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Soil Clean Up by *in-situ* Aeration. X. Vapor Stripping of Mixtures of Volatile Organics Obeying Raoult's Law

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Abstract

Mathematical models are developed for the soil vapor extraction of nonaqueous phase liquid mixtures obeying Raoult's law. The models make the local equilibrium assumption for vapor and liquid, and can handle up to three components. Vapor stripping in laboratory columns, by means of a single vertical well screened at the bottom (axial symmetry) and by means of a single horizontal slotted pipe (Cartesian symmetry), are modeled. The models run on IBM PC-AT compatible microcomputers. Some representative results are given.

INTRODUCTION

Soil vapor extraction (SVE) has become a well-recognized technique for the remediation of hazardous waste sites in which the vadose zone is contaminated with volatile organic compounds (VOCs). Pedersen and Curtis (*1*) recently provided a quite detailed review of the technology, together with an extensive list of references and a discussion of the assessment of the feasibility of the technique under any particular set of circumstances. Another recent review was by Hutzler and his coworkers (*2*). This was updated in a still more recent paper of ours (*3*), in which much of the mathematical modeling work in SVE was discussed.

Most of the models for soil vapor extraction describe the removal of a single compound having well-defined characteristics (solubility, Henry's constant, adsorption parameter(s), vapor pressure, etc.). However, many of the leaks and spills to be modeled involve mixtures such as gasoline or jet fuel, in which the range of some of these parameters (particularly vapor pressure) can be quite large. Johnson and his coworkers (Refs. *4–6*, for example) have stressed the importance of the variation of VOC mixture composition on soil vapor extraction when dealing with gasoline. Their work suggested to us the utility of extending SVE models of the type which we and others had developed (Refs. 7–9, for example) to Raoult's law mixtures.

ANALYSIS

Soil Gas Velocity Fields

If the soil permeability is assumed to be constant spatially and isotropic in the domain of interest, and if the gas is assumed to obey the ideal gas law $PV = nRT$, then the equation governing the steady-state pressure distribution in the vicinity of a vapor stripping well,

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

simplifies to Laplace's equation in P^2,

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

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

A solution to Eq. (2) is needed which satisfies the boundary conditions

$$P^2 = 1 \text{ atm}^2 \tag{3}$$

at the top of the vadose zone,

$$\partial P^2 / \partial n = 0 \tag{4}$$

at the bottom of the vadose zone, and which has a sink of the appropriate strength at the location of the vacuum well. Such solutions are readily constructed by the method of images from electrostatics (*10*). We first examine the case where the vacuum is produced by a long horizontal buried slotted pipe. Then we turn to the case of a single vertical well screened at the bottom.

Gas Flow Field around a Long Horizontal Buried Slotted Pipe

The geometry of the system is defined in Fig. 1. Let

h = thickness of vadose zone, m
$h - a$ = depth of well, m
r_w = radius of gravel packing around the horizontal slotted pipe, m
l = length of horizontal slotted pipe, m

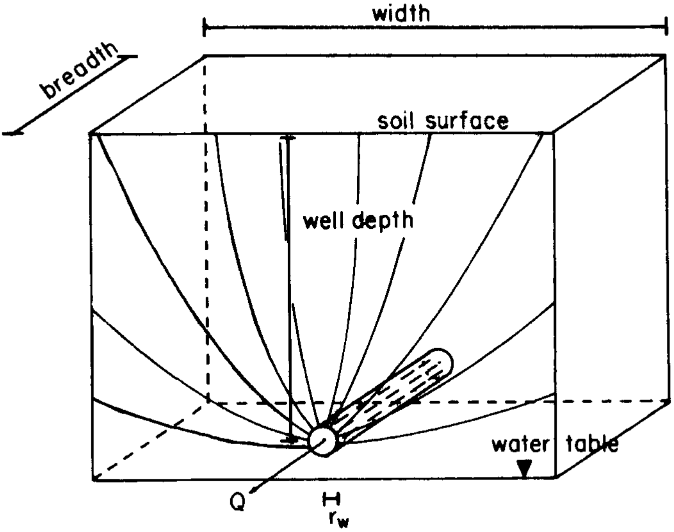

FIG. 1. Configuration for SVE with a buried horizontal slotted pipe.

We assume that l is sufficiently large that end effects can be neglected, so that Eq. (2) can be taken as

$$\frac{\partial^2 P^2}{\partial x^2} + \frac{\partial^2 P^2}{\partial y^2} = 0 \tag{5}$$

Then one can readily show by symmetry arguments that the following function W satisfies the conditions

$$W(x,h) = 0 \tag{6}$$

and

$$\partial W(x,0)/\partial y = 0 \tag{7}$$

where

$$1\ \text{atm}^2 - P^2(x,y)$$

$$= W(x,y) = A \sum_{n=-\infty}^{\infty} |\log_e \{x^2 + [y - (4n - 2)h - a]^2\}$$

$$+ \log_e \{x^2 + [y - (4n - 2)h + a]^2\} - \log_e \{x^2 + [y - 4nh - a]^2\}$$

$$- \log_e \{x^2 + [y - 4nh + a]^2\}| \tag{8}$$

We can also write this as

$$W(x,y) = A \sum_{n=-\infty}^{\infty} \log_e$$

$$\times \frac{\{x^2 + [y - (4n - 2)h - a]^2\}\{x^2 + [y - (4n - 2)h + a]^2\}}{\{x^2 + [y - 4nh - a]^2\}\{x^2 + [y - 4nh + a]^2\}} \qquad (9)$$

The constant A is evaluated as follows. Let P_w be the pressure in the well itself. Then

$$1 - P_w^2 = W(r_w,a) = A \sum_{n=-\infty}^{\infty} \log_e$$

$$\times \frac{\{r_w^2 + [y - (4n - 2)h - a]^2\}\{r_w^2 + [y - (4n - 2)h + a]^2\}}{\{r_w^2 + [y - 4nh - a]^2\}\{r_w^2 + [y - 4nh + a]^2\}} \qquad (10)$$

We define the sum on the right-hand side of Eq. (10) as $S(r_w,a,h)$. Then

$$A = \frac{1 - P_w^2}{S(r_w,a,h)} \qquad (11)$$

The soil gas velocity at the point (x,y) is given by Darcy's law as

$$v = -k\nabla P \qquad (12)$$

where k is the constant, isotropic permeability. From Eq. (8)

$$P^2(x,y) = 1 - W(x,y) \qquad (13)$$

from which

$$2P\nabla P = -\nabla W \qquad (14)$$

so

$$v = k\nabla W/2P \qquad (15)$$

where

$$P = P(x,y) = [1 - W(x,y)]^{1/2} \qquad (16)$$

We calculate the flow rate of the well as follows. Let Q be the molar flow rate of gas at the well, negative, mol/s. Then

$$Q = \int_0^l \int_0^{2\pi} c(r)\nu v_r(r) r d\theta dz \tag{17}$$

where $r^2 = x^2 + (y - a)^2$ is held constant and we are integrating over the surface of a cylinder of length l containing the vacuum pipe. Here $c(r)$ is the molar concentration of gas a distance r from the well, mol/m^3, and ν is the soil porosity, dimensionless. From the ideal gas law we have

$$c(r) = P(r)/RT \tag{18}$$

where $R = 8.206 \times 10^{-5}$ m^3·atm/mol·deg
T = temperature, kelvins

So

$$Q = \int_0^l \int_0^{2\pi} \frac{\nu P(r) v_r(r)}{RT} r d\theta dz \tag{19}$$

From Eq. (15) we find

$$P(r) v_r(r) = k\partial W/2\partial r \tag{20}$$

so

$$Q = \frac{\nu l k}{2RT} \int_0^{2\pi} \frac{\partial W}{\partial r} r d\theta \tag{21}$$

Examination of Eq. (8) shows that

$$W = A[-\log_e r^2 + \text{other terms which are bounded as } r \rightarrow 0] \tag{22}$$

So

$$\frac{\partial W}{\partial r} = -\frac{2A}{r} + \text{terms which are bounded as } r \rightarrow 0 \tag{23}$$

Therefore we can write

$$Q = \lim_{r \rightarrow 0} \frac{\nu l k}{2RT} \int_0^{2\pi} -\frac{2A}{r} r d\theta \tag{24}$$

and finally

$$Q = -\frac{\nu lkA}{RT} = -\frac{\nu lk(1 - P_w^2)}{RTS(r_w,a,h)} \tag{25}$$

where S is defined in Eq. (10). The negative sign indicates that the well is a sink rather than a source.

The velocity components v_x and v_y are obtained from Eq. (15):

$$v_x = \frac{k\partial W/\partial x}{2P} \tag{26}$$

$$v_y = \frac{k\partial W/\partial y}{2P} \tag{27}$$

The derivatives are given by

$$\frac{\partial W}{\partial x} = 2Ax \sum_{n=-\infty}^{\infty} \left[\frac{1}{x^2 + [y - (4n - 2)h - a]^2} + \frac{1}{x^2 + [y - (4n - 2)h + a]^2} - \frac{1}{x^2 + [y - 4nh - a]^2} - \frac{1}{x^2 + [y - 4nh + a]^2}\right] \tag{28}$$

and

$$\frac{\partial W}{\partial y} = 2A \sum_{n=-\infty}^{\infty} \left[\frac{y - (4n - 2)h - a}{x^2 + [y - (4n - 2)h - a]^2} + \frac{y - (4n - 2)h + a}{x^2 + [y - (4n - 2)h + a]^2} - \frac{y - 4nh - a}{x^2 + [y - 4nh - a]^2} - \frac{y - 4nh + a}{x^2 + [y - 4nh + a]^2}\right] \tag{29}$$

This, then, completes the calculation of the soil gas velocity field in the vicinity of a buried horizontal slotted pipe.

An alternative to the method of images for the calculation of the soil gas velocities is the use of a numerical relaxation method to solve Eq. (1) with the appropriate boundary conditions. This method is slower than the method of images, and probably slightly less accurate. It has a very great advantage over the method of images, however, in that the numerical relaxation method can handle anisotropic, spatially varying permeabilities, which cannot be done by the method of images. We have described this approach and its use in SVE modeling elsewhere (*11*) in some detail. In this approach the needed soil gas velocities are calculated separately and written to a file, from which they are then read by the program which models the SVE operation.

Gas Flow Field in the Vicinity of a Single Vertical Well Screened at the Bottom

The geometry of the system is defined in Fig. 2. Let

h = thickness of the vadose zone, m
$h - a$ = depth of well, m
r_w = effective radius of gravel packing around the screened portion of the well, m

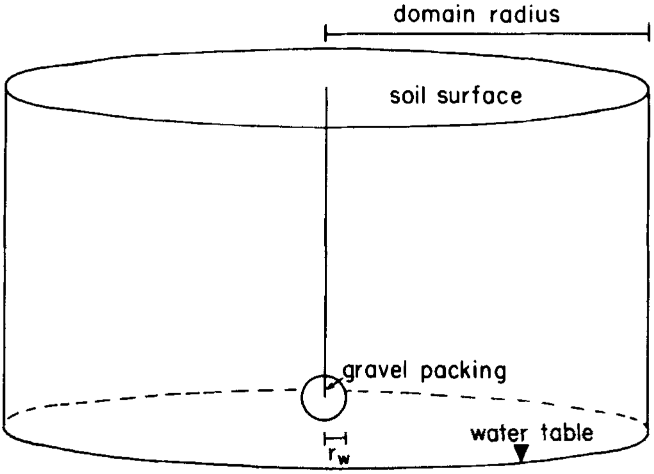

FIG. 2. Configuration for SVE by means of a single vertical well screened at the bottom.

We assume an isotropic, spatially constant permeability, so the system is axially symmetrical. Then Eq. (2) can be taken as

$$\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial(rP^2)}{\partial r}\right] + \frac{\partial^2 P^2}{\partial z^2} = 0 \tag{30}$$

which, together with the boundary conditions given by Eqs. (3) and (4) and the requirement that there be a sink of appropriate strength at $(0,a)$, determines P^2. We define

$$1 - P^2(r,z) = W(r,z) \tag{31}$$

and boundary conditions

$$W(r,h) = 0 \tag{32}$$

$$\partial W(r,0)/\partial z = 0 \tag{33}$$

From the symmetry of the problem it is readily seen that

$$\begin{aligned} W = A \sum_{n=-\infty}^{\infty} \Bigg[& \frac{1}{\{r^2 + [z - 4nh - a]^2]\}^{1/2}} \\ & + \frac{1}{\{r^2 + [z - 4nh - a]^2]\}^{1/2}} \\ & - \frac{1}{\{r^2 + [z - (4n - 2)h - a]^2]\}^{1/2}} \\ & - \frac{1}{\{r^2 + [z - (4n - 2)h + a]^2]\}^{1/2}} \Bigg] \end{aligned} \tag{34}$$

We evaluate the constant A as follows. Let P_w be the pressure in the well itself. Then

$$\begin{aligned} 1 - P_w^2 = W(r_w,a) = A \sum_{n=-\infty}^{\infty} \Bigg[& \frac{1}{\{r_w^2 + [-4nh]^2\}^{1/2}} \\ & + \frac{1}{\{r_w^2 + [2a - 4nh]^2\}^{1/2}} \\ & - \frac{1}{\{r_w^2 + [-(4n - 2)h]^2\}^{1/2}} \\ & + \frac{1}{\{r_w^2 + [2a - (4n - 2)h]^2\}^{1/2}} \Bigg] \end{aligned} \tag{35}$$

Let us define the sum on the right-hand side of Eq. (35) as $S'(r_w,a,h)$. Then

$$A = \frac{1 - P_w^2}{S'(r_w,a,h)} \tag{36}$$

The velocity of the soil gas at the point (r,z) is given by Darcy's law, as before; see Eq. (12). From Eq. (31) we have

$$P^2(r,z) = 1 - W(r,z) \tag{37}$$

So, as before,

$$v = k\nabla W/2P \tag{15}$$

with

$$P(r,z) = [1 - W(r,z)]^{1/2} \tag{38}$$

The flow rate of the well is calculated as follows. If we let Q be the molar gas flow rate to the well (mol/s), then

$$Q = \int_0^{2\pi} \int_0^{\pi} c(\rho)\nu v_\rho \rho^2 \sin\theta d\theta d\phi \tag{39}$$

where $\rho^2 = r^2 + (z - a)^2$ is held constant and we integrate over the surface of a sphere enclosing the sink. Here

$c(\rho)$ = molar concentration of gas a distance ρ from the sink, mol/m^3
ν = soil porosity

As before, we have

$$c(\rho) = P(\rho)/RT \tag{40}$$

So

$$Q = \frac{\nu}{RT} \int_0^{2\pi} \int_0^{\pi} P(\rho)v_\rho(\rho)\rho^2 \sin\theta d\theta d\phi \tag{41}$$

From Eq. (15) we see that

$$P(\rho)v_\rho(\rho) = \frac{k}{2}\frac{\partial W}{\partial \rho} \tag{42}$$

Then examination of Eq. (34) shows that

$$W = A\left[\frac{1}{\rho} + \text{terms which are regular as } \rho \rightarrow 0\right] \tag{43}$$

So

$$\lim_{\rho \rightarrow 0} \frac{\partial w}{\partial \rho}\rho^2 = -\frac{A}{\rho^2}\rho^2 = -A \tag{44}$$

Substitution of Eq. (44) into Eq. (42) and then of Eq. (42) into Eq. (41), followed by integration, yields

$$Q = -\frac{2\pi\nu kA}{RT} = -\frac{2\pi\nu k(1 - P_w^2)}{RTS'(r_w,a,h)} \tag{45}$$

where S' is defined in Eq. (35). As before, the negative sign indicates a sink at $(0,a)$.

Equation (15) gives the soil velocity components:

$$v_r = \frac{k\partial W/\partial r}{2P} \tag{46}$$

$$v_z = \frac{k\partial W/\partial z}{2P} \tag{47}$$

The derivatives are given by

$$\begin{aligned}\frac{\partial W}{\partial r} = -Ar \sum_{n=-\infty}^{\infty} \Bigg[& \frac{1}{\{r^2 + [z - 4nh - a]^2\}^{3/2}} \\ & + \frac{1}{\{r^2 + [z - 4nh + a]^2\}^{3/2}} \\ & - \frac{1}{\{r^2 + [z - (4n - 2)h - a]^2\}^{3/2}} \\ & - \frac{1}{\{r^2 + [z - (4n - 2)h + a]^2\}^{3/2}}\Bigg]\end{aligned} \tag{48}$$

and

$$
\begin{aligned}
\frac{\partial W}{\partial z} = -A \sum_{n=-\infty}^{\infty} \Bigg[& \frac{z - 4nh - a}{\{r^2 + [z - 4nh - a]^2\}^{3/2}} \\
& + \frac{z - 4nh + a}{\{r^2 + [z - 4nh + a]^2\}^{3/2}} \\
& - \frac{z - (4n - 2)h - a}{\{r^2 + [z - (4n - 2)h - a]^2\}^{3/2}} \\
& - \frac{z - (4n - 2)h + a}{\{r^2 + [z - (4n - 2)h + a]^2\}^{3/2}} \Bigg]
\end{aligned}
\tag{49}
$$

which completes the calculation of the soil gas velocities around a point sink in the vadose zone.

Distribution of VOCs between the Liquid and Vapor Phases

The next task we address is the calculation of the mole numbers of the component VOCs in the gas phase and in the liquid phase. We carry out the calculation for a single volume element. Notation is as follows.

ΔV = volume of the volume element, m^3
P_i^0 = vapor pressure of Component i in the pure state at the ambient soil temperature
ν = porosity of medium
n_i^g = number of moles of Component i in the vapor phase
n_i^l = number of moles of Component i in the liquid phase
n_i = total number of moles of Component i in the volume element
X_i = mole fraction of Component i in the liquid phase
P_i = vapor pressure of Component i in the volume element, atm
J = number of components in the mixture

Raoult's law gives

$$P_i = P_i^0 X_i \tag{50}$$

Also,

$$X_i = \frac{n_i^l}{\sum_{j=1}^{J} n_j^l} \tag{51}$$

Then the concentration of Component i in the vapor phase (mol/m^3) is given by

$$c_i^g = \frac{P_i^0}{RT} \frac{n_i^l}{\sum_j n_j^l} = \frac{n_i^g}{\nu \Delta V} \tag{52}$$

By definition

$$n_i = n_i^g + n_i^l \tag{53}$$

From Eq. (52) we have

$$n_i^g = \frac{VP_i^0}{RT} \frac{n_i^l}{\sum_j n_j^l} \tag{54}$$

Substitution of Eq. (54) into Eq. (53) yields

$$n_i = n_i^l \left[1 + \frac{\nu \Delta V P_i^0}{RT} \frac{1}{\sum_j n_j^l} \right] \tag{55}$$

Define

$$a_i = \frac{\nu \Delta V P_i^0}{RT} \tag{56}$$

$$u = \sum_j n_j^l \tag{57}$$

and rearrange Eq. (55) to obtain

$$n_i^l = \frac{n_i u}{a_i + u} \tag{58}$$

Sum Eq. (58) over i and use Eq. (57) to get

$$u = u \sum_i \frac{n_i u}{a_i + u}$$

or

$$1 = \sum \frac{n_i}{a_i + u} \tag{59}$$

Equation (59) is then solved numerically for u. Our programs use a simple binary search procedure, starting with $u_{\min} = 0$, $u_{\max} = \Sigma_i n_i$, $u = u_{\max}/2$. If no solution exists in this range, no liquid phase is present. Then $n_i^l = 0$ and $n_i^g = n_i$ for all i. If $0 < u < u_{\max}$, then Eq. (58) is used to obtain the n_i^l, after which the n_i^g are obtained from the equation

$$n_i^g = \frac{a_i n_i^l}{u} \tag{60}$$

The molar concentration of Component i in the vapor phase in this volume element is given by

$$c_i^g = n_i^g / v \Delta V \tag{61}$$

These vapor phase molar concentrations will be needed in modeling the advective transport of the VOCs in the next section.

Development of Soil Vapor Extraction Models

In this section we use the previously calculated soil gas velocities and vapor phase VOC concentrations to model the advective transport of VOCs to a vacuum well.

Model for Raoult's Law SVE with a Buried Horizontal Slotted Pipe

The domain to be stripped is diagrammed in Fig. 3. Its thickness is h, its breadth (parallel to the pipe) is l, and its width is $2b$ (all in m). We

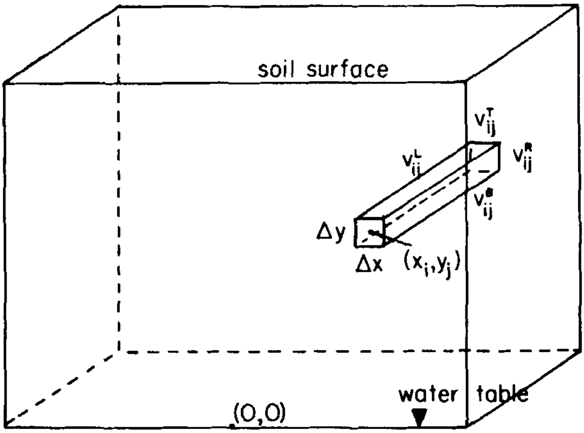

FIG. 3. Volume element and coordinates for SVE with a buried horizontal slotted pipe.

model only the right half of the domain, since the results for the left half are the mirror image of those for the right. The domain of interest is partitioned into volume elements ΔV such that

$$\Delta V = \Delta x \cdot \Delta y \cdot l \tag{62}$$

A mass balance is then carried out on Component α in the ijth volume element. Note that the coordinates of the center of the ijth volume element are

$$x_i = (i - \tfrac{1}{2})\Delta x \tag{63}$$

$$y_j = (j - \tfrac{1}{2})\Delta y \tag{64}$$

The mass balance gives

$$\begin{aligned}\frac{dn(\alpha,i,j)}{dt} = {} & \nu l \Delta y v_{ij}^{\mathrm{L}}[S(v^{\mathrm{L}})c^{g}(\alpha,i-1,j) + S(-v^{\mathrm{L}})c^{g}(\alpha,i,j)] \\ & - \nu l \Delta y v_{ij}^{\mathrm{R}}[S(-v^{\mathrm{R}})c^{g}(\alpha,i+1,j) + S(v^{\mathrm{R}})c^{g}(\alpha,i,j)] \\ & + \nu l \Delta x v_{ij}^{\mathrm{B}}[S(v^{\mathrm{B}})c^{g}(\alpha,i,j-1) + S(-v^{\mathrm{B}})c^{g}(\alpha,i,j)] \\ & - \nu l \Delta x v_{ij}^{\mathrm{T}}[S(-v^{\mathrm{T}})c^{g}(\alpha,i,j+1) + S(v^{\mathrm{T}})c^{g}(\alpha,i,j)], \\ & i = 1, 2, \ldots, n_x; \qquad j = 1, 2, \ldots, n_y\end{aligned} \tag{65}$$

Here

$$v_{ij}^{\mathrm{L}} = v_x[(i-1)\Delta x,(j - \tfrac{1}{2})\Delta y] \tag{66}$$

$$v_{ij}^{\mathrm{R}} = v_x[i\Delta x,(j - \tfrac{1}{2})\Delta y] \tag{67}$$

$$v_{ij}^{\mathrm{B}} = v_y[(i - \tfrac{1}{2})\Delta x,(j-1)\Delta y] \tag{68}$$

$$v_{ij}^{\mathrm{T}} = v_y[(i - \tfrac{1}{2})\Delta x,j\Delta y] \tag{69}$$

where v_x and v_y are given by Eqs. (26) and (27). Also,

$$\begin{aligned} S(u) &= 0 \quad \text{if} \quad u \leqslant 0 \\ &= 1 \quad \text{if} \quad u > 0 \end{aligned} \tag{70}$$

Some terms are omitted from Eq. (65) when one is dealing with border volume elements. These are just those terms for which the indices on $c^g(\alpha,p,q)$ lie out of range. Also, the mole numbers for the volume element containing the well are always set equal to zero.

The calculations are carried out as follows. After the model parameters are input, the coefficients in Eqs. (65) are calculated using Eqs. (66)–(69) and subroutines for v_x and v_y. The initial mole numbers in the volume elements, $n(\alpha,i,j)$, are assigned. The mole numbers for the liquid and gaseous phases are calculated from Eqs. (58) and (60) for each volume element, which requires many numerical solutions of Eq. (59). The $c^g(\alpha,i,j)$ are then calculated from the appropriate form for Eq. (61),

$$c^g(\alpha,i,j) = \frac{n^g(\alpha,i,j)}{v\Delta V} \tag{71}$$

These are then used to calculate the derivatives $dn(\alpha,i,j)/dt$ from Eq. (65), which permits one to step the system ahead in time by one time increment Δt. The new mole numbers are given by

$$n(\alpha,i,j,t + t) = n(\alpha,i,j,t) + \Delta t\frac{dn(\alpha,i,j)}{dt} \tag{72}$$

Computer memory limitations prevented the use of a more sophisticated integration formula such as a predictor-corrector.

The progress of the vapor stripping operation is readily followed by calculating the total residual component masses remaining in the domain as functions of the time. These are given (in kg) by

$$M(\alpha,t) = \sum_{i=1}^{n_x} \sum_{j=1}^{n_y} (\mathrm{MW})_\alpha n(\alpha,i,j) \tag{73}$$

where $(\mathrm{MW})_\alpha$ is the molecular weight of Component α in kg/mol.

Model for Raoult's Law SVE with a Single Vertical Well Screened at the Bottom

Figure 4 shows the domain to be stripped. Its thickness is h and its radius is b (m). The volume elements are ring-shaped, with volumes given by

$$V_{ij} = (2i - 1)\pi(\Delta r)^2\Delta z \tag{74}$$

The areas of the upper and lower surfaces of this volume element are $(2i - 1)\pi(\Delta r)^2$. The area of the inner surface is $2(i - 1)\pi\Delta r\Delta z$, and the

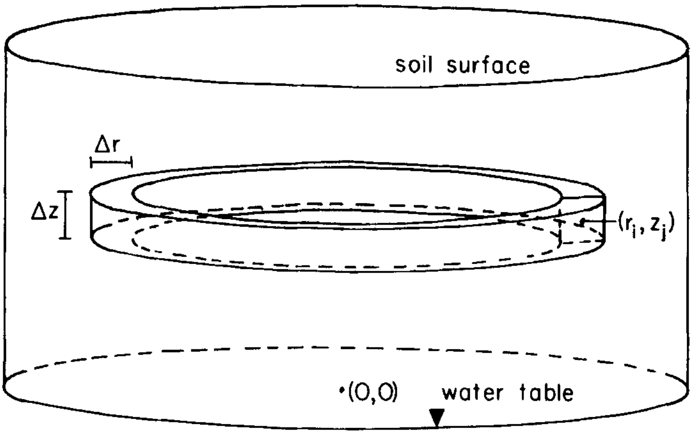

FIG. 4. Volume element and coordinates for SVE with a single vertical well screened at the bottom.

area of the outer surface is $2i\pi\Delta r\Delta z$. The coordinates of the middle of the *ij*th volume element (see Fig. 4) are

$$r_i = (i - \tfrac{1}{2})\Delta r \tag{75}$$

$$z_j = (j - \tfrac{1}{2})\Delta z \tag{76}$$

As before, a mass balance for Component α is carried out on the *ij*th volume element; the result is

$$\begin{aligned}\frac{dn(\alpha,i,j)}{dt} &= \nu 2(i - 1)\pi\Delta r\Delta z v_{ij}^{\mathrm{I}}[S(v^{\mathrm{I}})c^{g}(\alpha,i - 1,j) + S(-v^{\mathrm{I}})c^{g}(\alpha,i,j)] \\ &\quad - \nu 2i\pi\Delta r\Delta z v_{ij}^{\mathrm{B}}[S(-v^{\mathrm{B}})c^{g}(\alpha,i + 1,j) + S(v^{\mathrm{B}})c^{g}(\alpha,i,j)] \\ &\quad + \nu(2i - 1)\pi(\Delta r)^2 v_{ij}^{\mathrm{B}}[S(v^{\mathrm{B}})c^{g}(\alpha,i,j - 1) + S(-v^{\mathrm{B}})c^{g}(\alpha,i,j)] \\ &\quad - \nu(2i - 1)\pi(\Delta r)^2 v_{ij}^{\mathrm{T}}[S(-v^{\mathrm{T}})c^{g}(\alpha,i,j + 1) + S(v^{\mathrm{T}})c^{g}(\alpha,i,j)], \\ &\qquad i = 1, 2, \ldots, n_r; \quad j = 1, 2, \ldots, n_z\end{aligned} \tag{77}$$

Here, as before, the four pairs of terms in square brackets correspond to mass transport by advection through the four surfaces (inner, outer, bottom, top) of the *ij*th volume element.

The initial mole numbers in the contaminated volume elements are given by

$$n(\alpha,i,j) = c_\alpha \cdot \rho_{\text{soil}} \cdot \Delta V_{ij} \cdot 10^{-6} \qquad (78)$$

where c_α is the initial concentration of Contaminant α in the soil (mg/kg), and ρ_{soil} is the density of the soil (kg/m^3).

The differential equations, Eqs. (77), are then integrated forward in time by a scheme which is virtually identical to that described for the integration of Eqs. (65) for the buried horizontal pipe. The gaseous and liquid phase mole numbers are calculated from Eqs. (58) and (60) for each volume element ΔV_{ij}, after which the $c^g(\alpha,i,j)$ are calculated from

$$c^g(\alpha,i,j) = \frac{n^g(\alpha,i,j)}{v\Delta V_{ij}} \qquad (79)$$

These are then input to the formulas for the derivatives, Eqs. (77).

As before, boundary terms requiring $c^g(\alpha,p,q)$, where p and/or q are outside the acceptable ranges, are dropped, and the mole numbers of the on-axis volume element containing the well sink are always set equal to zero.

The progress of the clean up can be followed, as before, by calculating the total residual masses of the contaminants remaining in the domain of interest as a function of time. This is done by means of Eq. (73).

Preliminary Estimation of Gas Flow in Buried Horizontal Slotted Pipes and in Vertical Wells Screened at the Bottom

In the assignment of parameters for use in these models it is often convenient to have an easy means of estimating for a soil of known permeability the air flow of a well having a given packed radius and a given wellhead pressure (<1 atm). Such a formula would also provide a useful check on the coding of mathematical models. In this section we develop formulas for estimating the gas flow in SVE wells which are horizontal slotted pipes and which are vertical, with screening only along a short section at the bottom of the well.

We first consider the horizontal slotted pipe. For a single line sink of length l and running along the axis of a cylinder of porous medium of radius r_{max}, we can write

$$W = A \log_e (r/r_{\text{max}}) = 1 - P^2(r) \qquad (80)$$

as a solution to the two-dimensional Laplace equation having cylindrical symmetry and satisfying the boundary condition that $P = 1$ atm at the periphery of the cylinder. If the radius of the gravel packing of the well is r_w and the wellhead pressure is P_w, we can calculate A from the fact that

$$A \log_e (r_w/r_{\max}) = 1 - P_w^2 \tag{81}$$

so that

$$A = \frac{1 - P_w^2}{\log_e (r_w/r_{\max})} \tag{82}$$

and

$$W = \frac{1 - P_w^2}{\log_e (r_w/r_{\max})}(\log_e r - \log_e r_{\max}) \tag{83}$$

$$\frac{W}{r} = \frac{1 - P_w^2}{\log_e (r_w/r_{\max})} \frac{1}{r} \tag{84}$$

Now

$$\frac{\partial W}{\partial r} = -2P\frac{\partial P}{\partial r} \tag{85}$$

and

$$v_r = -k\frac{\partial P}{\partial r} \tag{86}$$

The gas flow rate to the well is given by

$$Q = \int_0^l \int_0^{2\pi} \nu c(r) v_r r d\theta dz = 2\pi \nu l c(r) v_r r \tag{87}$$

Since $c(r) = P(r)/RT$ and v_r is given by Eq. (86), this yields

$$Q = -\frac{2\pi l \nu k}{RT} P\frac{\partial P}{\partial r} r$$

Use of Eq. (85) then gives

$$Q = \frac{1 - P_w^2}{\log_e (r_w/r_{\max})} \frac{\pi l v k}{RT} \tag{88}$$

Note that Q is negative because the well is a sink. A rough lower bound for $r_{\max}$ is the depth of the well. For the well parameters used in the modeling discussed here (see Table 1), this yields a molar gas flow rate of 1.66 mol/s. The value calculated using the more elaborate calculation employing the method of images is 1.04 mol/s, about 63% of the value obtained by this rough approximation.

We next turn to the estimation of the flow rate to a single vertical well screened at the bottom. We consider a spherical domain of porous medium

TABLE 1
Parameters, Model for a Buried Horizontal Slotted Pipe

Depth to water table	6 m
Depth of well	5.5 m
Soil pneumatic permeability	0.1 m^2/atm·s
Soil porosity	0.3
Soil density	1.7 g/cm^3
Domain width	12 m
Domain breadth	6 m
Δx	1 m
Δy	1 m
Effective radius of well gravel packing	0.1 m
Wellhead pressure	0.85 atm
Ambient temperature	15°C
Components:	
Benzene:	
Molecular weight	78 g/mol
Vapor pressure	58.14 torr
Initial concentration	1000 mg/kg of soil
Toluene:	
Molecular weight	92 g/mol
Vapor pressure	15.97 torr
Initial concentration	1000 mg/kg of soil
p-Xylene:	
Molecular weight	106 g/mol
Vapor pressure	4.715 torr
Initial concentration	1000 mg/kg of soil
Calculated gas flow rate	1.038 mol/s 0.02454 m^3/s

of radius $r_{\max}$ with the well located at the center and having a packed radius of r_w. The expression for W, the desired solution to Laplace's equation, is

$$W = 1 - P(r)^2 = (A/r) + B \tag{89}$$

The constants A and B are calculated from the requirements that

$$P(r_w) = P_w \tag{90}$$

and

$$P(r_{\max}) = 1 \text{ atm} \tag{91}$$

These yield

$$W = \frac{1 - P_w^2}{(1/r_w - 1/r_{\max})}(1/r - 1/r_{\max}) \tag{92}$$

Since

$$k\nabla W = 2Pv \tag{93}$$

we obtain

$$Pv_r = -\frac{(1 - P_w^2)k}{2(1/r_w - 1/r_{\max})}\frac{1}{r^2} \tag{94}$$

The molar gas flow rate is obtained by integrating the gas flux $\nu Pv_r/RT$ over the surface of a sphere centered about the well; the result is

$$Q = \frac{2\pi\nu k(1 - P_w^2)r_{\max}r_w}{RT(r_{\max} - r_w)} \tag{95}$$

The flow rate calculated by this formula for the parameters given in Table 2 is 0.702 mol/s; that obtained by means of the more elaborate calculation using the method of images is 0.692 mol/s.

RESULTS

The models described above and a one-dimensional model of SVE in a lab column (not described above) were implemented in TurboBASIC and run on 286 and 386SX microcomputers equipped with math coprocessors

TABLE 2
Parameters, Model for a Well Screened at the Bottom

Depth to water table	6 m
Depth of well	5.5 m
Soil pneumatic permeability	0.1 $m^2/atm \cdot s$
Soil porosity	0.3
Soil density	1.7 g/cm^3
Domain radius	6 m
Δr	1 m
Δz	1 m
Effective radius of well gravel packing	0.3 m
Wellhead pressure	0.85 atm
Ambient temperature	15°C
Components:	
Benzene:	
Molecular weight	78 g/mol
Vapor pressure	58.14 torr
Initial concentration	1000 mg/kg of soil
Toluene:	
Molecular weight	92 g/mol
Vapor pressure	15.97 torr
Initial concentration	1000 mg/kg of soil
p-Xylene:	
Molecular weight	106 g/mol
Vapor pressure	4.715 torr
Initial concentration	1000 mg/kg of soil
Calculated gas flow rate	0.692 mol/s 0.01635 m^3/s

and running at 12 to 20 MHz. The runs reported here typically required 1 to 2 hours of machine time. The default parameters for the runs simulating operation of a horizontal buried slotted pipe SVE configuration are given in Table 1; those for simulation of a single vertical well screened at the bottom are given in Table 2. The vapor pressures of the three VOCs used (benzene, toluene, and *p*-xylene) were calculated at 15°C by means of the equation

$$\log_{10} P(T) = A - B/T \tag{96}$$

where the constants A and B were obtained by a least-squares fit to vapor pressure data taken from Montgomery and Welkom (*12*).

Plots of the residual masses of the three VOCs are shown in Figs. 5 and 6 for the horizontal buried slotted pipe configuration. The contaminated zone in Fig. 5 is 8 m wide by 6 m broad by 3 m deep; it is 10 by 6 by 4 m

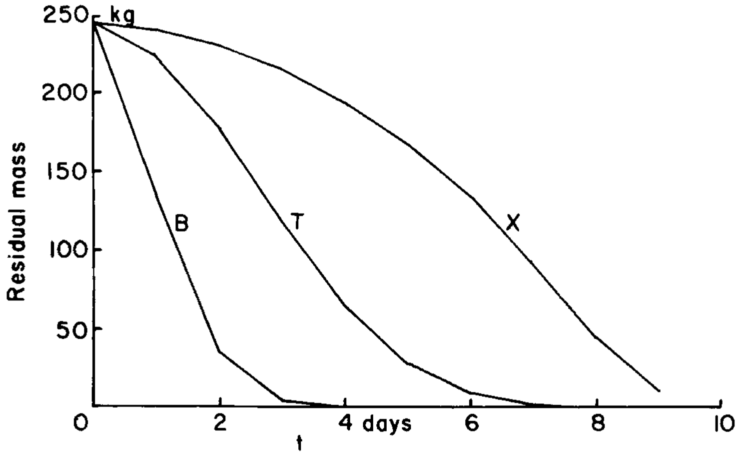

FIG. 5. Modeling SVE with a horizontal pipe. Plots of residual masses of benzene (B), toluene (T), and xylene (X) versus time. Model parameters are given in Table 1. The contaminated zone is of 8 m width, 6 m breadth, and extends to a depth of 3 m below the surface of the soil.

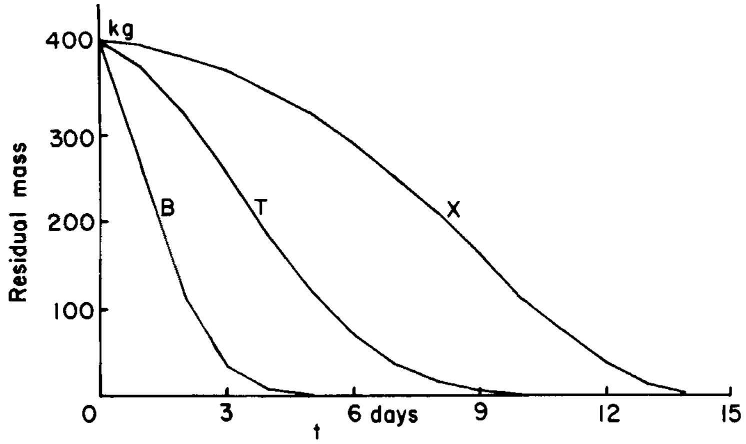

FIG. 6. Modeling SVE with a horizontal pipe. Plots of residual masses of benzene, toluene, and xylene versus time. Model parameters are given in Table 1. The contaminated zone is of 10 m width, 6 m breadth, and extends to a depth of 4 m below the surface of the soil.

in Fig. 6. As expected, we see most rapid removal of the most volatile component (benzene), followed by toluene, which is in turn followed by xylene. The rate of removal of xylene is seen to increase very markedly during the course of the run, since its mole fraction increases as the more volatile compounds are removed. This increases its vapor pressure quite substantially, resulting in its accelerated removal along toward the ends of the runs. The gas flow rate in these runs is 0.0245 m^3/s.

Figures 7 and 8 show runs modeling the removal of the same three VOCs, here by means of a single vertical well screened at the bottom. In Fig. 7 the contaminated zone is 4 m in radius by 3 m in depth; in Fig. 8, it is 6 by 4 m. The increased domain size requires roughly twice the time for clean up as the smaller one. The gas flow rate through these wells is 0.0164 m^3/s. If one normalizes the clean up times with respect to gas flow rate by taking the product of the clean up time for, say, benzene, times the gas flow rate, one concludes that the horizontal buried slotted pipe configuration is slightly over 50% more efficient in its use of gas than the single vertical well configuration. This is based on a comparison of Figs. 5 and 7, in which quite similar masses of VOCs are being removed. These results suggest a significant advantage to the use of horizontal buried slotted pipes in SVE, at least as long as the cost of putting these in is not excessive.

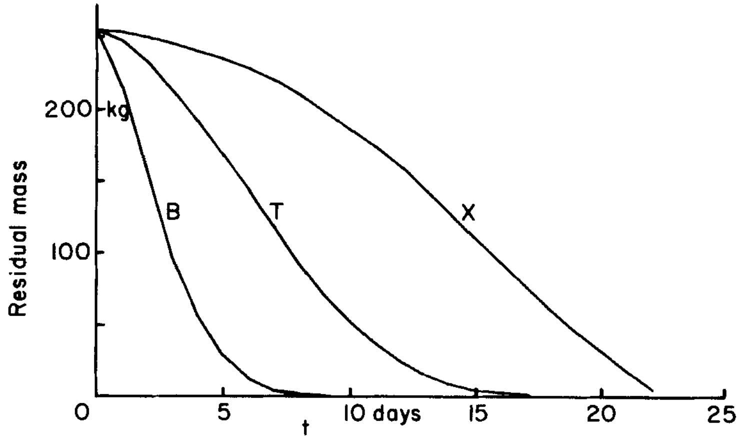

FIG. 7. Modeling SVE with a single vertical well screened at the bottom. Plots of residual masses of benzene, toluene, and xylene versus time. Model parameters are given in Table 2. The contaminated zone is of 4 m radius and extends to a depth of 3 m below the surface of the soil.

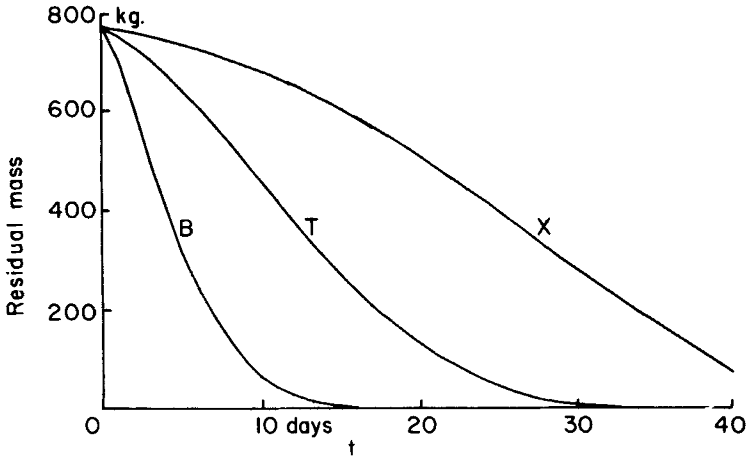

FIG. 8. Modeling SVE with a single vertical well screened at the bottom. Plots of residual masses of benzene, toluene, and xylene versus time. Model parameters are given in Table 2. The contaminated zone is of 6 m radius and extends to a depth of 4 m below the surface of the soil.

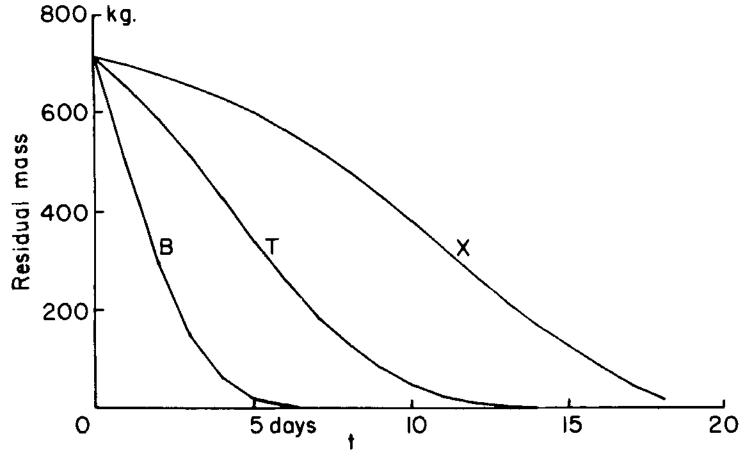

FIG. 9. Modeling SVE with a horizontal pipe. Plots of residual masses of benzene, toluene, and xylene versus time. Model parameters are given in Table 1. The contaminated zone is of 12 m width, 6 m breadth, and extends to a depth of 6 m below the surface of the soil, to the water table.

In Figs. 9 and 10 a horizontal pipe and a vertical well, respectively, are used to vapor strip a domain which is contaminated throughout. As one would expect, clean up times are somewhat longer than those found for the runs shown in Figs. 6 and 8, but the increases are not large and there is not a significant increase in tailing. This is presumably due to the use of a velocity field which does not have a no-flow condition at the outer boundaries of the domains, so that there are no volume elements in which the gas flow is essentially stagnant.

Figure 11 models a run with a horizontal pipe and a contaminated domain of the same size as that shown in Fig. 5; however, only xylene is present (at an initial concentration of 3000 mg/kg of soil) in the run shown in Fig. 11. Comparison of the results shown in Figs. 11 and 5 support the intuitively reasonable thesis that single component SVE models can be used to obtain upper bounds for the clean up times of mixtures if the component of lowest volatility is modeled.

The gas flow fields for the results reported above were calculated by the method of images. A second version of the model for horizontal buried pipes makes use of velocity fields calculated by a numerical solution of Laplace's equation by overrelaxation. The results are very similar to those reported above. This latter approach does permit one to include passive

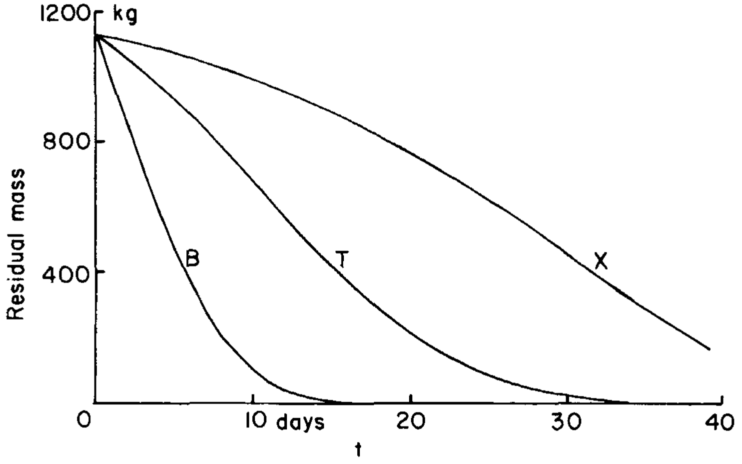

FIG. 10. Modeling SVE with a single vertical well screened at the bottom. Plots of residual masses of benzene, toluene, and xylene versus time. Model parameters are given in Table 2. The contaminated zone is of 6 m radius and extends to a depth of 6 m below the surface of the soil, to the water table.

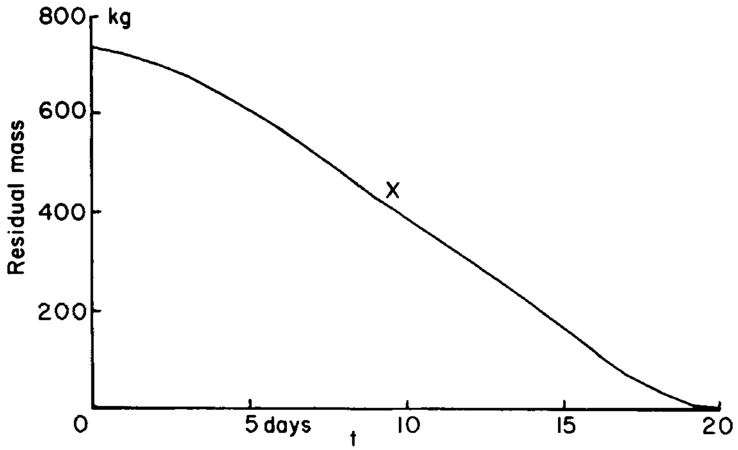

FIG. 11. Modeling SVE with a horizontal pipe, one VOC. Plot of residual mass of xylene versus time. Model parameters are given in Table 1. The contaminated zone is of 8 m width, 6 m breadth, and extends to a depth of 3 m below the surface of the soil, to the water table. The initial xylene concentration is 3000 mg/kg of soil.

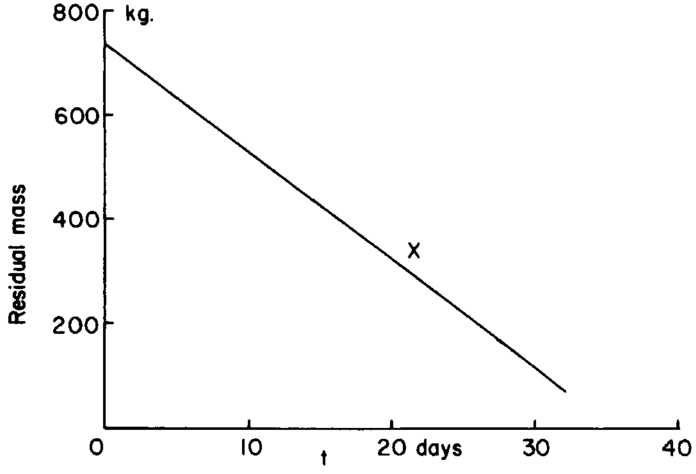

FIG. 12. Modeling SVE with a horizontal pipe, one VOC. The relaxation method is used to calculate the velocity field here. Model parameters are given in Table 3. The contaminant (xylene) is initially distributed uniformly throughout the entire domain.

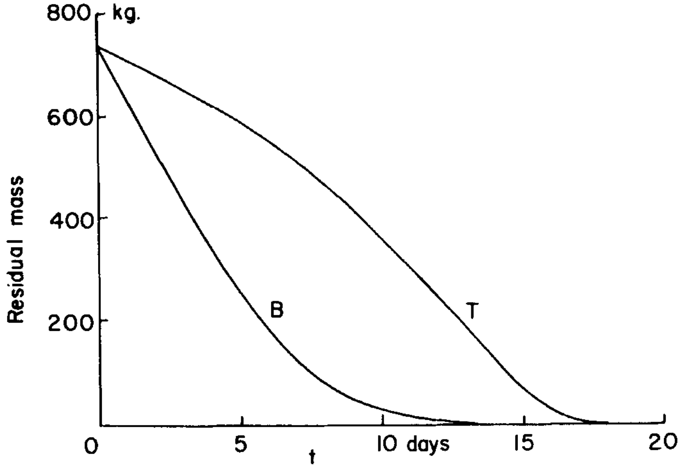

FIG. 13. Modeling SVE with a horizontal pipe. The relaxation method is used to calculate the velocity field here. Model parameters are given in Table 3. The contaminants (benzene and toluene) are initially distributed uniformly throughout the entire domain.

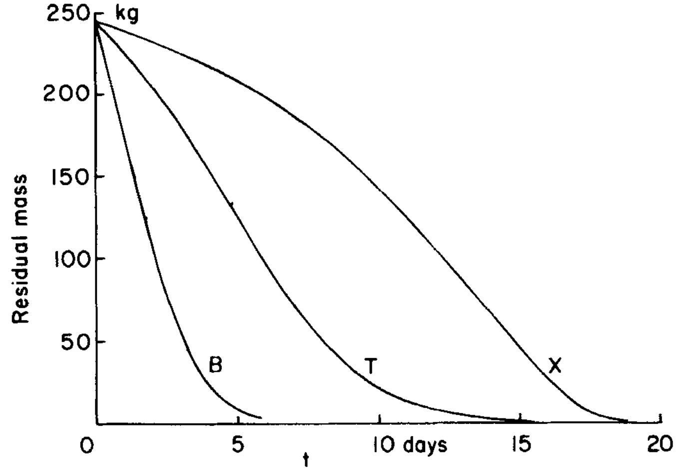

FIG. 14. Modeling SVE with a horizontal pipe. The relaxation method is used to calculate the velocity field here. Model parameters are given in Table 3. The contaminants (benzene, toluene, and xylene) are initially distributed uniformly throughout the entire domain.

TABLE 3
Parameters Used for Figures 12–14 (buried horizontal slotted pipe configuration)

Depth to water table	6 m
Depth of well	6 m
Soil pneumatic permeability	0.1 m^2/atm·s
Soil porosity	0.3
Soil density	1.7 g/cm^3
Domain width	11 m
Domain breadth	6 m
Δx	1 m
Δy	1 m
Wellhead pressure	0.85 atm
Gravel-packed radius of well	0.1 m
Ambient temperature	15°C
Molar gas flow rate (Note that the location of the pipe at the very bottom of the vadose zone cuts off about half of its flow as compared to the earlier runs)	0.463 mol/s
Properties of VOCs	See Table 1

TABLE 4
Vapor Pressure Parameters for Some Common Volatile Organics:[a]
$\log_{10} P(T) = A - B/T$, P in torr, T kelvins

Compound	Molecular weight	A	B
CCl_2F_2	120.9	7.5356	1131.8
CCl_4	153.8	7.8584	1737.1
$CHCl_3$	119.4	7.9412	1685.6
CH_2Cl_2	84.9	7.9629	1593.6
C_2Cl_4 (PCE)	165.8	8.2769	2089.5
C_2HCl_3 (TCE)	131.4	7.9635	1814.8
1,1,1-Trichloroethane	133.4	7.8744	1724.9
n-Pentane	72.1	7.6621	1476.8
n-Hexane	86.2	7.9399	1719.2
n-Heptane	100.2	8.1853	1946.6
n-Octane	114.2	8.6481	2239.5
n-Nonane	128.2	8.4220	2311.2
n-Decane	142.3	8.3351	2413.4
Chlorobenzene	112.5	8.2666	2149.2
Benzene	78.1	7.8948	1765.5
Toluene	92.1	8.2910	2041.3
p-Xylene	106.2	8.4075	2227.4

[a] Calculated from data taken from Ref. *13*.

vent wells, impermeable caps, and variable permeabilities, but requires the separate calculation of the velocity field. Plots of some representative runs are shown in Figs. 12–14. Run parameters are given in Table 3. For the run in Fig. 12 only xylene NAPL is present, and we see the expected linear rate of removal of the xylene down to nearly the end of the run. In Fig. 13 we start with equal masses of benzene and toluene, and see the expected inhibition of toluene removal by virtue of its dilution with benzene during the first 25 days or so of the run. The last run shows the removal of benzene, toluene, and xylene. Again the inhibition of toluene removal during the early stages of the run is quite clear. Comparison of Fig. 12 with Fig. 14 shows, as we saw before, that one can obtain an upper bound for the removal of mixtures simply by assuming that the mixture consists only of the compound having the lowest vapor pressure.

In order to use these models it is necessary to have the vapor pressures of the pure components of the mixture at ambient temperature. These are readily calculated by means of Eq. (96), together with the values of the constants A and B in this formula which are given in Table 4 for a number of common organic solvents. These constants were obtained by least-squares fits of Eq. (96) to data reported in Montgomery and Welcom (*12*) and Weast (*13*).

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