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David J. Wilson[a]; Ann N. Clarke[b]; James H. Clarke[b]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE [b] AWARE, INCORPORATED, NASHVILLE, TENNESSEE

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Soil Clean Up by *in-situ* Aeration. I. Mathematical Modeling

DAVID J. WILSON

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

ANN N. CLARKE and JAMES H. CLARKE

AWARE, INCORPORATED
NASHVILLE, TENNESSEE 37228

Abstract

Mathematical models are developed suitable for use in evaluating the feasibility of *in-situ* vapor stripping approaches for selected chemicals and site-specific environments. These models simulate the operation of both laboratory soil stripping columns and field-scale vacuum extraction wells (vent pipes). The effect of an anisotropic Darcy's constant is examined and the compressibility of the extracting gas is taken into account. The models incorporate the assumption of local equilibrium for the volatile compounds between the condensed and vapor phases. These models may use Henry's law or more complex isotherms for this equilibrium. A method is developed for calculating Henry's constant from field analytical data, and it is noted that use of Henry's constants calculated from laboratory data on solutions of volatile solutes in pure water can lead to very serious errors. It is shown that evacuation wells should be screened only down near the impermeable layer beneath the zone of stripping (unsaturated zone) for most efficient functioning.

I. INTRODUCTION

The remediation of environmental contamination caused by chemical releases from spills or so-called uncontrolled waste disposal sites is a national priority. The National Priority List developed by the USEPA currently contains over 800 sites, and current estimates for cleanup costs average in excess of $10 million per site. Literally thousands of other sites, not on the NPL list, will require remediation or correction actions as well. Remedial technologies which are both environmentally sound and cost effective are needed.

In the past, remedial efforts have focused largely on containment of contaminated materials and/or removal and off-site disposal in approved hazardous waste facilities. Thus, in either case, containment has typically been the solution, and the only reduction in toxic properties of these materials occurs through natural "degradation" processes. The recent Superfund amendments mandate that, where possible, remedial technologies be employed which detoxify the contaminated material or reduce the potential loading to the environment should a release occur. *In-situ* approaches which manage the contaminated material are attractive for several reasons, not the least of which is the much lower costs which are typically associated with *in-situ* approaches should they prove effective and appropriate. Two *in-situ* approaches which have been shown to be effective in certain site specific applications are *in-situ* biodegradation of hydrocarbons (*1*) and *in-situ* flushing with surfactant solutions (*2*); Clarke and Mutch have reviewed *in-situ* remediation techniques (*3*). Another *in-situ* approach currently being actively explored is *in-situ* vapor stripping. This approach has been used for the removal of volatile compounds from unsaturated soils at a number of sites, and indications are that it is effective (*4–7*).

This paper is organized as follows: The equations governing the flow of a compressible gas through a porous medium are presented and solved to obtain the gas flow fields in a laboratory soil stripping column and in the vicinity of a vent pipe with an impermeable boundary beneath it. The effects of anisotropic soil permeabilities are then examined. This is followed by the development of a model of soil vapor stripping in a laboratory column. The model incorporates the local equilibrium assumption and also the assumption that the partitioning of the volatile solute between the vapor and the condensed stationary phase is governed by Henry's law. We then turn to the modeling of vapor stripping in the field by evacuation through a vent terminating above a horizontal gas impervious layer (such as a water table). This model includes the same assumptions as the laboratory vapor stripping column model.

The adsorption isotherm is then considered in more detail. Generalizations of Henry's law are presented which should permit the description of soil containing very high concentrations of volatile solvents. Also, the effect of the curvature of the vapor–liquid interface on the Henry's constant is examined. The calculation of the effective Henry's constant from laboratory-scale experimental data on contaminated soil to be stripped is then discussed, and the resulting values are used in the field model to estimate the time required for remediation. Application to an actual site is made.

The gas velocity field in the vicinity of the evacuating vent pipe depends quite markedly on the position of the end of the pipe relative to the location of the impermeable boundary underlying the contaminated soil. The implications of this for optimal well design are presented.

We close with a number of cautions and caveats about the use of the models, the uncertainties in the parameters required by the models, and the fluctuations in the environment of a soil vapor stripping operation which make precise prediction of its behavior virtually impossible. Even so, it is expected that the models will be helpful in gaining insight into the process of *in-situ* soil vapor stripping and in making decisions concerning its use and applicability in remediating unsaturated soils contaminated with volatile organics.

II. GAS FLOWS IN POROUS MEDIA

A. Equations Governing the Flow of a Compressible Gas in an Isotropic Porous Medium

The continuity equation for a gas may be taken as

$$\partial c/\partial t = -\nabla \cdot (\bar{v}c) \tag{1}$$

where c = concentration of the gas, mol/cm^3
$\bar{v}$ = linear velocity of gas, cm/s

From the ideal gas law,

$$P = cRT \tag{2}$$

where P = pressure, atm
R = 82.06 cm$^3 \cdot$ atm/mol $\cdot$ deg
T = temperature, °K

From Darcy's law (*8*),

$$\bar{v} = -K_{\mathrm{D}}\nabla P \tag{3}$$

where K_D = Darcy's constant, $\text{cm}^2/\text{atm}\cdot\text{s}$.

For steady flow,

$$\partial c/\partial t = 0 \tag{4}$$

from which, on using Eqs. (1), (2), and (3), we obtain

$$0 = K_D \nabla \cdot \left(\frac{P}{RT} \nabla P\right) \tag{5}$$

Canceling out K_D/RT yields

$$\nabla \cdot (P \nabla P) = 0 \tag{6}$$

or

$$\nabla^2(P^2) = 0 \tag{7}$$

It is thus apparent that suitably chosen solutions to Laplace's equation, $\nabla^2 u = 0$, may be used, together with Eq. (3), to construct velocity fields for compressible gases in porous media. We employ this technique in the next section.

B. Determination of Gas Velocity Fields in a Laboratory Soil Column and in the Vicinity of a Vent Pipe in Field Aeration

In order to analyze the movement of a volatile and adsorbable compound through the soil, it is necessary to know the velocity field of the moving gas which is transporting the compound. The velocity fields for a laboratory column and a vent pipe are calculated in this section.

1. Laboratory Column

In the one-dimensional geometry appropriate to gas flow through a laboratory soil aeration column, Eq. (7) becomes

$$\frac{d^2(P^2)}{dx^2} = 0 \tag{8}$$

where x = distance measured from the inlet end of the column.

Integration of Eq. (8) yields

$$P^2(x) = a_1 x + a_2 \tag{9}$$

At the inlet end of the column $x = 0$, and

$$P_i^2 = a_2 \tag{10}$$

where P_i = column inlet pressure, atm. At the outlet end of the column $x = L$ (cm), the outlet pressure is P_f, and

$$P_f^2 = a_1 L + a_2 \tag{11}$$

from which, on use of Eq. (10), we get

$$a_1 = -\left(\frac{P_i^2 - P_f^2}{L}\right) \tag{12}$$

Substitution of Eqs. (12) and (10) in Eq. (9) then yields

$$P = \left[P_i^2 - \frac{P_i^2 - P_f^2}{L} x\right]^{1/2} \tag{13}$$

From Eq. (3),

$$v_x = -K_D \frac{dP}{dx} \tag{14}$$

which yields

$$v_x = \frac{K_D(P_i^2 - P_f^2)}{2L}\left[P_i^2 - \frac{(P_i^2 - P_f^2)}{L} x\right]^{-1/2} \tag{15}$$

as the linear velocity of the gas at point x in the column.

The pressure $P(x)$ and the gas linear velocity $v_x(x)$ are plotted in Figs. 1 and 2. Note that if $(P_i - P_f)/P_i$ is much larger than 0, the pressure drop in the column is not linear and the gas velocity increases significantly as one goes along the column, in contrast to the behavior of incompressible fluids.

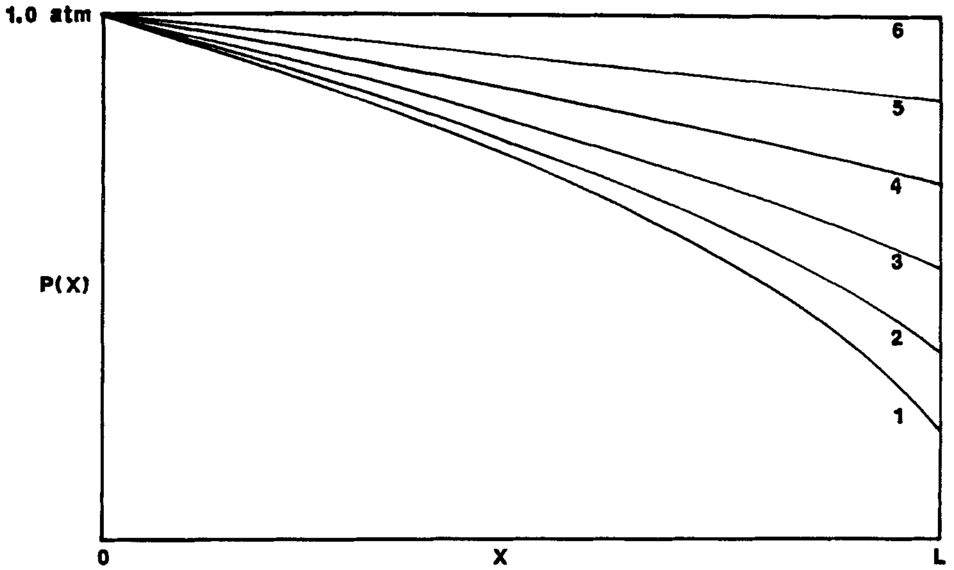


FIG. 1. Pressure gradients in aerated soil columns. Column length = 100 cm; column inlet pressure = 1.00 atm; column outlet pressure = 0.10, 0.36, 0.52, 0.68, 0.84, 1.00 atm (1 to 6).

2. Vent Pipe

The velocity field of an ideal gas in the vicinity of a sink (the vent pipe) at a depth a below the (horizontal) soil surface and having an impenetrable horizontal layer (the water table, perhaps) below the vent pipe is determined as follows. We use cylindrical corodinates (r,θ,z). The soil permeability is assumed to be constant throughout the region, and isotropic.

The sink is at $(0,0,-a)$, and the impermeable lower boundary is at $(r,\theta,-b)$, $b > a$. Since the gas may be assumed ideal, we have

$$\nabla^2(P^2) = 0 \qquad (7)$$

We use the method of images (*9*) to construct a solution to Eq. (7) satisfying the followings conditions:

(1) There must be a sink at $(0,0,-a)$.
(2) $P^2(r,\theta,0) = P_a^2, \qquad P_a = 1$ atm

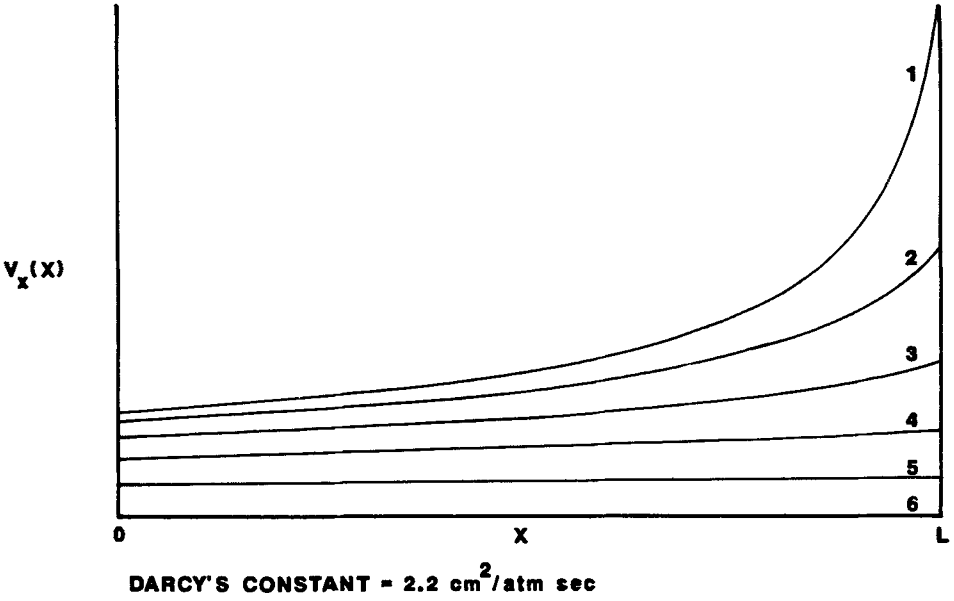


FIG. 2. Velocity profiles in aerated soil columns. Darcy's constant = 2.2 $cm^2/atm \cdot s$. Other data as in Fig. 1.

$$(3)\ \frac{\partial P}{\partial z}(r,\theta,-b) = 0 \tag{17}$$

(to allow for the impermeable lower boundary). An excellent approximation to the desired solution is obtained by regarding P^2 as an electrostatic potential, and constructing this potential by distributing point charges along the z-axis as indicated in Table 1. The charge actually generating the sink is q_7. The other charges are placed sequentially to satisfy Eqs. (16) and (17).

This distribution of charges gives an excellent approximation to the desired potential. We take

$$u = c\left[\sum_{i=1}^{13} \frac{q_i}{[r^2 + (z - z_i)^2]^{1/2}} - \frac{q_{13}}{|z_{13}|}\right] + P_2^a \tag{18}$$

$$u = P^2$$

TABLE 1
Charges and z-Coordinates for Generating an Image Potential Satisfying Conditions (1), (2), and (3)

i	q_i	z_i
1	+1	$6b - a$
2	+1	$4b + a$
3	−1	$4b - a$
4	−1	$2b + a$
5	+1	$2b - a$
6	+1	a
7	−1	$-a$
8	−1	$-2b + a$
9	+1	$-2b - a$
10	+1	$-4b + a$
11	−1	$-4b - a$
12	−1	$-6b + a$
13	+1	$-6b - a$

The constant term $-q_{13}/|z_{13}|$ is included to correct for the slight imbalance in terms above and below the plane $z = 0$, which causes a slight slowly varying violation of the boundary condition $u(z = 0) = P_a^2$. Then

$$2P \frac{\partial P}{\partial r} = -c \sum_{i=1}^{13} \frac{q_i r}{[r^2 + (z - z_i)^2]^{3/2}} \tag{19}$$

which gives

$$v_r = + \frac{K_{\mathrm{D}} c}{2P} \sum_{i=1}^{13} \frac{q_i r}{[r^2 + (z - z_i)^2]^{3/2}} \tag{20}$$

similarly

$$v_z = + \frac{K_{\mathrm{D}} c}{2P} \sum_{i=1}^{13} \frac{q_i (z - z_i)}{[r^2 + (z - z_i)^2]^{3/2}} \tag{21}$$

$$P = +c \sum_{i=1}^{13} \left[\frac{q_i}{[r^2 + (z - z_i)^2]^{1/2}} + P_a^2 - \frac{c q_{13}}{|z_{13}|} \right]^{1/2} \tag{22}$$

These equations then give the velocity field for a compressible gas in a porous (isotropic) medium having the geometry shown in Fig. 3.

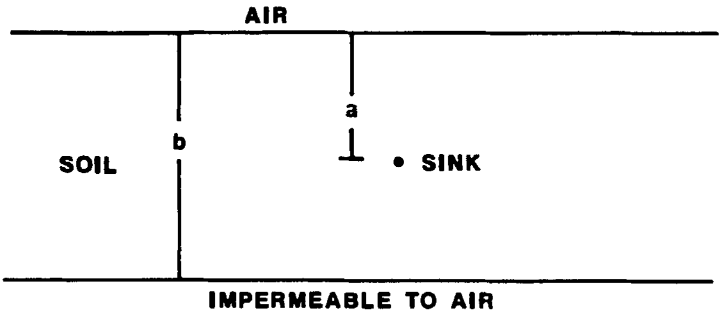


FIG. 3. Geometry for vent pipe velocity field calculation.

In Fig. 4 we see a diagram of the velocity field in the vicinity of a vent pipe which has been generated by this method. Figure 5 plots the streamlines of the gas flow for this model.

We still must determine the magnitude of the scale factor c in Eqs. (18) through (22). This is done as follows. We consider the immediate vicinity of the sink at $(0,0,-a)$, and use spherical coordinates (ρ,θ,ϕ) centered at this point. The net flux of gas to the sink is given by

$$Q = -\nu \int_0^{2\pi} \int_0^{\pi} v_\rho \frac{P}{RT} \cdot \rho^2 \sin\theta d\theta d\phi \tag{23}$$

where ν = voids fraction.

$$v_\rho = -[v_r^2 + v_z^2]^{1/2} \tag{24}$$

and

$$\rho = [r^2 + (z - z_7)^2]^{1/2} \tag{25}$$

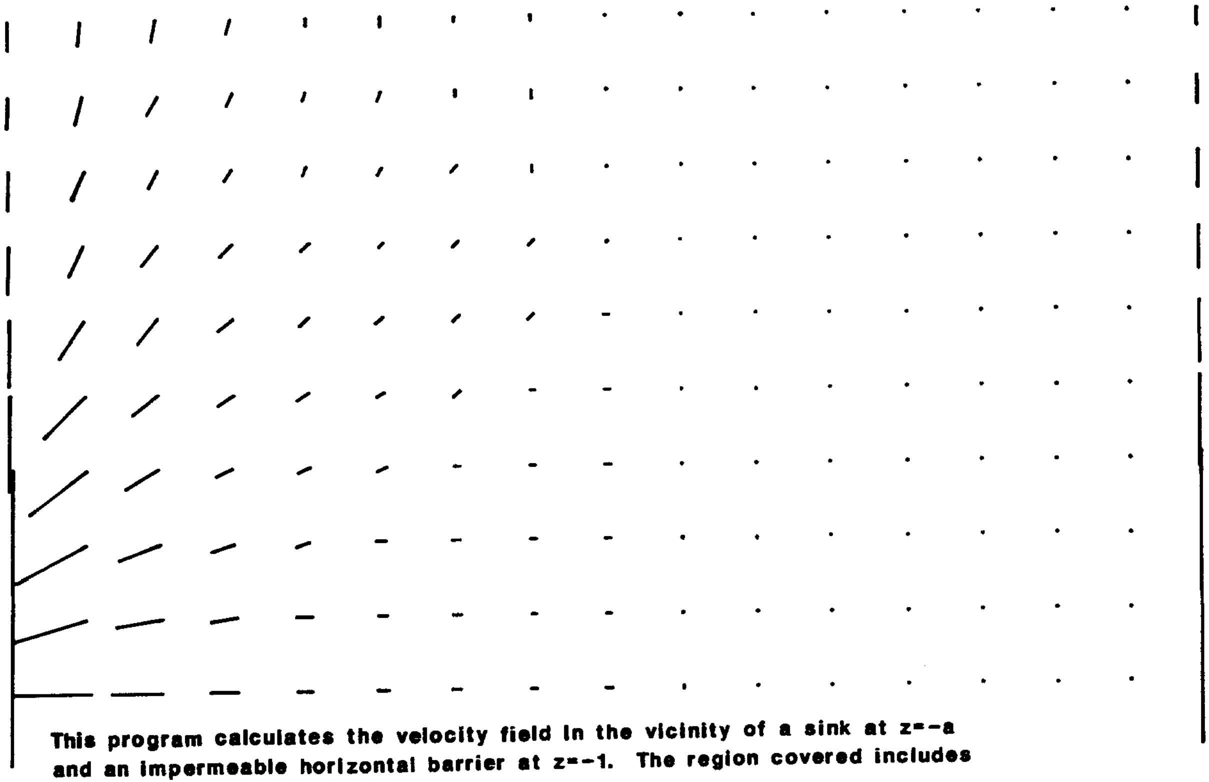
Then

$$Q = 4\pi\rho^2 \frac{\nu K_D c|q_7|[r^2 + (z - z_7)^2]^{1/2}}{2[r^2 + (z - z_7)^2]^{3/2}} \tag{26}$$

On using Eq. (25), this yields

$$Q = 2\pi\nu K_D q_7 c \tag{27}$$

so that



```
This program calculates the velocity field in the vicinity of a sink at z=-a
and an impermeable horizontal barrier at z=-1.  The region covered includes
[0 > z > -1] * [0 < x < 3].

   -a=-.9
   Velocity magnification factor= .1
   Step size= 20
```

FIG. 4. Gas flow velocity vectors in the vicinity of a vent pipe. The water table is at a depth of 10 m, and the vent pipe extends to a depth of 9 m. The distance from left to right is 30 m.

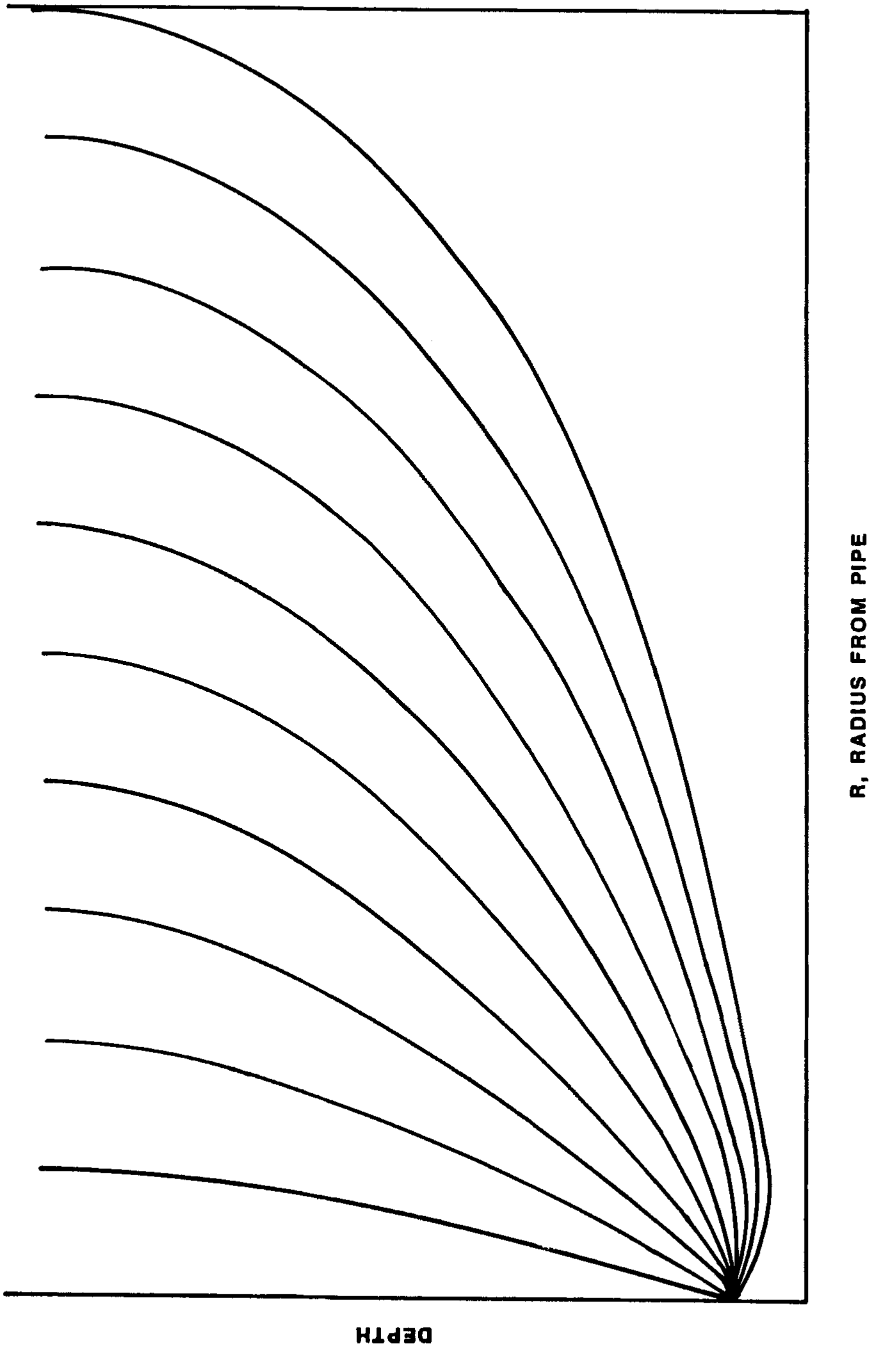


FIG. 5. Streamlines for compressible gas flow in the vicinity of a vent pipe. Parameters as in Fig. 4.

$$c = \frac{Q}{2\pi K_D |q_7| \nu} = \frac{Q}{2\pi K_D \nu} \tag{28}$$

It is still necessary to determine the permeability K_D in terms of easily observable quantities. We do so as follows. Assume that the sink is screened at a radius r_s. Then

$$P_f = \left[\frac{Q}{2\pi\nu K_D} \left(\sum_{i=1}^{13} \frac{q_i}{[r^2 + (z - z_i)^2]^{1/2}} - \frac{q_{13}}{|z_{13}|} \right) + P_a^2 \right]^{1/2} \tag{29}$$

where P_f = air pressure in the well
P_a = ambient pressure (1 atm)
$r^2 + (z - z_7)^2 = r_s^2$

An excellent approximation to this is

$$P_f = \left[\frac{Qq_7}{2\pi\nu K_D r_s} + P_a^2 \right]^{1/2} \tag{30}$$

Solving this for K_D and noting that $q_7 = -1$ then yields

$$K_D = \frac{Q}{2\pi\nu r_s(P_a^2 - P_f^2)} \tag{31}$$

Substituting this result into Eq. (28) for c gives

$$c = r_s(P_a^2 - P_f^2) \tag{32}$$

Thus it is possible to calculate both c and K_D in terms of flow rate, well radius r_s, and the air pressure (<1 atm) in the well, all readily accessible quantities.

C. Effect of Anisotropic Permeability on Gas Velocity Fields in Porous Media

Soil permeabilities are often anisotropic (*10*). A common pattern is that the permeability in the vertical direction is markedly less than that in a horizontal direction. Here we show how the effect of an anisotropic permeability can be taken into account in the calculation of the velocity field.

The continuity equation is

$$\partial c/\partial t = -\nabla \cdot (\bar{v}c) \tag{1}$$

and Darcy's law gives

$$\bar{v} = -\mathbf{K}_{\mathrm{D}}\nabla P$$

where $\mathbf{K}_{\mathrm{D}}$ is now to be regarded as a tensor. For steady flow we have

$$0 = \nabla \cdot (\mathbf{K}_{\mathrm{D}}\nabla P) \tag{33}$$

If we assume that the gas is ideal, use of Eq. (2) then gives

$$0 = \nabla \cdot (P\mathbf{K}_{\mathrm{D}}\nabla P) \tag{34}$$

Let us next perform a principal axis transformation, so that $\mathbf{K}_{\mathrm{D}}$ has nonzero elements only on its diagonal. In this coordinate system, Eq. (34) becomes

$$0 = \frac{\partial}{\partial x}\left(K_x \frac{P\partial P}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y P\frac{\partial P}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z P\frac{\partial P}{\partial z}\right) \tag{35}$$

We assume that K_x, K_y, and K_z are independent of position, which yields

$$0 = K_x\frac{\partial^2(P^2)}{\partial x^2} + K_y\frac{\partial^2(P^2)}{\partial y^2} + K_z\frac{\partial^2(P^2)}{\partial z^2} \tag{36}$$

Now transform to new coordinates X, Y, Z, given by

$$x = (K_x)^{1/2}X \tag{37}$$

$$y = (K_y)^{1/2}Y \tag{38}$$

$$z = (K_z)^{1/2}Z \tag{39}$$

In this coordinate system Eq. (36) becomes

$$0 = \frac{\partial^2(P^2)}{\partial X^2} + \frac{\partial^2(P^2)}{\partial Y^2} + \frac{\partial^2(P^2)}{\partial Z^2} \tag{40}$$

so again P^2 is a solution to Laplace's equation, albeit in the transformed coordinate system.

III. MODELING OF SOIL AERATION IN A LABORATORY COLUMN, HENRY'S LAW MODEL

The geometry for this case is shown in Fig. 6. It was shown in Section II.B.1 that the pressure and linear velocity in the column are given by

$$P(x) = \left[P_i^2 - \frac{P_i^2 - P_f^2}{L}x\right]^{1/2} \tag{13}$$

and

$$v_x = \frac{K_D(P_i^2 - P_f^2)}{2L}\left[P_i^2 - \frac{P_i^2 - P_f^2}{L}x\right]^{-1/2} \tag{15}$$

The flux of gas through the column is given by

$$Q\,(\text{mol/s}) = \pi r_c^2 c v_x \nu \tag{41}$$

where r_c = column radius, cm
c = gas concentration, mol/cm^3

Since

$$c = P/RT \tag{2'}$$

we have

$$Q = \pi r_c^2 \frac{P\nu}{RT} v_x \tag{42}$$

$$Q = \frac{\pi r_c^2 \nu}{RT} \cdot \frac{K_D(P_i^2 - P_f^2)}{2L} \tag{43}$$

From Eq. (43) we can calculate K_D in terms of readily measurable quantities, as seen in

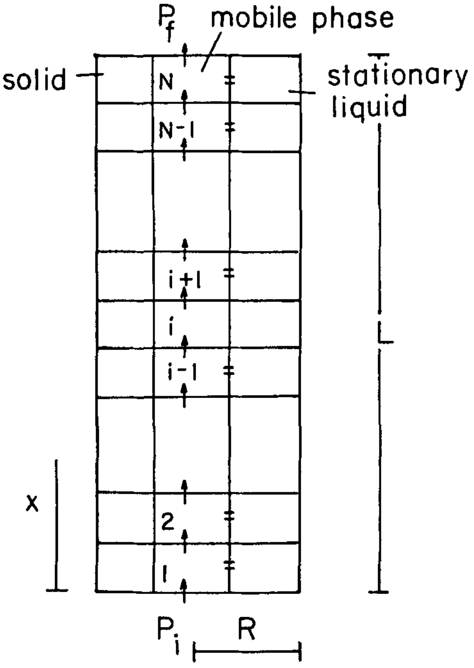


FIG. 6. Notation and column partitioning for laboratory aeration column model. P_i = inlet pressure, P_f = outlet pressure.

$$K_D = \frac{2QRTL}{\pi r_c^2(P_i^2 - P_f^2)} \tag{44}$$

The movement of a volatile compound in the soil column is determined as follows (we assume a Henry's law compound).

Let m_i = mass of compound in ith compartment, g

c_{vi} = vapor concentration of compound in ith compartment, g/cm^3

c_{li} = liquid concentration of compound in the stationary aqueous phase in ith compartment, g/cm^3

w = specific volume of water in the soil, dimensionless.

$K_H = c_v/c_l$, Henry's constant, dimensionless

A = cross-sectional area of column, πR^2

Then in the ith compartment we have

$$m_i = \Delta x A(wc_{li} + \nu c_{ci}) \tag{45}$$

$$= \frac{\Delta x \cdot A}{K_\mathrm{H}}(w + \nu K_\mathrm{H})c_{vi} \tag{46}$$

so

$$c_{vi} = \frac{K_\mathrm{H} m_i}{\Delta x A(w + \nu K_\mathrm{H})} \tag{47}$$

Now

$$dm_i/dt = (Q_\mathrm{air}c_v)_{i-1} - (Q_\mathrm{air}c_v)_i \tag{48}$$

and $Q_\mathrm{air}(x) = A\nu v(x)$ gives the local volumetric flow rate. Let

$$c_i = m_i/A\Delta x \tag{49}$$

be the total concentration of the compound per gram of soil. Use of Eqs. (47) and (49) in Eq. (48) then yields

$$\frac{dc_i}{dt} = \frac{\nu K_\mathrm{H}}{\Delta x(w + \nu K_\mathrm{H})}[(vc)_{i-1} - (vc)_i], \qquad i = 1, 2, \ldots, N \tag{50}$$

where we recall that

$$v_j \equiv v(x_j) = \frac{K_\mathrm{D}(P_i^2 - P_f^2)}{2L}\left[P_i^2 - \frac{P_i^2 - P_f^2}{L}x_j\right]^{-1/2} \tag{51}$$

Soil permeabilities (Darcy's constants) are generally drastically changed by the disturbances of sample collection, so that it is not realistic to use Darcy's constants obtained from measurements on essentially undisturbed samples in the modeling of lab column operation. We therefore present here a simple method by which this parameter can be computed from column parameters, the inlet and outlet pressures, and the volumetric flow rate of the gas.

The volumetric flow rate at the column outlet, Q_air, is related to the outlet linear gas velocity $v_x(L)$ by the equation

$$Q_\mathrm{air} = v_x(L) \cdot \nu \cdot \pi r^2$$

where r = column radius (cm)
ν = soil voids fraction

On setting $x = L$ in Eq. (15) and using the resulting expression for $v_x(L)$, we obtain

$$\frac{Q_{\text{air}}}{\pi r^2 \nu} = \frac{K_D(P_i^2 - P_f^2)}{2LP_f}$$

which yields the following equation for the permeability:

$$K_D = \frac{2Q_{\text{air}}LP_f}{\pi r^2 \nu (P_i^2 - P_f^2)}$$

One starts out initially with $c_j(t = 0) = c_0$, a constant, i.e., a uniformly contaminated column. The differential equations (Eq. 50) are then integrated forward in time to allow the elution of the column to develop. A standard predictor-corrector method is used for this; the algorithm is

Starter:

$$y^*(\Delta t) = y(0) + \frac{dy(0)}{dt}\,\Delta t \tag{52}$$

$$y(\Delta t) = y(0) + \left[\frac{dy(0)}{dt} + \frac{dy^*(\Delta t)}{dt}\right]\frac{\Delta t}{2} \tag{53}$$

Predictor:

$$y^*[(n+1)\Delta t] = y[(n-1)\Delta t] + \frac{dy}{dt}(n\Delta t)\cdot 2\Delta t \tag{54}$$

Corrector:

$$y[(n+1)\Delta t] = y(n\Delta t) + \left[\frac{dy}{dt}(n\Delta t) + \frac{dy^*}{dt}[(n = 1)\Delta t]\right]\frac{\Delta t}{2} \tag{55}$$

This algorithm is fast, readily programmed, stable, and quite accurate.

The total mass of compound remaining in the soil column at time t is given by

$$m_{\mathrm{total}}(t) = \sum_{i=1}^{N} A \cdot \Delta x \cdot c_i(t) \tag{56}$$

The model was programmed in BASICA to run on a Zenith 150 microcomputer; in compiled BASICA a typical run with 20 compartments required only a few minutes of machine time. The results of a run simulating a column containing soil from a site from which xylene is being removed by aeration are shown in Figs. 7 and 8. The xylene concentration profiles are shown in Fig. 7 at various times during the course of the aeration, and the total mass of xylene in the sample is plotted as a function of time in Fig. 8. The selection of the parameters used was based on data from an actual site; these will be discussed in more detail in Section V.C. Other parameters (column size, gas flow rate) were selected to correspond to values currently being used on lab column aerations of soil from this site.

IV. MODELING OF AERATION BY MEANS OF A VENT PIPE, HENRY'S LAW MODEL

We assume that our problem is axially symmetric, that the permeability is isotropic, that the vent pipe can be represented by a sink at $(0,0,-a)$, and that there is a horizontal, impervious boundary at $z = -b$.

Let $m(t,r,\theta,z)$ be the mass of volatile solute per unit per volume at the point (r,θ,z), and let $c^v(t,r,\theta,z)$ be the concentration of solute in the vapor phase at this point, both at time t. Then

$$\partial m/\partial t = -\nu\nabla \cdot (\bar{v}c^v) \tag{57}$$

if we neglect dispersion terms. c^v and m are related in the following way:

$$m = \nu c^v + wc^l \tag{58}$$

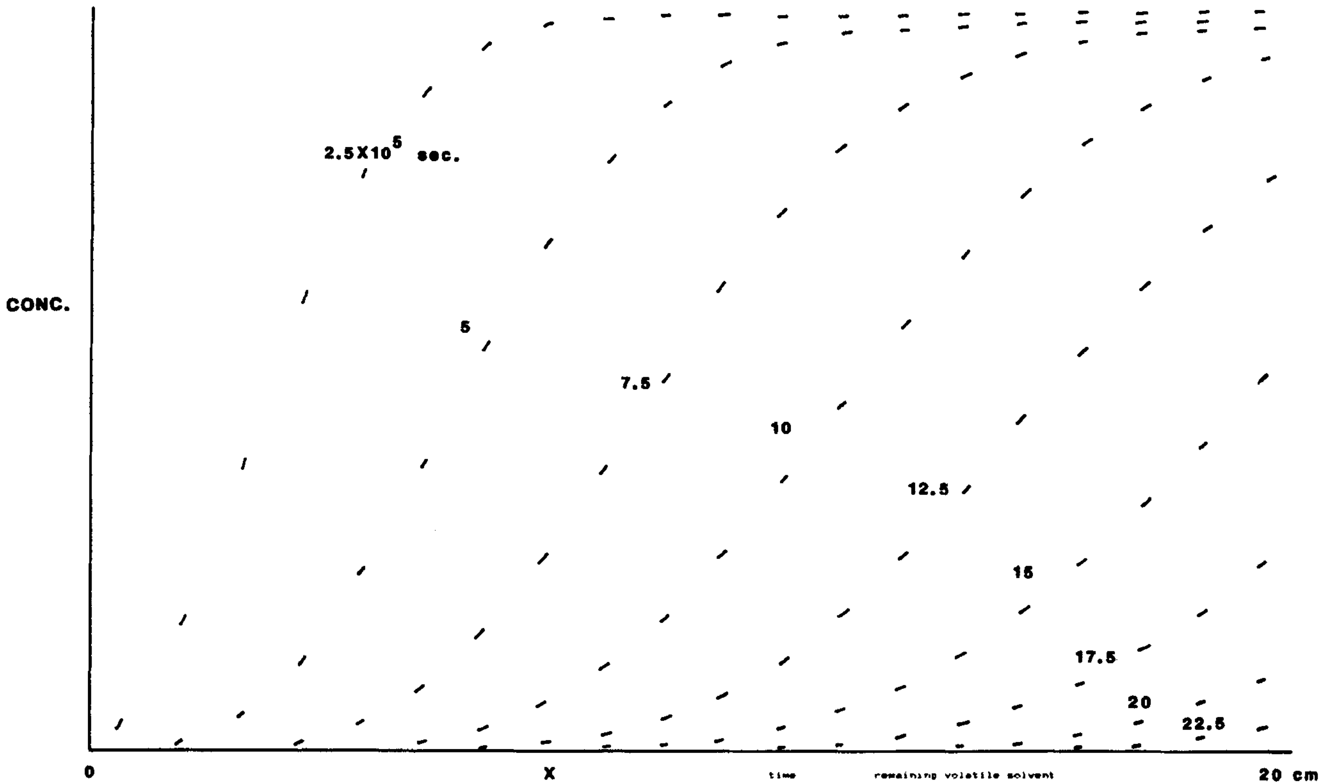
$$c^v = K_{\mathrm{H}}c^l \tag{59}$$

where c^l = volatile solute concentration in the soil condensed (liquid) phase

K_{H} = Henry's constant

w = specific volume of soil liquid phase

ν = specific volume of soil vapor phase (voids fraction)



```
time          remaining volatile solvent

50000         .964388
100000        .9313796
150000        .8984293
200000        .8655368
250000        .8327014
```

FIG. 7. Distribution of xylene in a simulated laboratory column aeration experiment at various times (0.25, 0.50, 0.75, . . . , 2.00, 2.25 × 10^5 s). Inlet pressure = 1.00 atm; outlet pressure = 0.95 atm; K_D = 2.2 cm^2/atm · s; specific volume of water in the soil = 0.2; voids fraction = 0.2; Henry's law constant = 0.00236; column length = 20 cm; column radius = 5 cm. The column is partitioned into 20 compartments. Initial volatile solute concentration = 0.635 mg/cm^3; airflow rate (1 atm) = 5.0 mL/min.

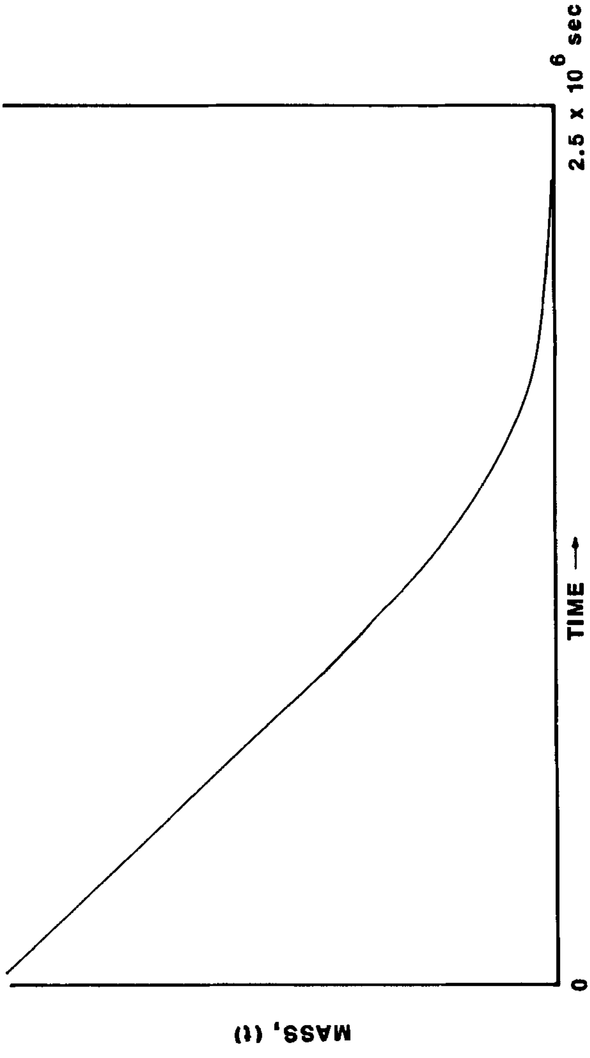


FIG. 8. Total mass of xylene remaining in the simulated column as a function of time. Parameters as in Fig. 7.

Then

$$m = [\nu + (w/K_{\mathrm{H}})]c^{v} \tag{60}$$

So Eq. (57) can be written as

$$\frac{\partial m}{\partial t} = -\frac{1}{[1 + w/\nu K_{\mathrm{H}}]}\nabla \cdot (\bar{v}m) \tag{61}$$

Because of the complicated nature of the velocity $\bar{v}$, it is necessary to numerically integrate Eq. (61). We consider a cylindrical volume of soil of radius r_v and extending from $z = 0$ to $z = -b$. The sink representing the vent pipe is located at $(0,0,-a)$. We set up a mesh of points as follows:

$$r_n = (n - \tfrac{1}{2})r, \qquad n = 1, 2, 3 \ldots, N \tag{62}$$

$$z_m = -(m - \tfrac{1}{2})\Delta z, \qquad m = 1, 2, 3, \ldots, N \tag{63}$$

Define V_{nm} = volume of an annular ring of inner radius $(n - 1)\Delta r$, outer radius $n\Delta r$, and thickness Δz. Then

$$V_{nm} = \pi(2n - 1)\Delta r^2 \Delta z \tag{64}$$

Since our system is axially symmetric, we can take the following equations as a discrete representation of Eq. (57):

$$\begin{aligned}
\frac{dM_{nm}}{dt} = {} & -v_r\left[n\Delta r, -\left(m - \frac{1}{2}\right)\Delta z\right] \cdot 2\pi n\Delta r\Delta z \cdot c_n^{v} + 1_{,m} \\
& + v_r\left[(n - 1)\Delta r, -\left(m - \frac{1}{2}\right)\Delta z\right] \cdot 2\pi(n - 1)\Delta r\Delta z \cdot c^{v}_{n+1,m} \\
& + \pi(2n - 1)\Delta r^2\left[-S\left[-v_z\left(\left(n - \frac{1}{2}\right)\Delta r, -(m - 1)\Delta z\right)\right]\right. \\
& \cdot v_z\left(\left(n - \frac{1}{2}\right)\Delta r, -(m - 1)\Delta z\right) \cdot c^{v}_{n,m-1} \\
& + S\left[v_z\left(\left(n - \frac{1}{2}\right)\Delta r, -mz\right)\right]v_z\left(\left(n - \frac{1}{2}\right)\Delta r, -m\Delta z\right) \cdot c^{v}_{n,m+1}
\end{aligned}$$

$$- S\left[-v_z\left(\left(n-\frac{1}{2}\right)\Delta r,-m\Delta z\right)\right]v_z\left(\left(n-\frac{1}{2}\right)\Delta r,-m\Delta z\right)$$

$$\cdot c^v_{n,m}\Bigg], \qquad n = 1, 2, 3, \dots, N;\ m = 1, 2, 3, \dots, N \tag{65}$$

Here

$$S(u) = 0, u \leqslant 0 \tag{66}$$

$$= 1, u \geqslant 0$$

The first two terms on the right-hand side of Eq. (65) describe the movement of volatile contaminant through the outer and inner cylindrical surfaces of the *nm* volume element. The last four terms describe the movement of volatile contaminant through the upper and lower faces of this volume element. In a Henry's law model

$$M_{nm} = V_{nm} \cdot [\nu + w/K_{\mathrm{H}}]c^v_{nm} \tag{67}$$

from Eq. (60).

The boundary conditions for the system are

$$c^v_{n,0} = 0 \text{ for all } n \tag{68}$$

This represents the requirement that uncontaminated air is being drawn down into the soil from the atmosphere.

$$c^v_{n+1,m} = 0 \tag{69}$$

or

$$c^v_{n+1,m} = c^v \text{ initial} \tag{70}$$

depending on whether the system is surrounded by clean soil (Eq. 69) or uniformly contaminated soil (Eq. 70). Since

$$v_z((n - \tfrac{1}{2})\Delta r, -N\Delta z) = 0 \tag{71}$$

no boundary condition is needed on the base of the cylinder. Since $n - 1 = 0$ when $n = 1$, no boundary condition is needed along the axis of the cylinder. These boundary conditions, the initial values $M_{nm}(0)$ of the masses of volatile solute in the volume elements V_{nm}, Eqs. (65), and Eqs. (67) completely specify the problem. In our work we assumed that the concentration of volatile solute in the cylinder was independent of position, so that

$$M_{nm}(0) = c_{\text{total}} V_{nm} \tag{72}$$

where c_{total} = initial solute concentration in the soil, g/cm^3.

Equations (65) were then integrated forward in time by the predictor-corrector method described earlier.

The displays shown later in this paper were constructed by printing the arrays $D(n,m)$ on the screen.

$$D(n,m) = \text{Int}\left(\frac{M_{nm}(t) \times 10}{M_{nm}(0)}\right) \tag{73}$$

Thus a value of 9 indicates between 0 and 10% removal, a value of 1 indicates between 80 and 90% removal, etc.

The total mass of solute remaining in the system at time t was calculated from

$$M_{\text{total}}(t) = \sum_{n}\sum_{m} M_{nm}(t) \tag{74}$$

Plots of $M_{\text{total}}(t)$ versus time are shown later in the paper.

The loss of material into the sink was handled by setting the solute concentrations of the compartment containing the sink and its five nearest neighbors equal to zero. Solute reaching these volume elements was assumed lost up the vent pipe.

A computer program implementing this model was written in BASICA and compiled. The results presented below were run on a Zenith 150 microcomputer. A typical run takes 90 min.

V. ADSORPTION ISOTHERMS

A. Generalizations of Henry's Law

Henry's law is the simplest isotherm which one could use in models such as those analyzed here. In this section we discuss two other isotherms which could be used without difficulty in these models if experimental results of sufficient accuracy were available to permit determination of the additional parameters. We note that Poe, Valsaraj, and Thibodeaux recently obtained data of sufficient accuracy to warrant the use of such more complex isotherms. They calculated adsorption isotherms of several volatile organics on a number of dry soils (*11*). These results should prove quite useful, and it is hoped that this work will be extended to include soils in equilibrium with atmospheres of various moisture content.

Henry's law is given by

$$c^v = K_H c^l \tag{59}$$

where c^v = vapor concentration of volatile solute, g/cm$_3$
c^l = concentration of volatile solute in the liquid phase
K_H = Henry's constant for the solute

If the liquid phase can be regarded as essentially water, then Henry's constant can be estimated from the vapor pressure and aqueous solubility of the volatile solvent, as shown in

$$K_H = 1.603 \times 10^{-3} \times \frac{(\mathrm{MW}) \times P_e}{TS} \tag{75}$$

where MW = solute molecular weight, g/mol
P_e = equilibrium vapor pressure of pure solute, torr
T = temperature, °K
S = solute aqueous solubility, g/100 mL

If the concentration of the volatile solute in the soil is sufficiently high, the aqueous phase may be saturated and there may be nonaqueous liquid phase present. Under these conditions the vapor phase concentration is simply that of the pure volatile solute,

$$c_e^v = \frac{1.603 \times 10^{-5}(\mathrm{MW}) \cdot P_e}{T} \tag{76}$$

where c_e^v is in g/cm^3. The isotherm is then given by

$$c^v = K_H c^l \tag{59}$$

if c^l is less than $S/100$, and

$$c^v = c_e^v$$

If c^l is greater than $S/100$, then c^l is given by

$$c^l = (c_{\text{total}} - \nu c^v)/w \tag{77}$$

where c_{total} = volatile solute concentration in the soil, g/cm^3
ν = voids fraction (specific volume of vapor phase)
w = liquid fraction (specific volume of liquid phase)

The isotherm is illustrated in Fig. 9.

The form of the second isotherm to be discussed is suggested by the shape of the plot in Fig. 9. We would like a function c^v which is linear in c^l at low concentrations and which approaches c_e^v asymptotically as c^l becomes large. Equation (78) satisfies these requirements.

$$c^v = \frac{K_{\text{H}} c^l}{1 + (K_{\text{H}}/c_e^v)c^l} \tag{78}$$

c^l is obtained from the soil concentration of volatile solute, c_{total} as follows:

$$c_{\text{total}} = wc^l + \nu c^l \tag{79}$$

$$= wc^l + \frac{\nu K_{\text{H}} c^l}{1 + bc^l} \tag{80}$$

where

$$b = K_{\text{H}}/c_e^v$$

This yields a quadratic in c^l, the desired solution to which is

$$c^l = \frac{B + \sqrt{B^2 - 4AC}}{2A} \tag{81}$$

where

$$A = wb \tag{82}$$

$$B = w + \nu K_{\text{H}} - bc_{\text{total}} \tag{83}$$

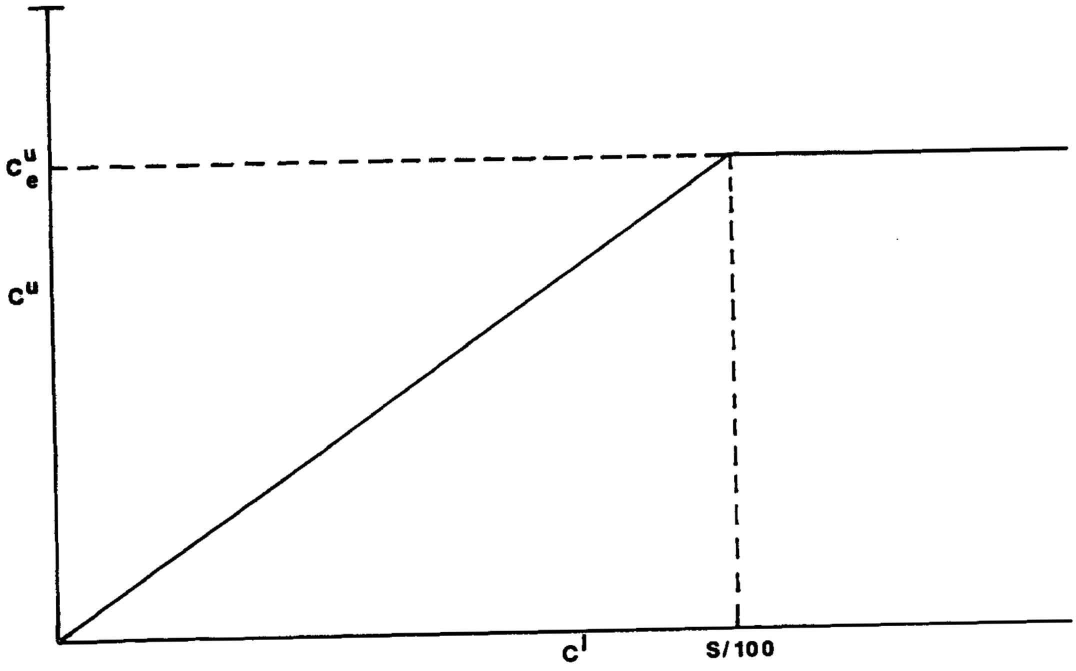


FIG. 9. Isotherm for Henry's law with saturation. S = solubility (g/100 mL of water).

$$C = -c_{\text{total}} \tag{84}$$

The use of either of these isotherms in the models discussed causes no computational difficulties. However, the uncertainties in the parameters (airflow rates, soil moisture, permeability, etc.) make the use of these refinements of questionable value at this time. The behavior of Eq. (78) is illustrated in Fig. 10.

B. Effect of Liquid-Vapor Surface Curvature on Henry's Constants

The vapor pressure of a pure liquid is affected by the signs and magnitudes of the radii of curvature of the liquid surface from which the compound is evaporating. The effect is described by the Kelvin equation,

$$\log_e \frac{P_l(R_1,R_2)}{P_l^\circ} = \frac{\gamma \bar{V}_l}{RT}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{85}$$

where γ = surface tension of liquid, dynes/cm
$\bar{V}_l$ = molar volume of liquid, cm^3
R_1, R_2 = principal radii of curvature of the liquid surface, cm
$P_l(R_1,R_2)$ = vapor pressure in equilibrium with the curved liquid surface
P_l° = vapor pressure in equilibrium with a plane liquid surface
R = gas constant, 8.314×10^7 erg/mol · deg
T = temperature, °K

For a derivation, see Adamson's text (*12*).

Here we wish to determine the extent of this effect in reducing the vapor pressure of a volatile solute in water which is in wetted capillary pores. Note that if the liquid surface is concave, as is the case here, the values of R_1 and R_2 are negative.

From the Young-Laplace equation, the pressure on the liquid in a wetted capillary (contact angle = 0) of radius r is given by

$$P(r) = P_{\text{ambient}} - \frac{2\gamma}{r} \tag{86}$$

We assume that the vapor phase may be treated as an ideal gas, so that the molar free energy of the volatile solute is given by

$$\bar{G}_2 = \bar{G}_2^\circ + RT \log_e P_2 \tag{87}$$

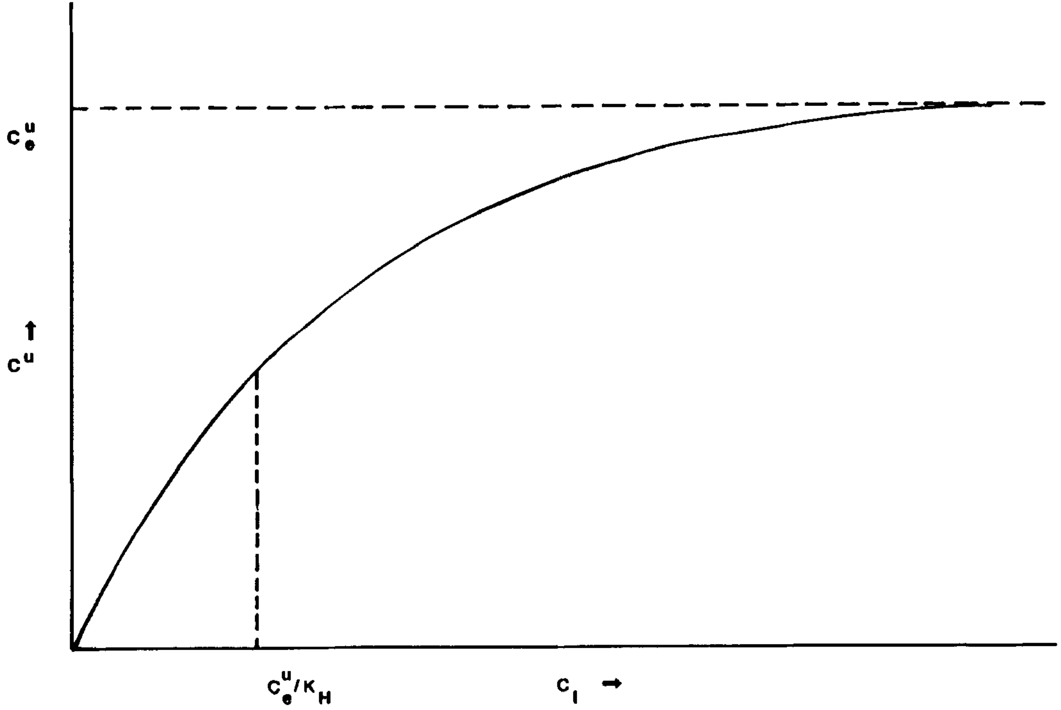


FIG. 10. A two-parameter isotherm. See text for parameter definitions.

where P_2 is the partial pressure of the solute vapor.

The change in molar free energy of the solute in the solution as the pressure is changed from P_{ambient} to $P' = P_{\text{ambient}} - 2\gamma/r$ is given by

$$\Delta\bar{G}_2 = \int_{P_{\text{ambient}}}^{P'} \bar{V}_2 dP = \frac{-2\bar{V}_2\gamma}{r} \tag{88}$$

The change in molar free energy of the solute in the vapor phase must be equal to the change in molar free energy of the solute in the liquid phase, since equilibrium between the liquid and the vapor phase requires that

$$\bar{G}_{2\ \text{vapor}} = \bar{G}_{2\ \text{liquid}} \tag{89}$$

This gives

$$\Delta\bar{G}_{2\ \text{vapor}} = RT \log_e P_2(r) - RT \log_e P_2^\circ \exp\left(-\frac{2\bar{V}_2\gamma}{rRT}\right) \tag{90}$$

from which we find

$$P_2(r) = P_2^\circ \exp\left(\frac{-2\bar{V}_2\gamma}{rRT}\right)$$

One may calculate P_2°, the vapor pressure of the volatile solute over the bulk solution, by Henry's law.

As an example, let us consider trichloroethylene, TCE: molecular weight = 131.40 g/mol, density = 1.4556 g/cm^3:

$$\bar{V}_2 = \frac{131.40}{1.4556} = 90.27 \text{ cm}^3/\text{mol}$$

The surface tension of water at room temperature is about 72 erg/cm^2. We assume that $T = 298$ °K. Then

$$\exp\left(-\frac{2\bar{V}_2\gamma}{rRT}\right) = \left(\frac{5247 \times 10^{-7}}{r}\right) \tag{91}$$

This yields the following values for $P_2(r)/P_2^\circ$:

r (cm)	$P_2(r)/P_2^\circ$
10^{-6}	.592
10^{-5}	.949
10^{-4}	.995
10^{-3}	.999

One should not extend this formula to values of r much less than 10^{-6} cm, since under these conditions the structure of liquid water is markedly changed by surface effects, as indicated by a substantial decrease in its surface tension.

C. Estimation of Henry's Constants from Data on Field Samples

We had initially assumed that Henry's constants could be readily estimated from vapor pressure data and the solubility of the volatile compound in water. The Henry's constant calculated in this way for *p*-xylene is 0.2 at 20°C, decreasing to about 0.14 at 12.8°C. However, when this Henry's constant was used to model removal of xylene from contaminated soil from the Tyson waste site (near Philadelphia), both the laboratory column model and the field vent pipe model predicted removal rates which were much too large. Furthermore, the soil moisture, soil concentration of xylenes, and initial soil gas xylene concentration were not consistent with the calculated value of K_H for xylenes; the initial soil gas xylenes concentration was far too low.

The soil samples from this site are quite black, and contain a good deal of sludgy humic material. (Septic tank waste was disposed of at the site, so this is not surprising.) In view of this, the assumption that the liquid phase in the soil can be regarded as water seems unrealistic, so that use of Henry's constants calculated for xylenes in water is not warranted.

The following approach was therefore used to estimate the Henry's constants for the volatile organics observed at this site. Laboratory vapor stripping data on soil samples from the site were obtained from ERM, Inc. (*13*). These data are given in Table 2. The parameters describing the vapor stripping column used are given in Table 3, and the parameters used in the mathematical simulations of the column operation are listed in Table 4.

Since the mathematical model is linear in concentration, the initial concentration of the volatile organic selected for percent removal calculations is arbitrary. A value of 0.001 g/mL was used in all but one of the runs made; one run was made with a value of 0.02 g/mL to verify that initial concentration has no effect on percent removal calculations.

TABLE 2
Average Percent Removal after 28 Days of Stripping, Lab Columns Aeration, Tyson Site[a]

Compound	Average initial concentration (μg/kg)	Average residual concentration (μg/kg)	Percent removal	Henry's constant × 10^3
Benzene	13,200	386	97	1.1
Bromoform	2,430	213	90	0.90
Chlorobenzene	484,000	42,400	91	0.92
Chloroform	376	ND	>87	>0.87
1,2-Dichlorobenzene	872,000	220	>99	>1.3
1,3-Dichlorobenzene	7,820	1,790	77	0.73
1,4-Dichlorobenzene	12,400	ND	>99	>1.3
1,1-Dichloroethane	460	365	21	0.19
1,2-Dichloroethane	541	ND	>99	>1.3
1,2-Dichloropropane	768	122	84	0.83
Ethyl benzene	611	506	17	0.16
Methylene chloride	2,120	155	93	0.97
Tetrachloroethene	324,000	106,000	67	0.63
Toluene	3,470,000	96,600	97	1.1
trans-1,2-Dichloroethene	714	277	61	0.57
Trichlorofluoromethane	78,000	187	>99	>1.3
Xylenes (total)	16,600,000	1,257,000	92	0.95
Average			>93	>0.97

[a] Data provided by ERM, Inc. (*13*).

Simulations were run for values of Henry's constant ranging from 0.0001 to 0.0013, and percent removals were calculated from the results; these are plotted in Fig. 11. Given a percent removal value from Table 2, one can then read off the value of Henry's constant for that compound from Fig. 11. Note that Fig. 11 pertains only to runs made using the parameters given in Table 4; if column dimensions or air flow rate are changed, it is necessary to run another set of simulations.

One expects Henry's constants for these soil samples which are quite different from those pertaining to the compounds of interest when the liquid phase is essentially pure water. Since septic tank waste has been disposed of at this site, these samples contained a good deal of humic material, and the liquid phase was very definitely not virtually pure water. [For benzene, toluene, ethylbenzene, and xylenes in water at room temperature, the Henry's constants are in the range of 0.1 to 0.2 (dimensionless).] The values of the Henry's constants calculated from Fig. 11 and the data in Table 2 are listed in the right-hand column in

TABLE 3
Lab Aeration Column Experimental Parameters, Tyson Site Runs[a]

Column inside diameter, 6.3 cm
Height of column of soil, 30 cm
Air flow rate (1 atm), 5 mL/min
Temperature, ~298 K
Duration of run, 28 d
Soil moisture, ~0.2 g/mL (the material was quite moist)
Soil voids fraction, ~0.2

---

[a]Data provided by AWARE, Inc. (*13*).

Table 2; they are about two orders of magnitude less than the constants calculated for these solutes in pure water.

Data were also taken from a report submitted to EPA by AWARE, Inc. (*7*). Henry's constants were calculated for several components in the samples from the Tyson site. The Henry's constants were calculated as described above, with the air flow rates and column dimensions that were used in this study. The values obtained are given in Table 5; these are seen to be comparable in magnitude to those calculated from the ERM data, where w = volume fraction liquid and v = voids fraction:

$$v = 0.40 - 0.20 = 0.20$$

Then

$$c_{\text{liquid}} = (c_{\text{total}} - vc_{\text{vapor}})/w \tag{92}$$

$$= .0085 \text{ g/cm}^3$$

TABLE 4
Parameters for Lab Column Simulation

Inlet pressure, 1 atm
Outlet pressure, 0.98 atm
Darcy's constant, 20.25 $\text{cm}^2/\text{atm} \cdot \text{s}$
Soil moisture, 0.2 g/mL
Voids fraction, ~0.2
Length of soil column, 30 cm
Column radius, 3,15 cm (column i.d., 6.3 cm)
Length of run, 2,420,000 s (28 d)
Air flow rate, 0.0833 mL/s (5.0 mL/min)
Time increment in numerical integration, 1000 s

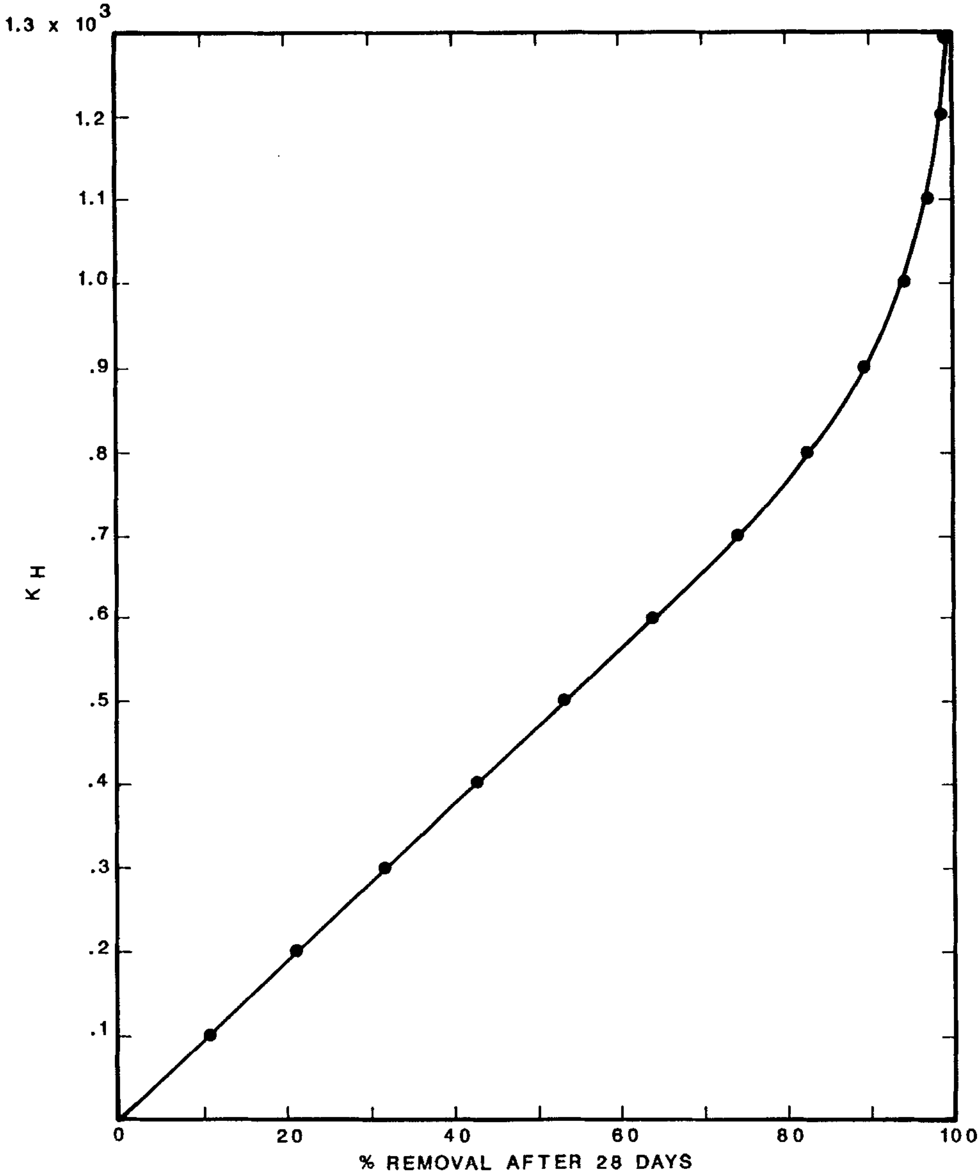


FIG. 11. Plot of Henry's constant versus percent removal after 28 d of vapor stripping. Lab column simulation. Column height = 32.1 cm; column radius = 3.15 cm; airflow rate = 5.0 mL/min; voids fraction = 0.2; specific moisture content = 0.2; Darcy's constant = 20.25 $cm^2/atm \cdot s$.

TABLE 5
Henry's Constant Calculated from Data Obtained in the Preliminary Soil Stripping Test, Tyson's Site[a]

Compound	Henry's constant (dimensionless)	
	1986 Data	1987 Data
TCP[c]	0.0025, 0.00086	No data
Toluene	0.0018, 0.0016, 0.00074	0.0011
Xylenes	0.0018, 0.0013, 0.0016, 0.0012	0.00095
Ethylbenzene	0.0011, 0.0013, 0.00096	0.00016[b]

[a] Data provided by AWARE, Inc. (*7*).
[b] Questionable.
[c] 1,2,3-Trichloropropane.

Henry's constant is given by

$$K_H = c_{\text{vapor}}/c_{\text{liquid}} \tag{93}$$

$$= 2.0 \times 10^{-5}/8.5 \times 10^{-3}$$

$$= 2.4 \times 10^{-3}$$

This value is approximately one hundredth the value of K_H for xylenes in pure water.

These results indicate the importance of using Henry's constants obtained from data on the soil to be aerated, rather than from lab data on solutes in pure water. Failure to use data representative of the material being aerated for the calculation of Henry's constants can result in conclusions which are very seriously in error.

V. MODELING OF AERATION IN THE FIELD—RESULTS

Data from Terra Vac, ERM, and AWARE were used to estimate the parameters required by the model in order to simulate aeration at the site. The data show a good deal of variation. The air flow rates at the four test wells at the Tyson site have been markedly different, and have increased very substantially during the course of the test run. The analyses of the soil gas also show a good deal of variation from well to well. The soil analysis data also exhibit variations which reflect the inhomogeneous distribution of contaminants in an inhomogeneous (gravelly) soil. One expects that soil moisture content changes substantially, both seasonally and as a result of the aeration treatment. It is therefore unwise to interpret thte result of the model in other than rough, semiquantitative fashion.

The parameters used in the first set of model calculations are as follows:

Water table depth		610 cm
Radius of influence		915 cm
Depth to vent pipe sink (the wells are screened from 7 to 20 ft)	570, 390, 210 cm	
Radius of vent pipe screen	12.7 cm	
Ambient pressure		1 atm
Pressure in vent pipe	0.866 atm	
Gas flow rate (1 atm)	23,600 cm^3/s	
Soil porosity (gas)	0.2	
Volume fraction soil moisture	0.2	
Soil density		2.67 g/cm^3
Compound		Xylene
Molecular weight		106 g/mol
Initial vapor concentration	20 mg/L	
Initial soil concentration	635 mg/kg	

The calculated value of K_H was 2.36×10^{-3}.

Since the wells are screened from 7 to 20 ft, while the model assumes a point sink, runs were made with the sink located at 19, 13, and 7 ft.

The boundary condition used for the calculations was the assumption that the soil surrounding the system contains no contaminant. If one is using an array of vent pipes, this is a more reasonable boundary condition than is the alternative assumption that the surrounding soil is uniformly contaminated.

The first run (Figs. 12a to 12d, 13) shows the changing distribution of xylene in the soil as the run proceeds for 292 h. Figure 13 is a plot of the totl mass of xylene in the system versus time. For this run, the sink is located at a depth of 570 cm. (The water table is at 610 cm.) Figure 13 indicates that about 98% of the xylene initially present is removed in the course of 292 h (12.2 d) of aeration. The original concentration of xylene in the soil would correspond to 239 ppm. The residual would be less than 5 ppm.

The run plotted in Fig. 14 has the sink located at a depth of 390 cm. Aeration was carried out for 292 h. The figure shows slightly less effective removal than was found with the preceeding run. About 97% of the xylene initially present is removed by 292 h of aeration.

The run plotted in Figure 15 has the sink located at a depth of 210 cm. As before, the duration of aeration was 292 h. Removal with this run is substantially poorer than in the other two; 86% of the initial xylene is removed.

```
   soil surface
0  0  0  1  1  1  2  2  3  3
2  2  2  3  4  4  5  6  6  6
4  4  5  6  6  7  8  8  8  6
6  6  7  7  8  8  9  9  8  6
7  7  8  9  9  9  9  9  8  5
8  8  9  9  9  9  9  9  7  4
8  9  9  9  9  9  9  8  7  3
0  0  9  9  9  9  9  8  6  3
•  0  9  9  9  9  8  7  6  2
0  0  9  9  9  9  8  7  5  2
   water table

12a. t = 41.7 hr. • denotes
     the location of the
     sink
```

```
0  0  0  0  0  0  0  0  1  1
0  0  0  0  0  1  2  2  3  3
0  0  1  1  2  3  4  5  5  3
1  1  2  3  4  5  6  7  6  3
2  3  4  5  6  7  7  7  6  3
3  4  5  7  7  8  8  7  5  2
4  5  7  8  8  8  7  6  4  1
0  0  8  8  8  7  6  5  3  1
*  0  8  8  7  6  5  4  2  0
0  0  7  7  6  6  5  3  2  0

12b.  t = 83.3 hr.
```

```
0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  1  1  1
0  0  0  0  0  1  2  2  2  2
0  0  0  1  2  2  3  4  3  2
0  1  1  2  3  4  5  5  3  1
1  1  3  4  5  5  5  4  3  1
1  3  4  5  6  6  5  4  2  0
0  0  5  6  6  5  4  3  1  0
*  0  5  5  5  4  3  2  1  0
0  0  4  4  3  3  2  1  0  0

12c. t = 125.0 hr.
```

```
0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0
0  0  0  0  0  1  1  0  0  0
0  0  0  1  1  1  1  0  0  0
0  0  1  1  1  1  0  0  0  0
*  0  1  1  1  0  0  0  0  0
0  0  0  0  0  0  0  0  0  0

12d. t = 205 hr.
```

FIG. 12a–d. Xylene distribution evolution during soil aeration with a single vent pipe. Parameters are given in the text. The vent pipe is located in the lower left corner at the asterisks. Duration of aeration = 41.7 (a), 83.3 (b), 125 (c), and 205 h (d).

In terms of the changes in soil gas composition (decreases in xylene concentration to about 20% of their initial values in about 430 h of aeration), the results of the model calculations appear to be of the right order of magnitude. Removal rates are proportional to air flow rate and Henry's constant; in view of the substantial uncertainties in the values of both parameters, our results seem to be in as good agreement with the soil gas composition data as we could reasonably expect.

We next turn to the calculation of upper bounds to the time required for remediation to a mean residual volatile organics concentration of 50 μg/kg, a level of remediation which has been proposed by EPA. Given the uncertainties in the parameters used in the model, it is probably unrealistic to attempt anything more precise than the estimation of upper bounds; this may be quite useful, however.

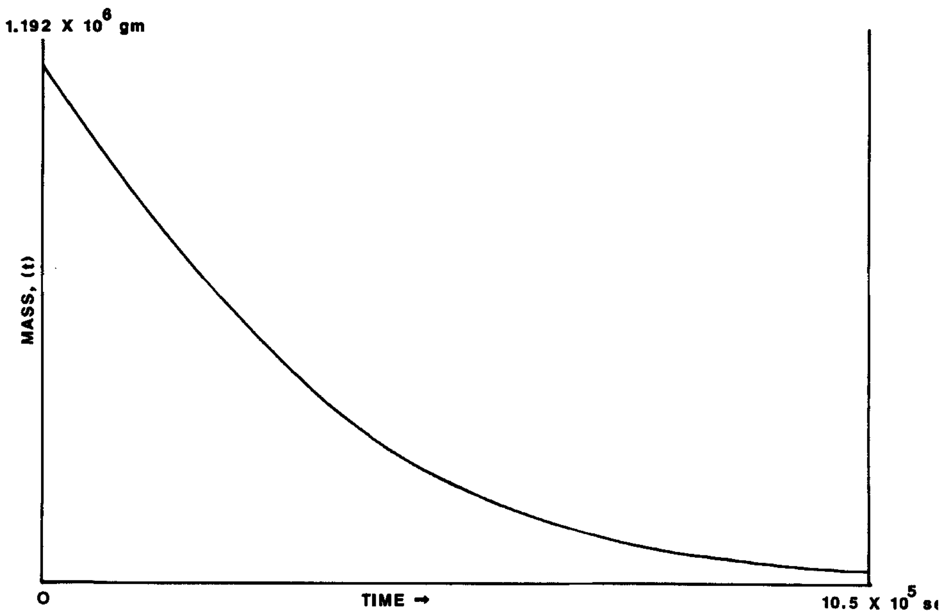
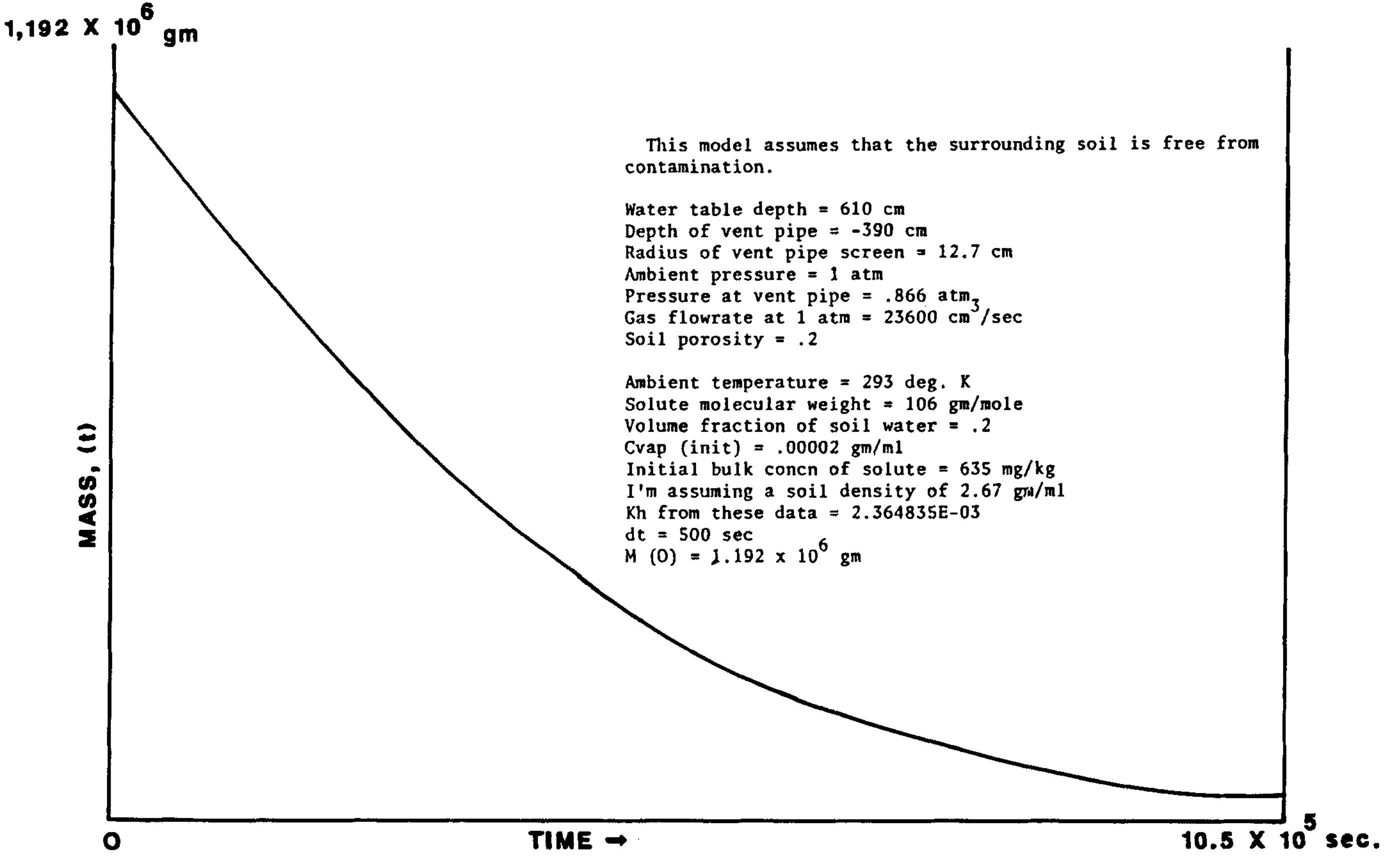


FIG. 13. Total mass of xylene in the cylinder of soil around the vent pipe as a function of time. Parameters as in Figs. 11 and 12. The depth of the vent pipe is 570 cm.

The parameters used for the field aeration calculations are given in Table 6; these are conservative choices within the framework of the values reported by Terra Vac for their test aeration wells at the Tyson site. We recall that the vent pipe is represented by a sink at the desired depth; this is underlain by a horizontal impermeable boundary layer. Given that the fractured rock beneath the soil layer is also to be aerated and appears to be of relatively high permeability, this gives a "worst case" geometry and boundary conditions.

Simulations were carried out with the model for the two values of the Henry's constant given in Table 6. The larger value, 0.00057, represents what we regard as a reasonable lower bound for the Henry's constants calculated for all of the volatile organics for all of the samples. Two compounds present are quite low concentrations gave outlier values for Henry's constant; the lower one of these (0.00016) was used as an "unreasonable" lower bound for the Henry's constants calculated for all of the volatile organics for all of the samples.

The larger of the two Henry's constants, 0.00057, gave a mean soil volatile organics concentration of 20 μg/kg after 139 d of aeration. We

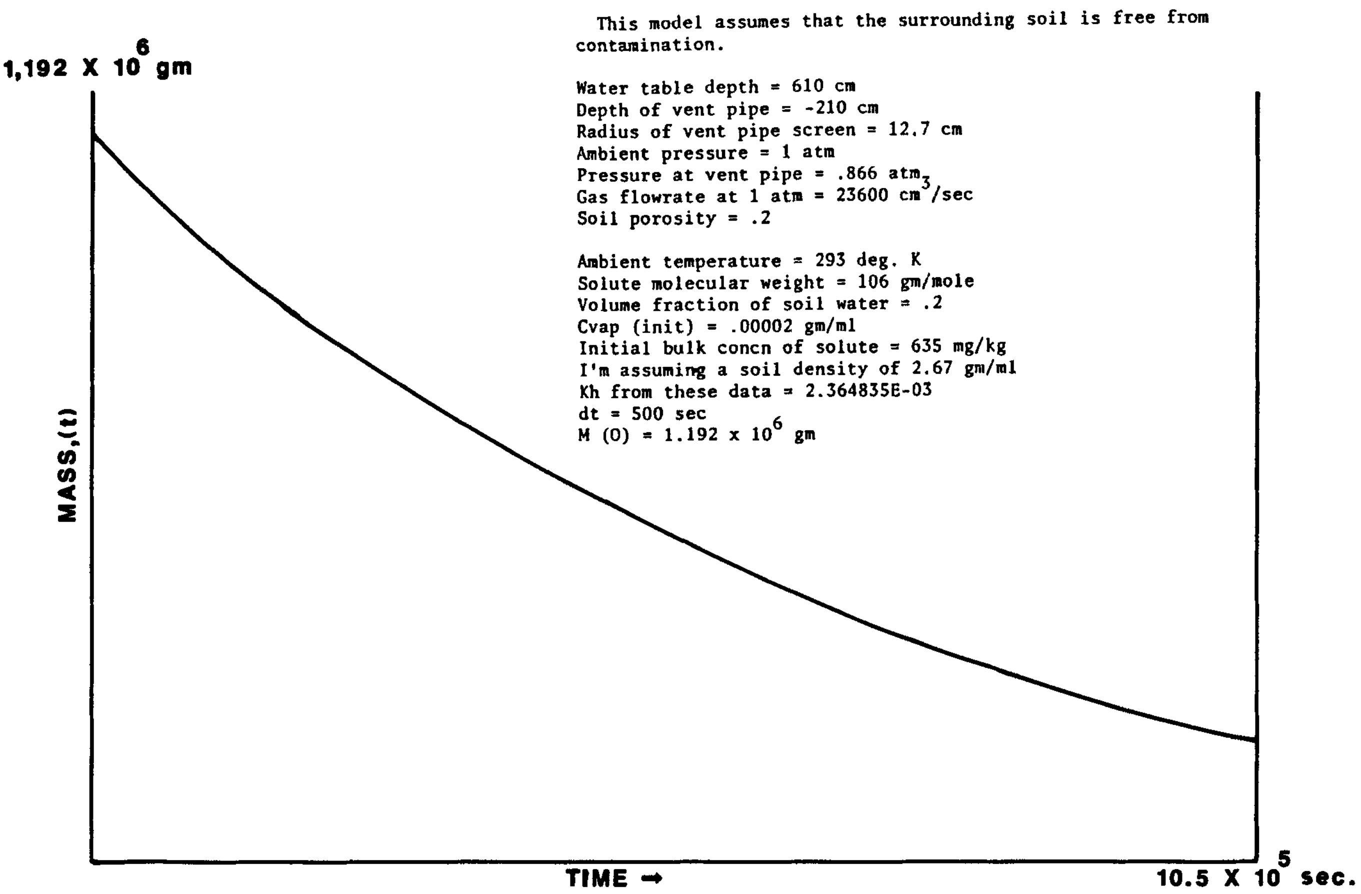


```
  This model assumes that the surrounding soil is free from
contamination.

Water table depth = 610 cm
Depth of vent pipe = -390 cm
Radius of vent pipe screen = 12.7 cm
Ambient pressure = 1 atm
Pressure at vent pipe = .866 atm
Gas flowrate at 1 atm = 23600 cm3/sec
Soil porosity = .2

Ambient temperature = 293 deg. K
Solute molecular weight = 106 gm/mole
Volume fraction of soil water = .2
Cvap (init) = .00002 gm/ml
Initial bulk concn of solute = 635 mg/kg
I'm assuming a soil density of 2.67 gm/ml
Kh from these data = 2.364835E-03
dt = 500 sec
M (O) = 1.192 x 10^6 gm
```

FIG. 14. Total mass of xylene in the cylinder of soil around the vent pipe as a function of time. Parameters as in Figs. 11 and 12, except that the depth of the vent pipe is 390 cm.



```
 This model assumes that the surrounding soil is free from
contamination.

Water table depth = 610 cm
Depth of vent pipe = -210 cm
Radius of vent pipe screen = 12.7 cm
Ambient pressure = 1 atm
Pressure at vent pipe = .866 atm
Gas flowrate at 1 atm = 23600 cm^3/sec
Soil porosity = .2

Ambient temperature = 293 deg. K
Solute molecular weight = 106 gm/mole
Volume fraction of soil water = .2
Cvap (init) = .00002 gm/ml
Initial bulk concn of solute = 635 mg/kg
I'm assuming a soil density of 2.67 gm/ml
Kh from these data = 2.364835E-03
dt = 500 sec
M (O) = 1.192 x 10^6 gm
```

FIG. 15. Total mass of xylene in the cylinder of soil around the vent pipe as a function of time. Parameters as in Figs. 11 and 12, except that the depth of the vent pipe is 210 cm.

TABLE 6
Parameters for the Mathematical Modeling of Field Aeration by a Single Vent Pipe

Water table depth, 610 cm
Depth of vent pipe, 570 cm
Radius of volume to be aerated, 610 cm
Ambient pressure, 1 atm
Pressure at vent pipe, 0.866 atm
Gas flow rate at 1 atm, 23,600 cm^3/s (50 cfm)
Soil voids fraction, 0.2 (volume/volume)
Temperature, 298 K
Henry's constant, 0.00057, 0.00016 (dimensionless)
Time increment in numerical integration, 1000 s
Initial volatile organics concentration, 40 g/kg (40,000,000 ppb)

therefore regard 139 d as a reasonable upper bound for the time needed to obtain the desired mean soil volatile organics concentration (50 μg/kg), given that the initial concentration is 4×10^7 μg/kg, that the vent pipes are located such that all portions of the soil to be vapor stripped are within 6.1 m of a vent pipes, that the vent pipes are evacuating air at a depth of 5.7 m or greater, and that the water table is at a depth of 6.1 m.

The smaller of the two Henry's constants, 0.00016, gave a mean soil volatile organics concentration of 42 μg/kg after 475 d of vapor stripping. We therefore regard 475 d as an "unreasonably" high upper bound for the time required to obtain a mean soil volatile organics concentration of 50 μg/kg, given the same parameters as were listed for the previous calculation.

A third field modeling run was made with the parameters given in Table 6 and a Henry's constant of 0.00095, corresponding to xylenes, the component present in the samples at the highest concentration. This run was simulated for a period of 21 d (the duration of Terra Vac's second test run at the Tyson site), and the xylenes concentration in the vent gas was plotted in order to compare its dependence on time with the experimental data obtained by Terra Vac on this test run (*14*). The model calculations indicate that the vent gas xylene concentration should be reduced to 17% of its initial value in the course of the 21-d run. See Fig. 16. The Terra Vac data show reductions in vent gas xylene concentration to 23, 10, 24, and 45% of the initial values. In view of the great heterogeneity of the material being vapor stripped at this site, and the quite substantial variations in air flow rate with time and from well to well, this is better agreement than one has a right to expect.

The variations in the Terra Vac data indicate that one would be ill-

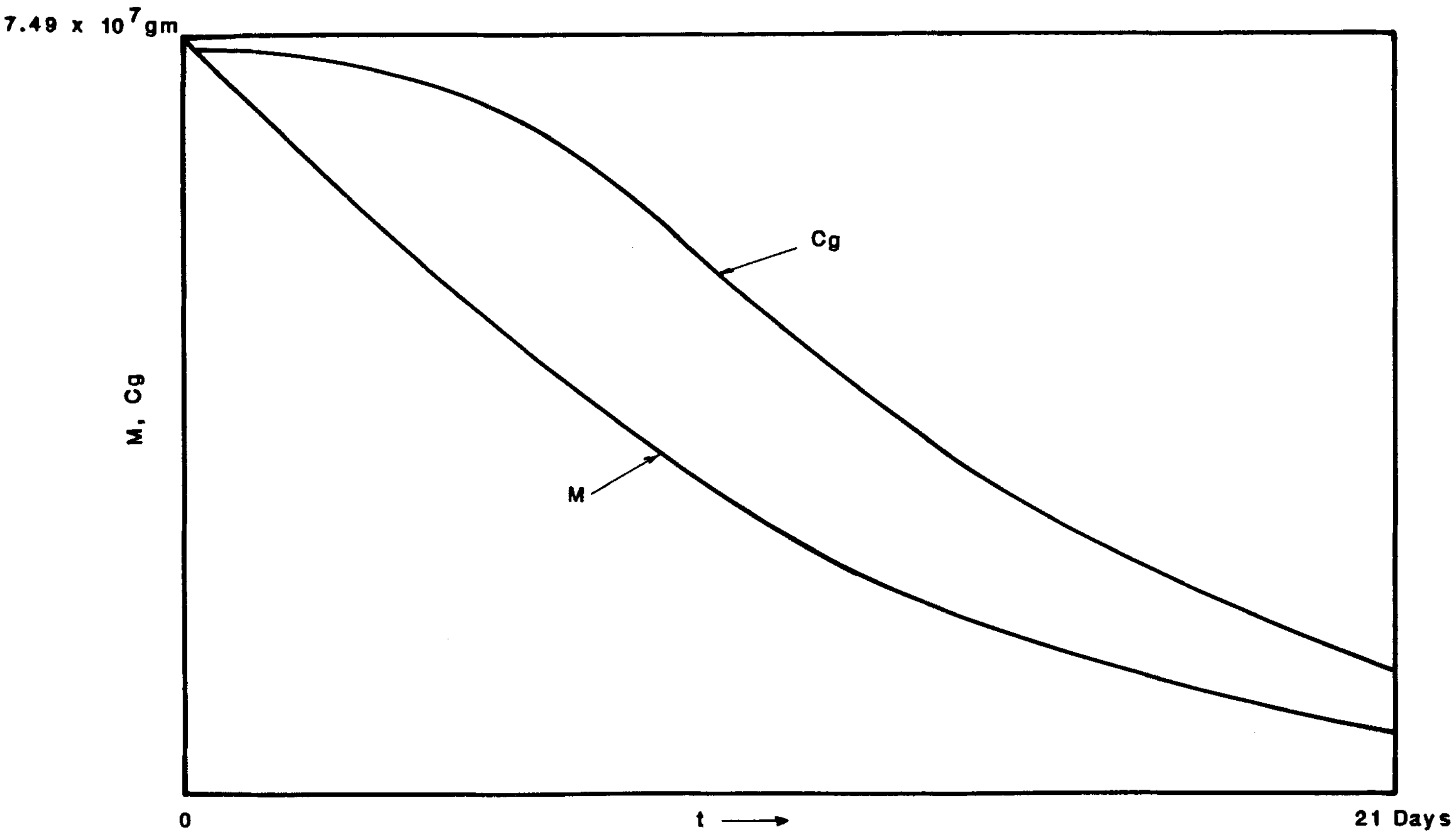


FIG. 16. Removal of xylene during a 21-d field vapor stripping test run, simulated. M = mass of xylene; C_g = vent gas xylene concentration. Henry's constant = 0.00095; dt = 2500 sed; initial total mass of xylene = 7.49×10^7 g; final total mass of xylene = 6.21×10^6 g; initial soil xylene concentration = 0.105 g/cm^3. Other parameters as in Table 6.

advised to rely solely on soil gas data in making a final assessment of the efficacy of cleanup. The semiquantitative agreement between the data and the theory do indicate, however, that soil gas analyses provide useful insight into the progress of clean-up. The model predicts that about 91% of the xylene has been removed from the cylinders of influence about the vent pipes in the course of the 21-d test run.

VI. IMPLICATIONS OF THE MODEL FOR WELL DESIGN

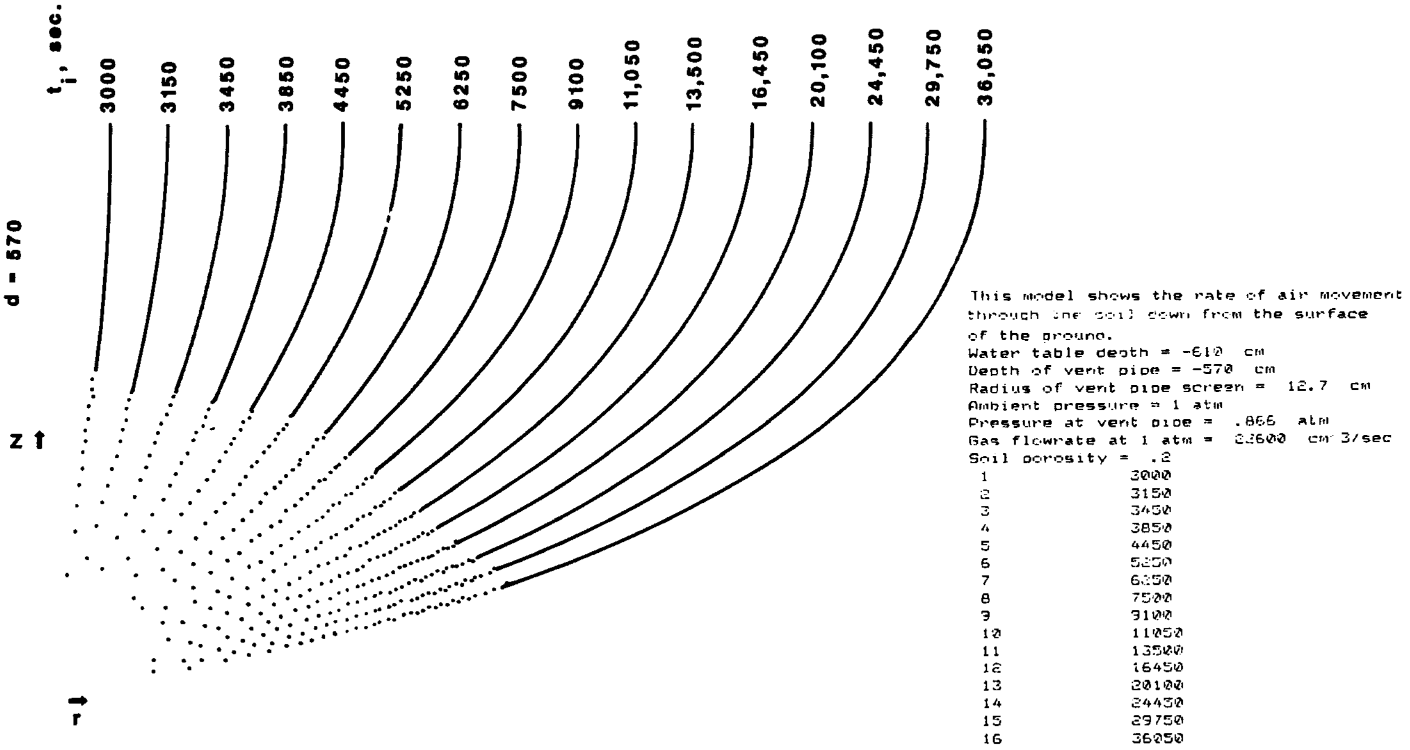
The results of Section V suggest that one increases removal efficiency by locating the sink as deeply as reasonably possible. In this section we explore this point more fully. In Section II, the gas velocity components v_r and v_z were calculated. Here we use these to calculate the streamlines of the gas flow through the soil to the sink, and the times required for gas to move from the surface of the soil along the streamline to the sink (t_i). These are shown in Figs. 17 (sink at 570 cm), 18 (sink at 390 cm), and 19 (sink at 210 cm).

For efficient cleanup, the transit times of gas moving to the sink from the outermost portions of the system should be as small as possible, and the streamlines should cover as much of the system volume as possible. It is apparent from the figures that, the shallower the well, the more slowly does air move along the outer streamlines, and the larger are the regions of stagnation (in which gas velocities are very small).

We therefore conclude that, other factors begin roughly equal, it is most effective to screen aeration wells only relatively near the water table (or gas-impermeable layer). For the wells modeled here, optimal screening would probably be from approximately 14 ft to the bottom of the wells at 20 ft. Screening higher in the well simply results in pumping more air through a portion of the system which will be very thoroughly cleaned up in any case.

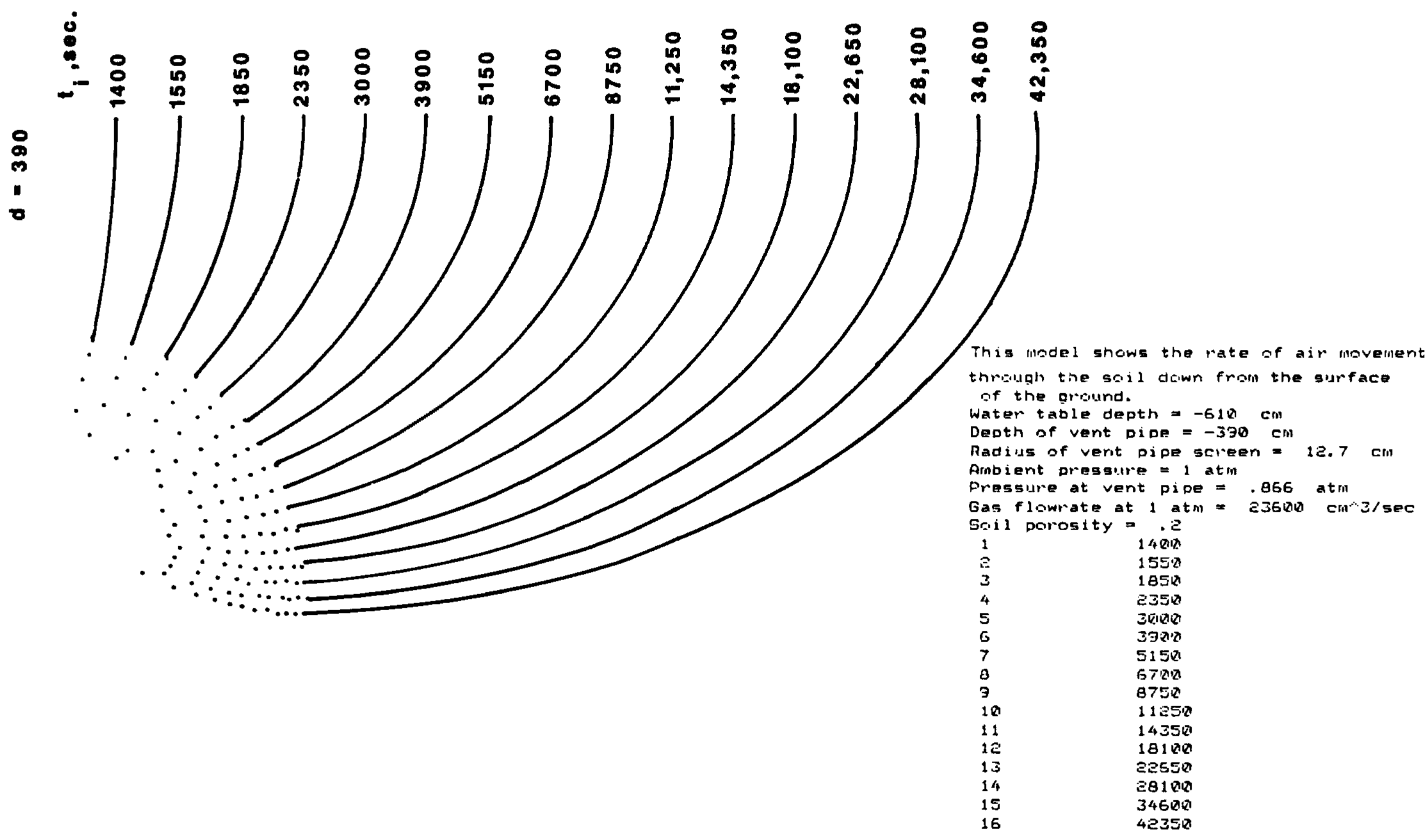
VII. CAVEATS AND CONCLUSIONS

We note again that the experimental data base used to get parameters for this model is relatively small and exhibits a good deal of variation. Removal rates are directly proportional to two parameters which are known with very poor precision—the gas flow rate and the Henry's constant. Removal rate is approximately inversely proportional to soil moisture content. The very large changes in air flow rate in the data from the site suggest substantial changes in soil moisture. The assumptions of



```
This model shows the rate of air movement
through the soil down from the surface
of the ground.
Water table depth = -610  cm
Depth of vent pipe = -570  cm
Radius of vent pipe screen =  12.7  cm
Ambient pressure = 1 atm
Pressure at vent pipe =  .866  atm
Gas flowrate at 1 atm =  22600  cm 3/sec
Soil porosity =  .2
 1                3000
 2                3150
 3                3450
 4                3850
 5                4450
 6                5250
 7                6250
 8                7500
 9                9100
 10               11050
 11               13500
 12               16450
 13               20100
 14               24450
 15               29750
 16               36050
```

FIG. 17. Flow lines and gas transit times t_i in the vicinity of a vent pipe at a depth of 570 cm. Other parameters as in Figs. 11 and 12. t_i is the time required for air to move from the surface of the ground at the indicated point down along the streamline to the vent pipe.



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This model shows the rate of air movement
through the soil down from the surface
 of the ground.
Water table depth = -610  cm
Depth of vent pipe = -390  cm
Radius of vent pipe screen =  12.7  cm
Ambient pressure = 1 atm
Pressure at vent pipe =  .866  atm
Gas flowrate at 1 atm =  23600  cm^3/sec
Soil porosity =  .2
 1              1400
 2              1550
 3              1850
 4              2350
 5              3000
 6              3900
 7              5150
 8              6700
 9              8750
 10             11250
 11             14350
 12             18100
 13             22650
 14             28100
 15             34600
 16             42350
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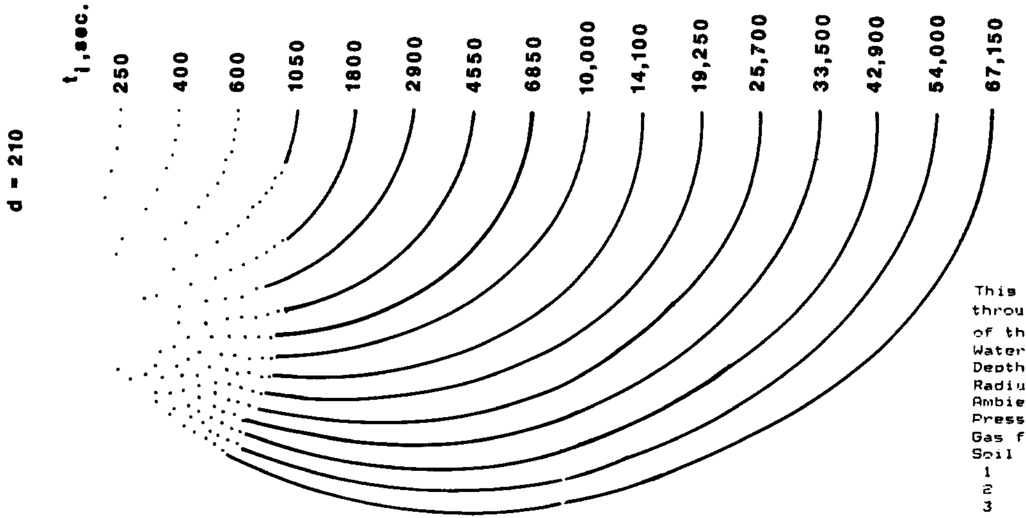
FIG. 18. Flow lines and gas transit times in the vicinity of a vent pipe at a depth of 390 cm. Other parameters as in Figs. 11 and 12.



```
This model shows the rate of air movement
through the soil down from the surface
of the ground.
Water table depth = -610  cm
Depth of vent pipe = -210  cm
Radius of vent pipe screen =  12.7  cm
Ambient pressure = 1 atm
Pressure at vent pipe =  .866  atm
Gas flowrate at 1 atm =  23600  cm^3/sec
Soil porosity =  .2
 1             250
 2             400
 3             600
 4             1050
 5             1800
 6             2900
 7             4550
 8             6850
 9             10000
 10            14100
 11            19250
 12            25700
 13            33500
 14            42900
 15            54000
 16            67150
```

FIG. 19. Flow lines and gas transit times in the vicinity of a vent pipe at a depth of 210 cm. Other parameters as in Figs. 11 and 12.

constant soil moisture content, constant and isotropic permeability, uniform initial system composition, and constant air flow rate are therefore at best considered bulk or time-weighted averages.

Nevertheless, the model, when used with Henry's constants derived from soil xylene concentration and soil moisture content, appears to yield results which are in fairly good agreement with Terra Vac's soil gas data on xylene during the course of their run. The model requires further testing, both on laboratory column experiments and on field data from the site. At present, it appears that the model will be a useful tool for design purposes and for making semiquantitative predictions about the progress and cost of soil aeration cleanups.

Acknowledgments

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