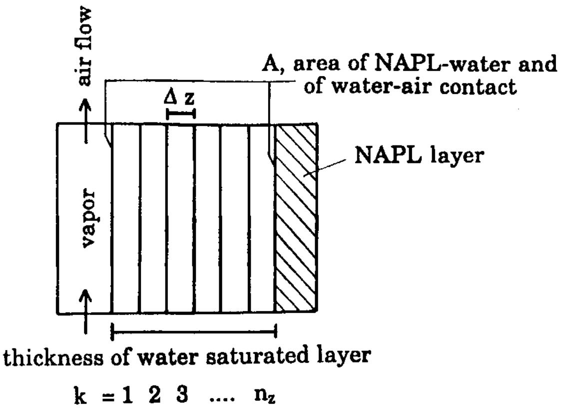

FIG. 2 Schematic detail of diffusion mass transport from a layer of NAPL through an aqueous layer to the advecting soil gas.

and mass transport factors controlling the release of the VOC being vapor stripped, and the merging of the two to form the model.

Gas Flow Field

We shall assume that we are dealing with a porous medium of constant, isotropic permeability, so that we may use the method of images from electrostatics (35) for calculating the soil gas pressures in the vicinity of the SVE well. We shall model only the right-hand side of the domain, since from symmetry the left is just a mirror image of the right. Let

h = thickness of porous medium (depth to water table), m
$x_{\max}$ = half-width of domain of interest (at right angles to the axis of the SVE pipe), m
L = length of horizontal slotted SVE pipe, m
r_w = radius of gravel packing of the horizontal slotted pipe, m
P_w = wellhead gas pressure (<1 atm), atm
P_a = ambient pressure, atm
$P(x, y)$ = soil gas pressure at the point (x, y), atm
K_D = Darcy's constant, $m^2/atm \cdot s$
a = distance of well above the water table, m
Q = molar gas flow rate to well, mol/s
q = standard volumetric gas flow rate to well, m^3/s
v_x = x-component of superficial velocity, m/s ($m^3/m^2 \cdot s$)
v_y = y-component of superficial velocity, m/s ($m^3/m^2 \cdot s$)

R = gas constant, 8.206×10^{-5} m^3·atm/mol·deg
T = temperature, degrees Kelvin

It is readily shown that the pressure of an ideal gas in a porous medium satisfies the equation

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

which for our system is

$$\frac{\partial^2 P^2}{\partial x^2} + \frac{\partial^2 P^2}{\partial y^2} = 0 \tag{2}$$

in Cartesian coordinates, where we are assuming that we can neglect effects at the ends of the pipe. The solution to this equation must satisfy the boundary conditions

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

and

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

Also, a sink (to represent the vacuum well) is needed at $(0, a)$.

We define the velocity potential as

$$W(x, y) = P^2(x, y) - P_a^2 \tag{5}$$

The following expression for W can easily be shown by symmetry arguments to satisfy the boundary conditions, and has a sink at $(x, y - a)$.

$$\begin{aligned} W = B \sum_{n=-\infty}^{\infty} [&\log\{x^2 + (y - 4nh - a)^2\} \\ &+ \log\{x^2 + [y - 4nh + a]^2\} \\ &- \log\{x^2 + [y - (4n - 2)h - a]^2\} \\ &- \log\{x^2 + [y - (4n - 2)h + a]^2\}] \end{aligned} \tag{6}$$

The superficial gas velocity is assumed to be given by Darcy's law,

$$v = -K_D \nabla P = -(K_D/2P)\nabla W \tag{7}$$

which, with Eq. (5), gives

$$v = -K_D \nabla W/[2(P_a^2 + W)^{1/2}] \tag{8}$$

The concentration of gas at the point (x, y), c, is given by

$$c = P/RT \tag{9}$$

so the molar flow rate of the well is

$$Q = -L \int_0^{2\pi} cv \cdot r d\theta \tag{10}$$

$\{r$ = radial distance from well, $[x^2 + (y - a)^2]^{1/2}\}$ which yields

$$Q = (\pi L K_D / RT) \nabla_r W \cdot r \tag{11}$$

In the vicinity of the well, we have (approximately)

$$W = B \cdot \log(r^2) + C \tag{12}$$

$$\nabla_r W = 2B/r \tag{13}$$

from which, together with Eq. (11), we obtain

$$B = QRT/(2\pi L K_D) \tag{14}$$

To obtain K_D we evaluate Eq. (12) at $r = r_w$ and at $r = r_a = h - a$, the depth of the well. This yields

$$B = \frac{P_a^2 - P_w^2}{2 \log(r_a/r_w)} \tag{15}$$

This, with Eq. (14), gives

$$K_D = \frac{QRT \cdot \log(r_a/r_w)}{\pi L (P_a^2 - P_w^2)} \tag{16}$$

Since the volumetric flow rate q is given by $q = QRT$, this can also be written as

$$K_D = \frac{q \cdot \log(r_a/r_w)}{\pi L (P_a^2 - P_w^2)} \tag{17}$$

Henceforth we shall use Eq. (15) to calculate B in Eq. (6) and other equations involving W.

Calculating the soil gas superficial velocity components requires $\partial W/\partial x$ and $\partial W/\partial y$. These are given by

$$\begin{aligned}\frac{\partial W}{\partial x} = 2B \Bigg[\sum_{n=-\infty}^{\infty} & \frac{x}{x^2 + [y - 4nh - a]^2} \\ & + \frac{x}{x^2 + [y - 4nh + a]^2} \\ & - \frac{x}{x^2 + [y - (4n - 2)h - a]^2} \\ & - \frac{x}{x^2 + [y - (4n - 2)h + a]^2} \Bigg]\end{aligned} \tag{18}$$

and

$$\frac{\partial W}{\partial y} = 2B\left[\sum_{n=-\infty}^{\infty} \frac{y - 4nh - a}{x^2 + [y - 4nh - a]^2} + \frac{y - 4nh + a}{x^2 + [y - 4nh + a]^2} - \frac{y - (4n - 2)h - a}{x^2 + [y - (4n - 2)h - a]^2} - \frac{y - (4n - 2)h + a}{x^2 + [y - (4n - 2)h + a]^2}\right] \tag{19}$$

The soil gas superficial velocity components are then calculated by using Eqs. (6), (18), and (19) in Eq. (8).

Equilibrium and Mass Transport

Refer to Fig. 2 for a schematic of how equilibrium and mass transport are handled. The block represents a volume element ΔV in the domain being vapor stripped. The picture we are using to represent diffusion transport of VOC from NAPL is as follows. We assume that the NAPL present forms films within the lamellae of low permeability, and that a film is in turn overlain by a layer of water-saturated soil through which the VOC which dissolves from the NAPL must diffuse before reaching the advecting gaseous phase. This picture is rather simplified, but it represents a major improvement over our previous lumped parameter method, and it computes fast, unlike our earlier model. Terms are defined as follows.

ΔV = volume of a volume element, $= \Delta x \Delta y L$
σ = air-filled porosity of the medium
ω = water-filled porosity of the medium
l = thickness of water layer coating the soil particles, m
n_z = number of slabs into which the water layer is partitioned for analysis
Δz = thickness of one of these slabs, l/n_z
A = area of NAPL–water contact (assumed equal to area of water–air contact) within the volume element, m^2; $A = \Delta V \omega / l$
C_{sat} = water solubility of VOC, kg/m^3
K_{H} = Henry's constant of VOC, dimensionless
D = diffusivity of the VOC in water, m^2/s
C^g = concentration of VOC in the gas phase, kg/m^3
C_k^w = concentration of VOC in the kth slab of the aqueous phase in the volume element, kg/m^3

m = mass of NAPL in the volume element, kg. This is assumed to be coating the soil particles and in turn to be coated by the water layer.

We then carry out a mass balance on each of the compartments into which this volume element is partitioned; the gas phase, n_z slabs of aqueous phase, and the NAPL phase. For the gas phase the mass balance is as follows.

$$\Delta V \sigma \frac{dC^g}{dt} = \text{advection terms involving other volume elements} + \frac{AD}{\Delta z/2}\left(C_1^w - \frac{C^g}{K_H}\right) \tag{20}$$

For the first aqueous slab (adjacent to the gas phase) it is

$$\frac{\Delta V \omega}{n_z}\frac{dC_1^w}{dt} = \frac{AD}{\Delta z/2}\left(\frac{C^g}{K_H} - C_1^w\right) + \frac{AD}{\Delta z}(C_2^w - C_1^w) \tag{21}$$

For an interior aqueous slab we have

$$\frac{\Delta V \omega}{n_z}\frac{dC_k^w}{dt} = \frac{AD}{\Delta z}(C_{k-1}^w - 2C_k^w + C_{k+1}^w) \tag{22}$$

For the aqueous slab adjacent to the NAPL phase (if there is one), the material balance equation is

$$\frac{\Delta V \omega}{n_z}\frac{dC_{n_z}^w}{dt} = \frac{AD}{\Delta z}[C_{n_z-1}^w - C_{n_z}^w + 2S(m)(C_{\text{sat}} - C_{n_z}^w)] \tag{23}$$

where

$$\begin{aligned} S(m) &= 1 \quad \text{if} \quad m > 0 \\ &= 0 \quad \text{if} \quad m = 0 \end{aligned}$$

For the NAPL phase immediately adjacent to the soil surface,

$$\frac{dm}{dt} = -\frac{2AD}{\Delta z} S(m)(C_{\text{sat}} - C_{n_z}^w) \tag{24}$$

Completion of the Model

Construction of the SVE model simply requires the combining of the advective terms mentioned in Eq. (20) with the mass transport terms. This is straightforward.

To describe the advection which appears in Eq. (20) we introduce subscripts *i,j* to specify the various volume elements. As seen in Fig. 1,

$$x_i = (i - 0.5)\Delta x \tag{25}$$

$$y_j = (j - 0.5)\Delta y \tag{26}$$

The normal superficial gas velocity components at the centers of the Left, Right, Top, and Bottom surfaces of the *ij*th volume element are then given by

$$v_{ij}^{\mathrm{L}} = v_x[(i - 1)\Delta x, (j - 0.5)\Delta y] \tag{27}$$

$$v_{ij}^{\mathrm{R}} = v_x[i\Delta x, (j - 0.5)\Delta y] \tag{28}$$

$$v_{ij}^{\mathrm{B}} = v_y[(i - 0.5)\Delta x, (j - 1)\Delta y] \tag{29}$$

$$v_{ij}^{\mathrm{T}} = v_y[(i - 0.5)\Delta x, j\Delta y] \tag{30}$$

where v_x and v_y are specified by Eq. (8). Again we define a step function, this time with velocity as argument. It is

$$\begin{aligned} S(v_{ij}^{\mathrm{Q}}) = S(v^{\mathrm{Q}}) &= 1 \quad \text{if} \quad v_{ij}^{\mathrm{Q}} > 0,\ Q = \mathrm{L, R, B, or\ T} \\ &= 0 \quad \text{if} \quad v_{ij}^{\mathrm{Q}} \leq 0 \end{aligned}$$

Omission of the subscripts *i* and *j* causes no problems because these are always the subscripts of the velocity factor preceeding the term in which the $S(v)$ appear. The advection terms are then

$$\begin{aligned} \left[\Delta V\sigma \frac{dC_{ij}^{g}}{dt}\right]_{\mathrm{advect}} &= L\Delta y v_{ij}^{\mathrm{L}}\{S(v^{\mathrm{L}})C_{i-1,j}^{g} + S(-v^{\mathrm{L}})C_{ij}^{g}\} \\ &+ L\Delta y v_{ij}^{\mathrm{R}}\{-S(-v^{\mathrm{R}})C_{i+1,j}^{g} - S(v^{\mathrm{R}})C_{ij}^{g}\} \\ &+ L\Delta x v_{ij}^{\mathrm{B}}\{S(v^{\mathrm{B}})C_{i,j-1}^{g}) + S(-v^{\mathrm{B}})C_{ij}^{g}\} \\ &+ L\Delta x v_{ij}^{\mathrm{T}}\{-S(-v^{\mathrm{T}})C_{i,j+1}^{g} - S(v^{\mathrm{T}})C_{ij}^{g}\} \end{aligned} \tag{31}$$

Inclusion of these terms in Eq. (20) and solution of Eqs. (20) through (24) for the derivatives completes the derivation of the modeling equations. These, written with the space subscripts included, are as follows.

$$\begin{aligned}\frac{dC^g_{ij}}{dt} = {} & \frac{1}{\sigma\Delta x} v^{\mathrm{L}}_{ij}[S(v^{\mathrm{L}})C^g_{i-1,j} + S(-v^{\mathrm{L}})C^g_{ij}] \\ & + \frac{1}{\sigma\Delta x} v^{\mathrm{R}}_{ij}[-S(-v^{\mathrm{R}})C^g_{i+1,j} - S(v^{\mathrm{R}})C^g_{ij}] \\ & + \frac{1}{\sigma\Delta y} v^{\mathrm{B}}_{ij}[S(v^{\mathrm{B}})C^g_{i,j-1} + S(-v^{\mathrm{B}})C^g_{ij}] \\ & + \frac{1}{\sigma\Delta y} v^{\mathrm{T}}_{ij}[-S(-v^{\mathrm{T}})C^g_{i,j+1} - S(v^{\mathrm{T}})C^g_{ij}] \\ & + \frac{2\omega D}{n_z(\Delta z)^2\sigma}(C^w_{ij1} - C^g_{ij}/K_{\mathrm{H}}) \end{aligned} \tag{32}$$

$$\frac{dC^w_{ij1}}{dt} = \frac{D}{(\Delta z)^2}[C^w_{ij2} - C^w_{ij1} + 2(C^g_{ij}/K_{\mathrm{H}} - C^w_{ij1})] \tag{33}$$

$$\frac{dC^w_{ijk}}{dt} = \frac{D}{(\Delta z)^2}(C^w_{ij,k+1} - 2C^w_{ijk} + C^w_{ij,k+1}) \tag{34}$$

$$\frac{dC^w_{ij,n_z}}{dt} = \frac{D}{(\Delta z)^2}[C^w_{ij,n_z-1} - C^w_{ij,n_z} + 2S(m_{ij})(C_{\mathrm{sat}} - C^w_{ij,n_z})] \tag{35}$$

and

$$\frac{dm_{ij}}{dt} = -\frac{2\Delta V\omega DS(m_{ij})}{n_z(\Delta z)^2}(C_{\mathrm{sat}} - C^w_{ij,n_z}) \tag{36}$$

The initial conditions are determined as follows (34). If the initial total concentration of VOC in a volume element is C_{tot}, then

$$C_{\mathrm{tot}} = \sigma C^g + \omega C^w + C^{\mathrm{NAPL}} \tag{37}$$

We assume that $C^{\mathrm{NAPL}} = 0$, and that C^g and C^w are in equilibrium. Since we are also assuming that the VOC obeys Henry's law, this gives

$$C_{\mathrm{tot}} = \sigma K_{\mathrm{H}} C^w + \omega C^w \tag{38}$$

so

$$C^w = \frac{C_{\mathrm{tot}}}{\sigma K_{\mathrm{H}} + \omega} \tag{39}$$

If this value of C^w is less than C_{sat} (the aqueous solubility of the VOC), then C^w is correct, $C^g = K_{\mathrm{H}}C^w$, and $C^{\mathrm{NAPL}} = 0$ for that volume element. If $C^w \geq C_{\mathrm{sat}}$, then the solution is in fact saturated, so that

$$\begin{aligned} C^w &= C_{\mathrm{sat}} \\ C^g &= K_{\mathrm{H}} C_{\mathrm{sat}} \end{aligned} \tag{40}$$

and from Eq. (37)

$$C^{\mathrm{NAPL}} = C_{\mathrm{tot}} - \sigma C^{g} - \omega C^{w} \tag{41}$$

The initial values of the model variables for the volume element are then

$$C_{ij}^{g} = C^{g} \tag{42}$$

$$C_{ijk}^{w} = C^{w}, \qquad k = 1, 2, \ldots, n_z \tag{43}$$

$$m_{ij} = \Delta V \cdot C^{\mathrm{NAPL}} \tag{44}$$

After initialization the equations are integrated forward in time by a simple Gaussian method or by the predictor-corrector method. In the initial stages of a run, diffusion transport is very rapid, which can lead to instabilities if the time increment Δt is too large. This is governed by the Courant condition on the time increment, namely that

$$\frac{D\Delta t}{(\Delta z)^2} < 1 \tag{45}$$

if integration is to be stable.

The total residual mass of VOC in the system is calculated by Eq. (46).

$$M_{\mathrm{tot}} = \sum_{i=1}^{n_x} \sum_{j=1}^{n_y} \left[\left(\sigma C_{ij}^{g} + \sum_{k=1}^{n^z} \frac{\omega C_{ijk}^{w}}{n_z} \right) \Delta V + m_{ij} \right] \tag{46}$$

The VOC concentration in the effluent gas was calculated by Eq. (47), and is just the gas-flux-weighted average of the VOC concentrations in the volume elements surrounding the element containing the well.

$$C_{\mathrm{effl}}^{g} = \frac{v^{\mathrm{T}} A^{\mathrm{T}} C_{1,J+1}^{g} + v^{\mathrm{R}} A^{\mathrm{R}} C_{2,J}^{g} + v^{\mathrm{B}} A^{\mathrm{B}} C_{1,J-1}^{g}}{v^{\mathrm{T}} A^{\mathrm{T}} + v^{\mathrm{R}} A^{\mathrm{R}} + v^{\mathrm{B}} A^{\mathrm{B}}} \tag{47}$$

where v^{T}, v^{R}, and v^{B} are the superficial gas velocities entering the top, right, and bottom faces of the volume element containing the well; and A^{T}, A^{R}, and A^{B} are the areas of the top, right, and bottom faces of this volume element.

In fact, one would not expect the thicknesses of the aqueous layers to have a single fixed value; there would be some sort of distribution of thicknesses. If one attempts to handle this by including a distribution of thicknesses in each volume element, one increases the number of differential equations to be integrated by a factor roughly equal to the number of different thicknesses which are to be taken into account. This immediately puts the problem beyond the scope of readily available microcomputers.

We took this distribution of thicknesses into account by making a number of random selections of thicknesses equal to the number of volume elements used to represent the system, and then assigning one value of the water layer thickness to each volume element. The recipe to select values of the thickness was as follows.

$$l_{ij} = \langle l \rangle + g[-0.5 + \mathrm{RND}] \tag{48}$$

Here $\langle l \rangle$ is a mean value of the water layer thickness (m), g is the spread between possible maximum and minimum values, and RND is a uniformly distributed pseudo-random number between 0 and 1 which is generated by the random number subroutine in TurboBASIC.

The amounts of computer time required to simulate runs with the scheme described above are rather long, since the differential equations of the model are rather stiff. Small values of Δt are required, while the time period modeled may be of the order of months. We therefore describe two approximations which result in quite substantial reductions.

The first involves making the steady-state approximation for the gas phase concentrations C_{ij}^{g}. The advective terms in the equations for dC_{ij}^{g}/dt provide a limit on Δt in that the volume of gas flowing into (and out of) each volume element during the time interval Δt must be substantially less than the volume of gaseous phase contained in that volume element if these differential equations are to be integrated in the normal way. As discussed in more detail in earlier papers (30, 32), one expects that for virtually the entire duration of an SVE cleanup the derivatives dC_{ij}^{g}/dt will be sufficiently small that they can be set equal to zero. The resulting algebraic equations can then be solved for the C_{ij}^{g}, and the limit on Δt associated with advection is thereby avoided. They are as follows.

$$C_{ij}^{g} = \frac{\begin{aligned}\Bigg[&\frac{1}{\sigma\Delta x} v_{ij}^{\mathrm{L}} S(v^{\mathrm{L}}) C_{i-1,j}^{g} - \frac{1}{\sigma\Delta x} v_{ij}^{\mathrm{R}} S(-v^{\mathrm{R}}) C_{i+1,j}^{g} \\ &+ \frac{1}{\sigma\Delta y} v_{ij}^{\mathrm{B}} S(v^{\mathrm{B}}) C_{i,j-1}^{g} - \frac{1}{\sigma\Delta y} v_{ij}^{\mathrm{T}} S(-v^{\mathrm{T}}) C_{i,j+1}^{g} + \frac{2\omega D}{n_z(\Delta z)^2} C_{ij1}^{w}\Bigg]\end{aligned}}{\begin{aligned}\Bigg[&-\frac{1}{\sigma\Delta x} v_{ij}^{\mathrm{L}} S(-v^{\mathrm{L}}) + \frac{1}{\sigma\Delta x} v_{ij}^{\mathrm{R}} S(v^{\mathrm{R}}) - \frac{1}{\sigma\Delta y} v_{ij}^{\mathrm{B}} S(-v^{\mathrm{B}}) \\ &+ \frac{1}{\sigma\Delta y} v_{ij}^{\mathrm{T}} S(v^{\mathrm{T}}) + \frac{2\omega D}{\sigma n_z(\Delta z)^2 K_{\mathrm{H}}}\Bigg]\end{aligned}} \tag{49}$$

In solving these equations for the C_{ij}^{g}, one sets all concentrations which lie outside the domain equal to zero, and one calculates the C_{ij}^{g} in order of decreasing j and decreasing i. If the SVE horizontal pipe is near the bottom of the domain, as is usually the case, this permits exact solution, since each equation uses only C^g_{ij}'s which have already been computed. In this way one is able to avoid lengthy solutions of sets of linear equations.

The diffusion process is handled in a somewhat similar manner to avoid the restriction imposed by the Courant condition, Eq. (45). After the initial stages of the cleanup but before the NAPL has been eliminated from any of the volume elements, one can make the steady-state assumption for the concentrations C^w_{ijk} in the aqueous boundary layers, i.e., $dC^w_{ijk}/dt = 0$. This gives linear concentration distributions in the aqueous layers, in which the concentrations are given by

$$C^w_{ijk} = \frac{C^g_{ij}}{K_H} + \left[C_{\text{sat}} - \frac{C^g_{ij}}{K_H}\right]\frac{(k - 1/2)\Delta z}{l}, \qquad k = 1, 2, \ldots, n_z \tag{50}$$

This then replaces all of the differential equations in the model with algebraic equations except for the equations for the dm_{ij}/dt.

Therefore, after the initial transients of the cleanup (involving less than a minute of computer time), one can shift from the exact model in which all concentrations are calculated by means of the differential equations to the steady-state model in which the VOC concentrations in the gas and aqueous phases are calculated by algebraic steady-state approximations. At this point the time increment can be greatly increased, since it is controlled only by the differential equations for the m_{ij}. The program can be run in this regime until one or more of the m_{ij} becomes zero. At this point the steady-state approximation for the C^g_{ij} is still valid, but that for the C^w_{ijk} is not. One therefore shifts to an algorithm in which the differential equations for the C^w_{ijk} and the m_{ij} are used, along with the algebraic (steady-state) equations for the C^g_{ij}. This approach should make use of this distributed diffusion model on relatively slow microcomputers quite feasible.

RESULTS

The model was implemented in TurboBASIC and run on a 386 NX Canon laptop computer operating at 20 MHz and equipped with a math coprocessor. Typical runs using only the differential equations (no steady-state approximations) required about 40 minutes.

Near the end of the study some runs were made using a 486 DX machine running at 50 MHz. Without the steady-state approximations a typical run required 300 to 400 seconds on this machine. With the steady-state approximations typical runs were from 2.35 to 4.0 times as fast. When the steady-state approximations are used, runs in which there is lengthy tailing are not speeded up as much as runs in which tailing is relatively short, as expected, since the steady-state approximations are in operation only during the period in which the effluent soil gas concentration is on a plateau. The appearances of graphs and the cleanup times obtained with the two methods were identical.

Default values of the parameters used with the model are given in Table 1. The runs were made in two sets; in the first the thickness of the water layer is held constant over the domain being modeled, while in the second set it varies from volume element to volume element according to Eq. (47). In the first set of runs we explore the dependence of SVE on various model parameters; in the second we focus on the effects of the distribution of water layer thicknesses on the behavior of SVE. In reporting both sets we shall include the time-dependence of both the total residual mass of VOC (which is what everyone is most interested in) and the VOC concentrations in the effluent soil gas (which is what we can actually measure). In all cases we plot (total residual mass of VOC at time t)/(total initial mass of VOC) and (C^g_{effl} at time t)/($K_H \cdot C_{\text{sat}}$), so the ordinates of the graphs are dimensionless.

TABLE 1
Default Parameters Used in the Diffusion-Limited SVE Model

	First set	Second set
Width of domain to be stripped, m	10	10
Depth to water table, m	5	5
Length of horizontal slotted pipe, m	10	10
Depth of well, m	4.5	4.5
Wellhead pressure, atm	0.9	0.9
Gas flow rate of well, SCFM	25	25
Well gravel packing diameter, cm	30	30
Identity of VOC	TCE, trichloroethylene	
Solubility of VOC, mg/L	1100	1100
Henry's constant of VOC, dimensionless	0.2821	0.2821
Density of VOC, g/mL	1.46	1.46
Diffusion constant of VOC in water, m^2/s	2×10^{-10}	2×10^{-10}
Soil density, g/cm^3	1.7	1.7
Soil air-filled porosity, dimensionless	0.2	0.2
Soil water-filled porosity, dimensionless	0.2	0.2
Thickness of water diffusion layer, cm	0.4	0.4 ($\langle l \rangle$)
n_x	5	5
n_y	5	5
n_z	5	5
Total initial VOC concentration, mg/kg of soil	2000	2000
Δt, seconds	50, 100	100
Length of run, days	30	50

In Figs. 3(a) and 3(b) we see plots of total residual VOC mass and effluent soil gas VOC concentration for gas flow rates of 12.5, 25, and 50 SCFM (0.00590, 0.0118, and 0.0236 m^3/s). The thickness of the water diffusion layer is 0.5 cm in these runs. In all cases the effluent soil gas VOC concentration C^{g}_{effl} drops quite rapidly from its initial value (satura-

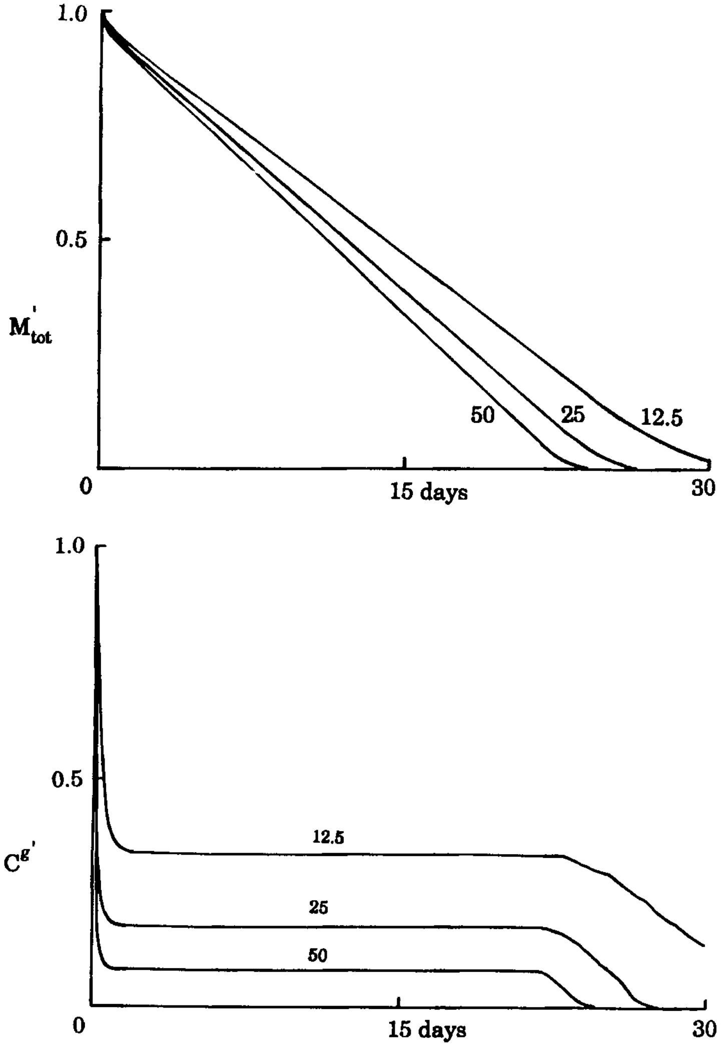

FIG. 3 Plots of reduced total residual VOC mass (a) and reduced effluent soil gas VOC concentration (b) versus time; effect of gas flow rate. Gas flow rates are 12.5, 25, and 50 SCFM as indicated. Set 1.

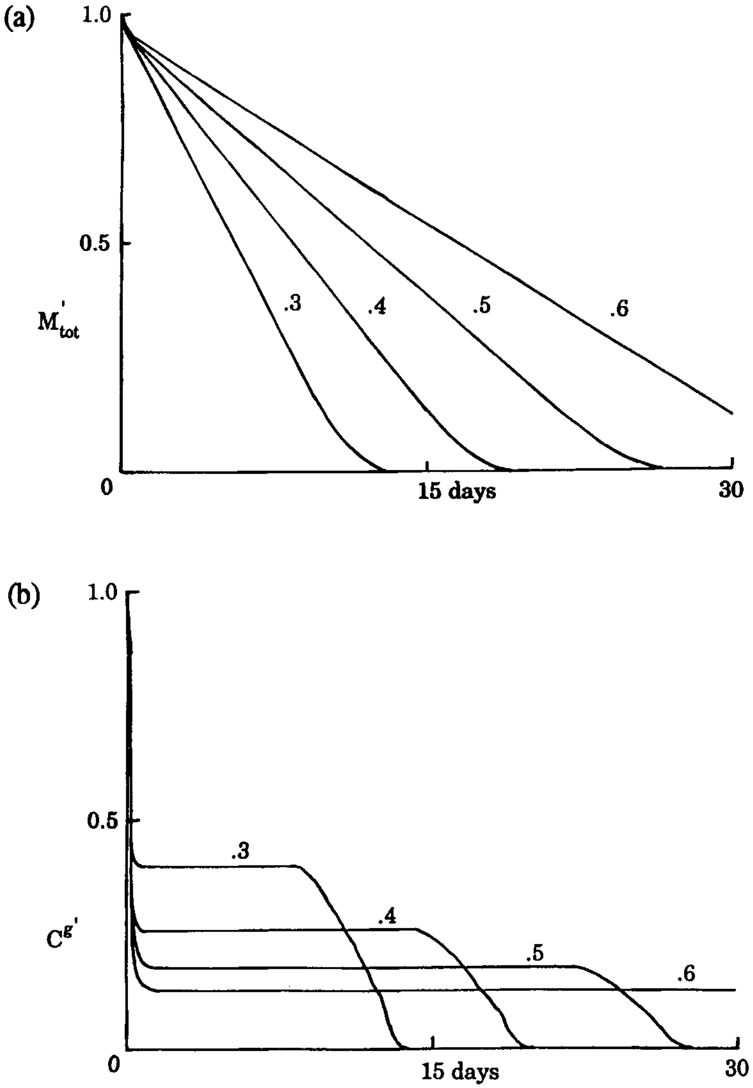

FIG. 4 Plots of reduced total residual VOC mass (a) and reduced effluent soil gas VOC concentration (b) versus time; effect of water diffusion layer thickness. l = 0.3, 0.4, 0.5, and 0.6 cm. Set 1.

tion), levels off to form a plateau value which is maintained for the bulk of the run, and then drops off relatively abruptly to zero as one achieves essentially 100% removal. If one were to assume that C^g_{effl} provides a measure of the extent of removal, these long flat plateaus would be extremely discouraging. In fact, as indicated by the plots of total residual VOC mass (M_{tot}), the cleanups progress in good order.

The fact that the plateau VOC concentrations are far less than the saturation gas concentration indicates that these three runs are all quite limited by mass transport kinetics. The 99.5% cleanup times in these three runs are 23.59, 26.13, and 31.29 days for gas flow rates of 50, 25, and 12.5 SCFM, respectively. The volumes of effluent soil gas requiring treatment are 17.0, 9.4, and 5.8 × 10^5 SCFM, respectively. Evidently one can substantially reduce off-gas treatment costs at the expense of relatively modest increases in cleanup times by properly selecting the gas flow rate of the system.

The effect of the thickness of the water diffusion layer—the thickness of the low-permeability porous lamellae—is shown in Figs. 4(a) and 4(b). In these runs the gas flow rate is 25 SCFM, and the thickness of the water diffusion layer is 0.3, 0.4, 0.5, and 0.6 cm. The 99.5% cleanup times are 12.69, 18.55, 26.13, and 35.49 days. As expected, there is a strong correlation between cleanup time and the thickness of the water diffusion layer. A nonlinear least-squares program was used to fit the equation

$$t_{99.5} = B' + C'l^n \tag{51}$$

to the data given in Table 2. The parameter values obtained are given in Table 2. In the strictly diffusion-limited region one would expect that $n = 2$ and $B' = 0$.

TABLE 2
Dependence of 99.5% Cleanup Time $t_{99.5}$ on Water Diffusion Layer Thickness l

l (cm)	$t_{99.5}$ (days) from model	$t_{99.5}$ from statistical fit
0.2	8.56	8.503
0.3	12.69	12.733
0.4	18.55	18.620
0.5	26.13	26.155
0.6	35.49	35.332
0.7	46.07	46.147

Nonlinear least-squares fit to $t_{99.5} = B' - C'l^n$: $B' = 5.075592$, $C' = 83.29427$, $n = 1.982385$, $r^2 = 0.999969$
rms error = 0.11724 days

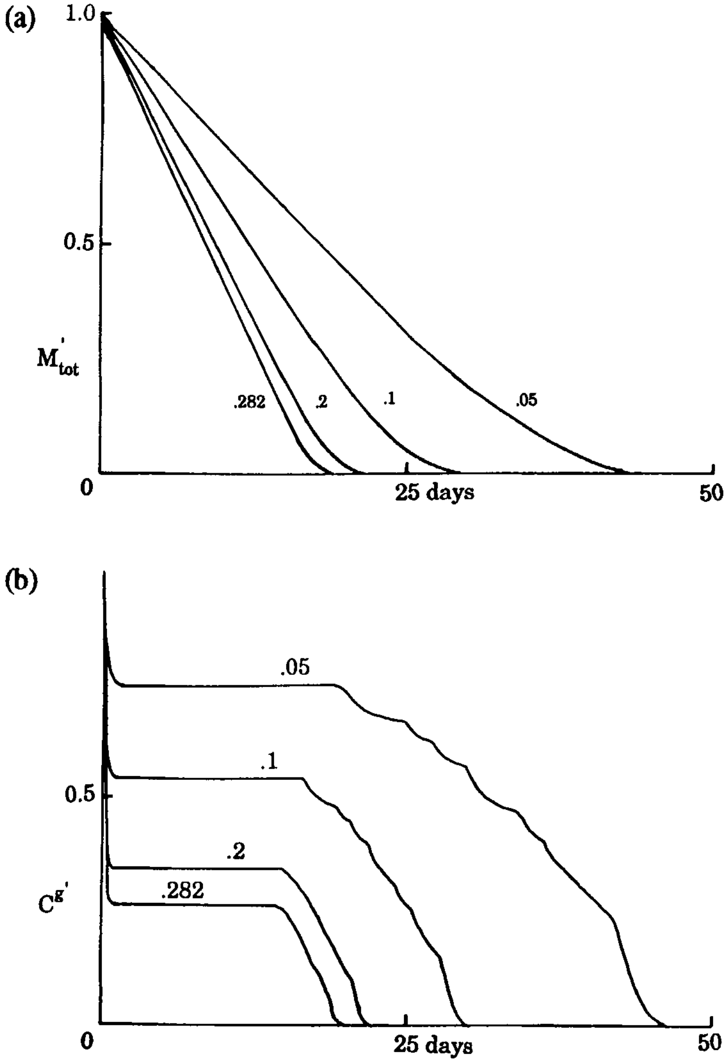

FIG. 5 Plots of reduced total residual VOC mass (a) and reduced effluent soil gas VOC concentration (b) versus time; effect of Henry's constant. K_H = 0.05, 0.1, 0.2, and 0.2821 as indicated. Set 1.

The dependence of SVE on the Henry's constant of the VOC is illustrated in Fig. 5. Since the process is somewhat diffusion-limited under these conditions, we do not find that the cleanup time is inversely related to K_H, but the correlation is negative, as expected.

We next turn to the second set of results, obtained with distributions of water diffusion layer thickness. Figure 6 shows plots of M_{tot} and C^{g}_{effl} for a single representative run for which the range of the distribution is rather narrow, only 0.2 cm, so that l ranges from 0.3 to 0.5 cm. In Fig. 7 we have plots of M_{tot} and C^{g}_{effl} for a run for which the range of the distribution is 0.6 cm, with l ranging from 0.1 to 0.7 cm. Both plots show a large initial rate of removal which rapidly decreases to a plateau. The constant plateau is narrower than was the case with the runs in set 1, however, and we see a substantially longer tailing region toward the run in which l ranges from 0.1 to 0.7 cm than it is for the other run with the narrower range of l. The time required for 99.5% cleanup is quite a bit larger for the run with the wider range, despite the fact that the two runs have nearly identical average water layer thicknesses.

Sets of 10 runs each were made for $\langle l \rangle = 0.4$ cm and $g = 0.2$, 0.4, and 0.6 cm. The values of $t_{99.5}$ for these sets of runs are given in Table 3, together with the mean value and standard deviation of $t_{99.5}$ for each set. The tendency noticed above of $t_{99.5}$ to increase with increasing upper limit to the range of the water diffusion layer thicknesses is strongly confirmed

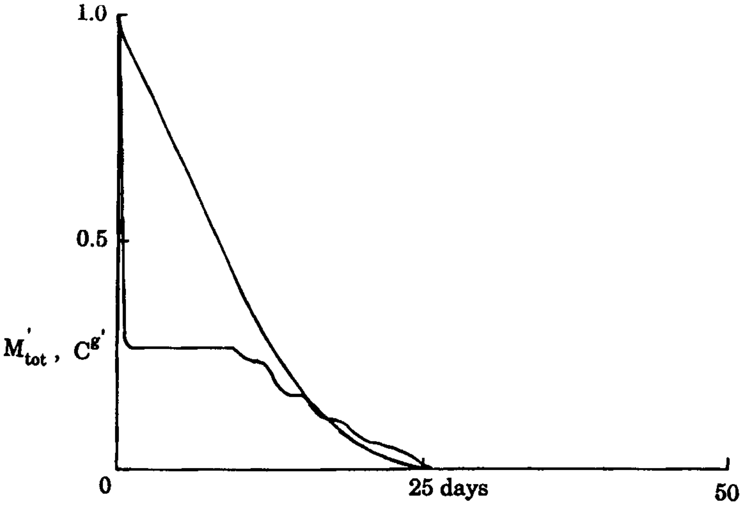

FIG. 6 Plots of reduced total residual VOC mass and reduced effluent soil gas concentration for a narrow range (g = 0.2 cm) of water diffusion layer thicknesses. Set 2.

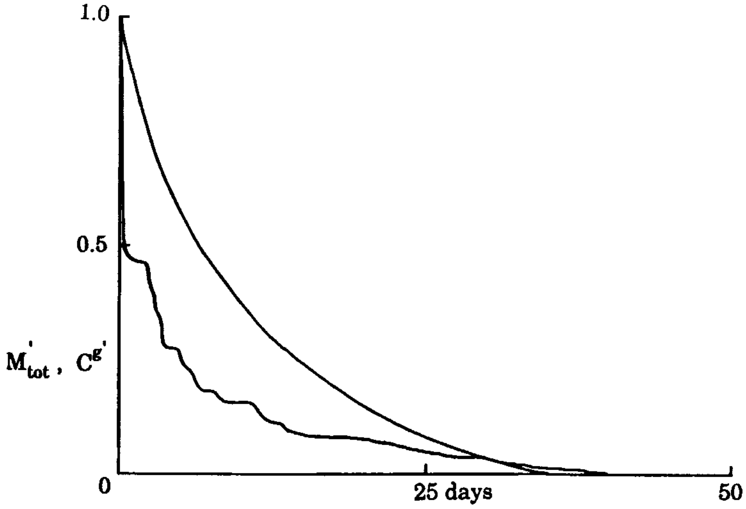

FIG. 7 Plots of reduced total residual VOC mass and reduced effluent soil gas concentration for a wide range (g = 0.6 cm) of water diffusion layer thicknesses. Set 2.

TABLE 3

Results for Set 2; Values of $t_{99.5}$ (days) for Sets of Runs Having Various Ranges of Values of Water Diffusion Layer Thickness

$\langle l \rangle = 0.4$, $g = 0$	$\langle l \rangle = 0.4$, $g = 0.2$	$\langle l \rangle = 0.4$, $g = 0.4$	$\langle l \rangle = 0.4$, $g = 0.6$
18.53	23.60	30.44	42.44
	22.62	31.33	39.00
	22.84	31.69	41.33
	24.16	32.18	41.11
	22.40	31.62	43.56
	22.44	28.56	39.89
	22.78	31.40	38.44
	23.33	29.51	42.22
	21.67	28.76	36.56
	23.67	28.89	39.27
$\overline{t_{99.5}} = 18.53$	22.96	30.44	40.38
σ_t = —	0.70	1.32	2.02

here. A nonlinear least-squares correlation of $t_{99.5}$ with the upper limit $l_{\max}$ to the water diffusion layer thickness yielded

$$\overline{t_{99.5}} = 13.755 + 80.657(l_{\max})^{3.103} \tag{52}$$

with a coefficient of determination of 0.99976 and an rms error of 0.257.

CONCLUSIONS

A mathematical model for soil vapor extraction has been developed which includes what is hoped to be a rather realistic picture of diffusion-limited mass transport between the NAPL and aqueous phases and between the aqueous and gaseous phases. The model is simple enough to be run on readily available microcomputers (i.e., 386 SX 12 MHz or better, with a math coprocessor). SVE cleanup times correlate very strongly with the upper limit to the thickness of the aqueous diffusion layer. Effluent soil gas VOC concentration plots commonly show very high initial values which drop off extremely quickly, followed by a virtually flat plateau, followed by terminal tailing, the extent of which increases with increasing upper limit to the distribution of values of the diffusion layer thickness.

The results suggest that it is futile to try to design short-term pilot-scale experiments which will estimate cleanup times at all accurately. The extent of the tailing which may result toward the end of the cleanup is determined by the slow release of VOC through thick diffusion layers, and there is no way by which this can be assessed by short-term experiments, given the likelihood of a substantial range of diffusion layer thicknesses.

On the other hand, the results also suggest that finding that the effluent soil gas VOC concentrations are not definitely decreasing with time during the course of cleanup is no cause for alarm, in that plateaus in C^{g}_{effl} are quite normal when diffusion of VOC from NAPL through aqueous boundary layers is occurring.

This exercise, combined with earlier results on the effects of spatial variations in the pneumatic permeability on SVE cleanup times, provides a warning that highly precise predictions of SVE cleanup times are probably not possible unless one is willing to spend quite large amounts of money and time to characterize the site in great detail.

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REFERENCES

1. T. A. Pedersen and J. T. Curtis (Eds.), *Soil Vapor Extraction Technology Reference Handbook*, Risk Reduction Engineering Laboratory, U.S. EPA Report EPA/540/2-91/003, 1991. Reprinted as *Soil Vapor Extraction Technology. Pollution Technology Review 204*, Noyes Publications, Park Ridge, New Jersey, 1991.
2. J. P. Stumbar and J. Rawe, *Guide for Conducting Treatability Studies under CERCLA: Soil Vapor Extraction Interim Guidance*, U.S. EPA Report EPA/540/2-91/019A, 1991.
3. W. J. Lyman and D. C. Noonan, "Assessing UST Corrective Action Technologies: Site Assessment and Selection of Unsaturated Zone Treatment Technologies," in *Cleanup of Petroleum Contaminated Soils at Underground Storage Tanks*, by W. J. Lyman, D. C. Noonan, and P. J. Reidy, Noyes Data Corp., Park Ridge, New Jersey, 1990.
4. P. J. Reidy, W. J. Lyman, and D. C. Noonan, "Saturated Zone Corrective Action Technologies," in *Cleanup of Petroleum Contaminated Soils at Underground Storage Tanks*, by W. J. Lyman, D. C. Noonan, and P. J. Reidy, Noyes Data Corp., Park Ridge, New Jersey, 1990.
5. D. DiGiulio (Project Officer), *Proceedings, Symposium on Soil Venting, April 29–May 1, 1991, Houston, Texas*, U.S. EPA Report EPA/600/R-92/174.
6. N. J. Hutzler, B. E. Murphy, and J. S. Gierke, "State of Technology Review: Soil Vapor Extraction Systems," *J. Hazard. Mater.*, *26*(2), 225 (1991).
7. N. J. Hutzler, B. E. Murphy, and J. S. Gierke, *Review of Soil Vapor Extraction System Technology*, Presented at Soil Vapor Extraction Technology Workshop, U.S. EPA RREL, June 28–29, Edison, New Jersey. Reprinted in *Soil Vapor Extraction Technology. Pollution Technology Review 204* (T. A. Pedersen and J. T. Curtis, Eds.), Noyes Publications, Park Ridge, New Jersey, 1991, p. 136.
8. D. J. Wilson and A. N. Clarke, "Soil Vapor Extraction," in *Hazardous Waste Site Soil Remediation: Theory and Application of Innovative Technologies* (D. J. Wilson and A. N. Clarke, Eds.), Dekker, New York, 1993, p. 171.
9. A. L. Baehr, G. E. Hoag, and M. C. Marley, "Removing Volatile Contaminants from the Unsaturated Zone by Inducing Advective Air-Phase Transport," *J. Contam. Hydrol.*, *4*, 1 (1989).
10. G. E. Hoag, *Soil Vapor Extraction Research Developments*, Presented at Soil Vapor Extraction Technology Workshop, U.S. EPA RREL, June 28–29, 1989, Edison, New Jersey. Reprinted in *Soil Vapor Extraction Technology. Pollution Technology Review 204* (T. A. Pedersen and J. T. Curtis, Eds.), Noyes Publications, Park Ridge, New Jersey, 1991, p. 286.
11. G. E. Hoag, C. J. Bruell, and M. C. Marley, *Study of the Mechanisms Controlling Gasoline Hydrocarbon Partitioning and Transport in Ground Water Systems*, USGS Report G832-06, available from NTIS as PB85-242907/AS, 1984.
12. G. E. Hoag, M. C. Marley, B. L. Cliff, and P. Nangeroni, "Soil Vapor Extraction Research Developments," in *Hydrocarbon Contaminated Soils and Ground Water: Analysis, Fate, Environmental and Public Health Effects, and Remediation*, Lewis Publishers, Chelsea, Michigan, 1991, p. 187.
13. M. C. Marley, "Development and Application of a Three-Dimensional Air Flow Model in the Design of a Vapor Extraction System," in *Proceedings, Symposium on Soil*

Venting, April 29–May 1, 1991, Houston, Texas (D. DiGiulio, Project Officer), U.S. EPA Report EPA/600/R-92/174, 1992, p. 125.

14. M. C. Marley, P. E. Nangeroni, B. L. Cliff, and J. D. Polonsky, "Air Flow Modeling for In Situ Evaluation of Soil Properties and Engineered Vapor Extraction System Design," in *Proceedings, 4th National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, May 14–17, 1992, Las Vegas, Nevada*, p. 651.
15. M. C. Marley, S. D. Richter, B. L. Cliff, and P. E. Nangeroni, *Design of Soil Vapor Extraction Systems—A Scientific Approach*, Presented at Soil Vapor Extraction Technology Workshop, U.S. EPA RREL, June 28–29, 1989, Edison, New Jersey. Reprinted in *Soil Vapor Extraction Technology. Pollution Technology Review 204* (T. A. Pedersen and J. T. Curtis, Eds.), Noyes Publications, Park Ridge, New Jersey, 1991.
16. P. C. Johnson, M. W. Kemblowski, and J. D. Colthart, *Practical Screening Models for Soil Venting Applications*, Presented at Workshop on Soil Vacuum Extraction, April 27–28, 1989, RSKERL, Ada, Oklahoma.
17. P. C. Johnson, M. W. Kemblowski, and J. D. Colthart, "Quantitative Analysis for the Cleanup of Hydrocarbon-Contaminated Soils by In Situ Soil Venting," *Ground Water, 28*, 413 (1990).
18. P. C. Johnson, M. W. Kemblowski, J. D. Colthart, D. L. Byers, and C. C. Stanley, *A Practical Approach to the Design, Operation, and Monitoring of In-Situ Soil Venting Systems*, Presented at Soil Vapor Extraction Technology Workshop, June 28–29, 1989, U.S. EPA Risk Reduction Engineering Laboratory (RREL), Edison, New Jersey. Reprinted in *Soil Vapor Extraction Technology. Pollution Technology Review 204* (T. A. Pedersen and J. T. Curtis, Eds.), Noyes Publications, Park Ridge, New Jersey, 1991, p. 195.
19. P. C. Johnson, C. C. Stanley, M. W. Kemblowski, D. L. Byers, and J. D. Colthart, "Practical Approach to the Design, Operation and Monitoring of In Situ Soil Venting Systems," *Ground Water Monit. Rev., 10*, 159 (1990).
20. M. W. Kemblowski and S. Chowdery, "Soil Venting Design: Models and Decision Analysis," in *Proceedings, Symposium on Soil Venting, April 29–May 1, 1991, Houston, Texas* (D. DiGiulio, Project Officer), U.S. EPA Report EPA/600/R-92/174, 1992, p. 73.
21. J. S. Cho, *Forced Air Ventilation for Remediation of Unsaturated Soils Contaminated by VOC*, U.S. EPA Report EPA/600/2-91/016, July 1991.
22. J. C. Walton, R. G. Baca, J. B. Sisson, and T. R. Wood, "Application of Soil Venting at a Large Scale: A Data and Modeling Analysis," in *Proceedings, 4th National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, May 14–17, Las Vegas, Nevada*, 1990, p. 559.
23. J. C. Walton, R. G. Baca, J. B. Sisson, A. J. Sondrup, and S. O. Magnusen, "Application of Computer Simulation Models to the Design of a Large-Scale Soil Venting System and Bioremediation," in *Proceedings, Symposium on Soil Venting, April 29–May 1, 1991, Houston, Texas* (D. DiGiulio, Project Officer), U.S. EPA Report EPA/600/R-92/174, 1992, p. 91.
24. D. J. Wilson, A. N. Clarke, and J. H. Clarke, "Soil Cleanup by In-Situ Aeration. I. Mathematical Modeling," *Sep. Sci. Technol., 23*, 991 (1988).
25. K. Gannon, D. J. Wilson, A. N. Clarke, R. D. Mutch, and J. H. Clarke, "Soil Cleanup by In-Situ Aeration. II. Effects of Impermeable Caps, Soil Permeability, and Evaporative Cooling," *Ibid., 24*, 831 (1989).
26. A. N. Clarke, M. M. Megehee, and D. J. Wilson, "Soil Cleanup by In-Situ Aeration. XII. Effect of Departures from Darcy's Law on Soil Vapor Extraction," *Ibid., 28*, 1671 (1993).

27. W. R. Roy and R. A. Griffin, *In-Situ Extraction of Organic Vapors from Unsaturated Porous Media* (Open File Report 24), Environmental Institute for Waste Management Studies, University of Alabama, Tuscaloosa, 1989.
28. M. C. Marley and G. E. Hoag, "Induced Venting for the Recovery/Restoration of Gasoline Hydrocarbons in the Vadose Zone," Presented at *NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, Houston, Texas,* November 5–7, 1984.
29. D. C. DiGiulio, J. S. Cho, R. R. Dupont, and M. W. Kemblowski, "Conducting Field Tests for Evaluation of Soil Vacuum Extraction Application," in *Proceedings, 4th National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, May 14–17, Las Vegas, Nevada,* 1990, p. 587.
30. J. M. Rodríguez-Maroto and D. J. Wilson, "Soil Cleanup by In-Situ Aeration. VII. High-Speed Modeling of Diffusion Kinetics," *Sep. Sci. Technol., 26,* 743 (1991).
31. J. M. Rodríguez-Maroto, C. Gómez-Lahoz, and D. J. Wilson, "Mathematical Modeling of SVE: Effects of Diffusion Kinetics and Variable Permeabilities," in *Proceedings, Symposium on Soil Venting, April 29–May 1, 1991, Houston, Texas* (D. DiGiulio, Project Officer), U.S. EPA Report EPA/600/R-92/174, 1992, p. 103.
32. C. Gómez-Lahoz, R. A. Garcia-Delgado, F. Garcia-Herruzo, J. M. Rodríguez-Maroto, and D. J. Wilson, "Extraccion a Vacio de Contaminantes Organicos del Suelo. Fenomenos de No-Equilibrio," Presented at *III Congreso de Ingenieria Ambiental, Proma '93, Bilbao, Spain,* 1993.
33. C. Gómez-Lahoz, J. M. Rodríguez-Maroto, and D. J. Wilson, "Biodegradation Phenomena during Soil Vapor Extraction: A High-Speed Nonequilibrium Model," *Sep. Sci. Technol., 29,* 429 (1994).
34. D. J. Wilson, C. Gómez-Lahoz, and J. M. Rodríguez-Maroto, "Soil Cleanup by In-Situ Aeration. XVI. Solution and Diffusion in Mass Transport-Limited Operation and Calculation of Darcy's Constants," *Ibid., 29,* 1133 (1994).
35. W. R. Smythe, *Static and Dynamic Electricity,* 4th ed., McGraw-Hill, New York, 1953.

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