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Soil Clean Up by *in-situ* Aeration. V. Vapor Stripping from Fractured Bedrock

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Soil Clean Up by *in-situ* Aeration.
V. Vapor Stripping from Fractured Bedrock

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Abstract

A mathematical model for soil vapor stripping is presented which permits one to model vapor stripping from porous fractured bedrock, where one cannot make the assumption of local equilibrium between the stationary condensed phase and the moving vapor phase with respect to contaminant transport. Models for lab column operation and field operation of a vapor stripping well are presented. A lumped parameter approach is used to handle the kinetics of diffusion of the volatile contaminant from the interiors of the pieces of bedrock out to the moving soil gas. A method for estimating the time constant for this diffusion transport is presented, and the effects of the time constant on the performance of vapor stripping operations are assessed. The effects of impermeable circular caps on vapor stripping wells with and without passive vent wells are examined.

INTRODUCTION

There are now more than 1200 sites on the Superfund list, and it is estimated that several thousand other sites will have to be cleaned up if protection of groundwater resources from toxic contaminants is to be achieved. Many of these sites are contaminated with volatile hydrophobic organics which, as Schwille (*1*) has shown, move rapidly in both the vadose zone and the zone of saturation. These chemicals can be removed by *in-situ* soil vapor stripping, the advantages of which have been described in our earlier work (*2–5*). This technique is now coming into fairly common use.

Laboratory-scale studies include Wootan and Voynick's work on vapor stripping gasoline from a large-scale sand aquifer (*6*) and Clarke's work on the vapor stripping of several volatile organics in laboratory columns (*7*). A pilot scale vapor stripping operation near Tacoma, Washington, was described by Woodward-Clyde Consultants (*8*), and Anastos et al. (*9*) discussed a pilot study of the removal of trichloroethylene and other compounds at the Twin Cities Army Ammunition Plant, Minnesota. Crow, Anderson, and Minugh (*10*) reported on vapor stripping at a petroleum fuels terminal, and Bailey and Gervin (*11*) described a pilot study of the vapor stripping of chlorinated solvents. Lord (*12*) demonstrated that gasoline can be vapor stripped in the vicinity of streets and buildings, and Terra Vac recently carried out a demonstration test at Groveland, Massachusetts (*13*). Mutch et al. (*15*) described pilot vapor stripping work at a site in eastern New Jersey, and Dalfonso and Navetta discussed the use of biologically enhanced vapor stripping to decontaminate a soil stockpile contaminated with kerosene, bunker oil, and solvents (*14*).

We have developed mathematical models for lab column and field-scale vapor stripping, and have described the use of lab column experimental data with the lab column model to obtain effective Henry's constants for the field scale model. The effects of well depth, impermeable overlying caps, spacing of the wells, well packing radius, evaporative cooling, impermeable obstacles in the soil, and passive vent wells were explored. The removal of underlying nonaqueous phase liquid (NAPL) by vapor stripping was modeled. The calculation of the soil gas velocity fields has been extended to permit the use of the variable, anisotropic pneumatic permeabilities (*2–5, 16, 17*). Baehr, Hoag, and Marley recently described lab scale experimental work on the removal of gasoline, a local equilibrium model, and the use of the model in connection with a site contaminated with gasoline (*18*). Fall et al, (*19*) described the use of vapor stripping to remove gasoline at a site in California.

In all of our previous work on soil vapor stripping it was assumed that local equilibrium existed between volatile contaminant in the condensed, stationary phase(s) and the volatile contaminant present in the adjacent moving vapor phase. If one is dealing with sand, gravel, or unconsolidated sediments, the assumption of local equilibrium is probably quite good. If, however, one is vapor stripping from fractured bedrock or other "lumpy" media in which volatile contaminant must diffuse out from the interiors of the lumps before it can be swept away by the soil gas as it moves through the interstices between the lumps, then the assumption of local equilibrium could be quite poor. This seems to have been observed by Fall et al. (*19*). We here address the modeling of soil vapor stripping from fractured bedrock.

Such a model, if constructed rigorously, is computationally quite formidable; one must integrate a partial differential equation in two or three macroscopic space variables, one space variable which refers to diffusion within the porous pieces of rock, and one time variable. This would require a substantial amount of time on a mainframe computer, and would markedly reduce the utility of the model. We therefore make use of a lumped parameter method for handling diffusion from the pieces of rock, and also assume that the geometry of the vapor stripping well is cylindrically symmetrical. This permits us to construct a model which can be run on microcomputers such as the IBM PC-AT and its clones. We have used this approach previously in modeling the water flushing of soluble contaminants from fractured bedrock (*20*).

TIME CONSTANT FOR DIFFUSION

The model is illustrated schematically in Fig. 1. The domain of interest is partitioned into an array of volume elements as shown, and mass transfer of volatile contaminant between volume elements is assumed to take place by advection and dispersion. Each volume element is partitioned into two domains. The first corresponds to fractures, and is linked to similar domains in the adjacent volume elements by advection and dispersion. The second domain corresponds to the immobile pore liquid and/or sorption sites within the blocks of matrix; this is assumed to be linked only to the first domain in the same volume element by a diffusion term. Diffusion within a piece of porous but low-permeability medium is thus handled by a one-compartment model.

The time constant for diffusion of contaminant from a block of this matrix is calculated by approximating the block as spherical, for instance, and then calculating the lowest nonzero eigenvalue for the appropriate diffusion problem. If we assume spherical symmetry, the appropriate diffusion equation is

$$\frac{\partial c}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) \tag{1}$$

where D is the diffusion constant, $c(r,t)$ is the solute concentration at a dis-

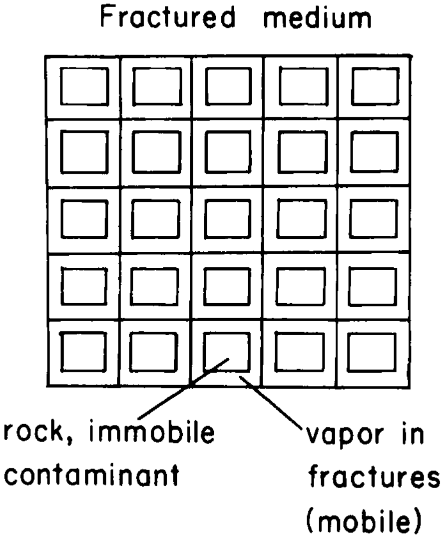

FIG. 1. Lumped parameter model for vapor stripping from fractured bedrock.

tance r from the center of the block and time t, and the boundary conditions are

$$\begin{aligned} &c(a,t) = 0 \\ &c(0,t) \text{ is bounded} \end{aligned} \tag{2}$$

The partial differential equation is solved by separation of variable $[c(r,t) = R(r)*T(t)]$ and the substitution $R = u/r$. The second boundary condition leads to a solution of the form

$$c_\lambda(r,t) = \sum_\lambda \frac{B_\lambda}{r} \sin \sqrt{\frac{\lambda}{D}}\, r \exp(-\lambda t) \tag{3}$$

Use of Eq. (2) then yields

$$\lambda = \lambda_n = \left(\frac{n\pi}{a}\right)^2 D, \qquad n = 1, 2, 3, \ldots \tag{4}$$

for the eigenvalues of the system. The lowest nonzero eigenvalue is

$$\lambda_1 = D(\pi/a)^2 \tag{5}$$

A similar calculation for a rectangular solid having edges *a, b,* and *c* yields

$$\lambda_1 = D\pi^2(a^{-2} + b^{-2} + c^{-2}) \tag{6}$$

The time constants for a sphere of diameter $2a$ and a cube having edges of length $2a$ are $D\pi^2/a^2$ and $3D\pi^2/4a^2$, respectively, indicating that the details of the shapes of the blocks are not likely to be important in the calculations.

LABORATORY COLUMN MODEL

The model for lab column vapor stripping of fractured bedrock is illustrated in Fig. 2. Notation is as follows.

A = cross-sectional area of column, cm^2
ν = voids fraction associated with mobile gas, dimensionless
w = voids fraction associated with immobile pore liquid and adsorption sites within the block of medium
Q = gas flow rate, mL/s
c_i^v = contaminant concentration in the vapor phase, *i*th compartment, g/mL
c_i^s = contaminant concentration in the condensed phase, *i*th compartment, g/mL
K_H = effective Henry's constant, dimensionless
m_i = contaminant mass in the *i*th compartment

Then

$$m_i = A\Delta x \nu c_i^v + A\Delta x w c_i^s \tag{7}$$

We assume a lumped parameter model for mass transport from the interior of the medium blocks by diffusion, which yields

$$dc_i^s/dt = -\lambda(c_i^s - c_i^v/K_H) \tag{8}$$

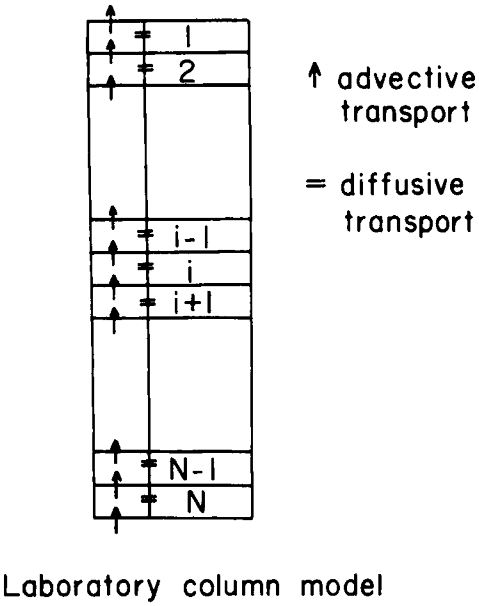

FIG. 2. Model for laboratory column vapor stripping from fractured bedrock.

and

$$\left(\frac{\partial c_i^v}{\partial t}\right)_{\text{mass trans}} = \frac{\lambda w}{\nu}(c_i^s - c_i^v/K_{\mathrm{H}}) \tag{9}$$

Then

$$\frac{dm_i}{dt} = Q(c_{i-1}^v - c_i^v) = A\Delta x\left(\nu\frac{dc_i^v}{dt} + w\frac{dc_i^s}{dt}\right) \tag{10}$$

which, on use of Eq. (7), gives for the differential equations modeling the column operation

$$dc_i^s/dt = -\lambda(c_i^s - c_i^v/K_{\mathrm{H}}) \tag{8}$$

and

$$\frac{dc_i^v}{dt} = \frac{w\lambda}{v}\left(c_i^s - \frac{c_i^v}{K_H}\right) + \frac{Q}{Av\Delta x}(c_{i-1}^v - c_i^v) \tag{11}$$

If we wish to modify this to permit the handling of time constants such that $1/\lambda$ is comparable in magnitude to or smaller than the time increment in the numerical integration, Eqs. (8) and (11) can be replaced by

$$\frac{dc_i^s}{dt} = \left(\frac{c_i^v}{K_H} - c_i^s\right)\frac{1 - \exp(-\lambda\Delta t)}{\Delta t} \tag{12}$$

and

$$\frac{dc_i^v}{dt} = \frac{Q}{Av\Delta x}(c_{i-1}^v - c_i^v) - \frac{w}{v}\,\frac{1 - \exp(-\lambda\Delta t)}{\Delta t}\left(\frac{c_i^v}{K_H} - c_i^s\right) \tag{13}$$

MODEL OF A FIELD VAPOR STRIPPING WELL

The model assumed for the operation of a field vapor stripping well is sketched in Fig. 3. The soil gas velocity field generated by the vapor stripping well is calculated by the relaxation method described previously (*5*); this calculation and the actual modeling of the stripping well operation assume that the system is axially symmetric. The pneumatic permeability tensor can vary with depth and can also be anisotropic ($K_z \neq K_r$). It is also possible to include an impermeable circular cap at the surface of the soil and coaxial with the well. Insofar as possible, we use the same notation as was used for modeling lab column operation; here, however, SI units are used instead of cgs units.

The volume of interest is partitioned into a number of ring-shaped volume elements as indicated in Fig. 3; we let $dr = dz = \delta$. Then

$(i + 1/2)\delta$ = radius drawn to the midpoint of the *ij*th ring
$(j + 1/2)\delta$ = distance of the midpoint of the *ij*th ring above the water table
$V_{ij} = \pi(2i + 1)\delta^3$ is the volume of the *ij*th ring

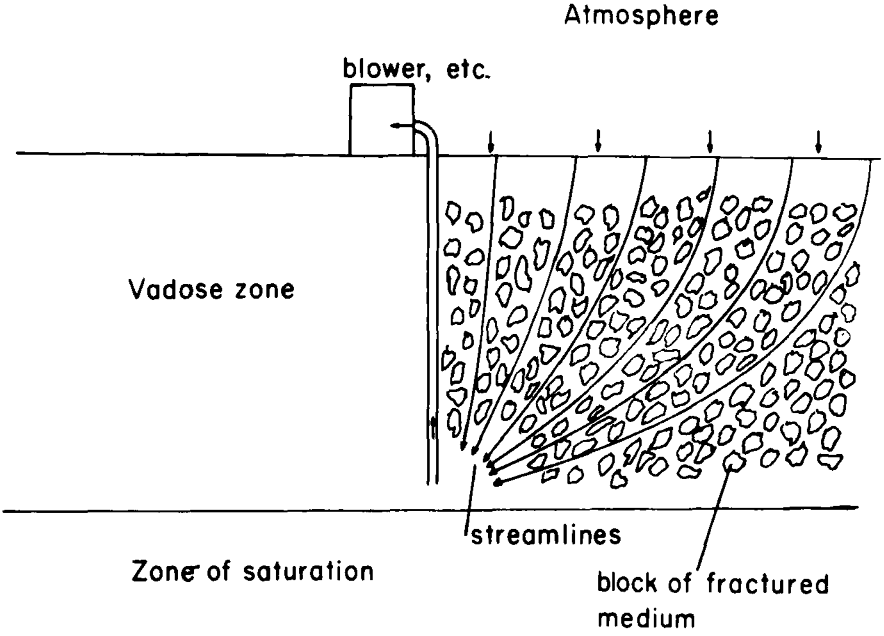

FIG. 3. Model for operation of a field vapor stripping well in fractured bedrock.

The upper, lower, inner, and outer surfaces of the volume elements are calculated, and the net flux of contaminant into the ijth volume element is then calculated in the usual way. The contaminant concentrations in the mobile and stationary phases in the volume element are related to the mass of contaminant in the volume element by

$$m_{ij} = V_{ij}(\nu c_{ij}^{v} + wc_{ij}^{s}) \tag{14}$$

We use our lumped parameter approximation to obtain Eq. (15), analogous to Eq. (8):

$$dc_{ij}^{s}/dt = -\lambda(c_{ij}^{s} - c_{ij}^{v}/K_{\mathrm{H}}) \tag{15}$$

This result, Eq. (14), and a material balance on the ijth volume element allow us to construct Eq. (16):

$$\begin{aligned}\frac{dc^{\upsilon}_{ij}}{dt} = \Bigg[& -\upsilon_r((i+1)\delta,(j+\tfrac{1}{2})\delta)\cdot\frac{2(i+1)}{2i+1}\, c^{\upsilon}_{i+1|j} + \upsilon_r(i\delta,(j+\tfrac{1}{2})\delta) \\ & \cdot\frac{2i}{2i+1}\, c^{\upsilon}_{ij} - \upsilon_z((i+\tfrac{1}{2})\delta,(j+1)\delta)\{S(-\upsilon_z)c^{\upsilon}_{i,j+1} - S(\upsilon_z)c^{\upsilon}_{i,j}\} \\ & + \upsilon_z((i+\tfrac{1}{2})\delta|j\delta)\{S(\upsilon_z)c^{\upsilon}_{ij-1} + S(-\upsilon_z)c^{\upsilon}_{ij}\}\Bigg]/\delta \\ & + (\lambda w/\nu)(c^{s}_{ij} - c^{\upsilon}_{ij}/K_{\mathrm{H}}) \qquad (16)\end{aligned}$$

Here υ_r = r-component of the velocity for the given values of the coordinates

υ_z = z-component of the velocity

$S(\upsilon) = 0$ if $\upsilon < 0$

$S(\upsilon) = 1$ if $\upsilon > 0$

It is necessary to include the unit step function factors $S(\upsilon_z)$ in Eq. (16) to take into account the fact that υ_z takes on both positive and negative values in the domain of interest, so that contaminant may be flowing into a volume element from above or from below. This is not necessary with the radial velocity terms, since the radial velocity is negative over the entire domain.

An initial contaminant distribution in the domain of interest is specified, and Eqs. (15) and (16) are then integrated forward in time by means of the predictor-corrector method used previously (*2–5*).

In preliminary work it is often desirable to estimate a value for the Darcy's constant ($\mathbf{K}_\mathrm{D}$, pneumatic permeability) which appears in the equations from which the soil gas velocity field is calculated,

$$\mathbf{K}_\mathrm{D}\nabla P = \vec{\upsilon} \qquad (17)$$

and

$$\nabla\cdot\mathbf{K}_\mathrm{D}P^2 = 0 \qquad (18)$$

Relatively few Darcy's constants for air in soils are available, but one can estimate these from the intrinsic permeability, k, as follows. We use notation from Freeze and Cherry (*21*).

$$\vec{\upsilon} = -K\nabla h \qquad (19)$$

where k = hydraulic conductivity, m/s
h = hydraulic head

Now

$$\nabla h = \frac{1}{\rho g} \nabla P \qquad (20)$$

where ρ = fluid density, kg/m^3
g = gravitational constant, m/s^2
P = pressure, N/m^2

Freeze and Cherry define intrinsic permeability k by

$$K = k\rho g/\mu \qquad (21)$$

where μ = fluid viscosity, kg/ms.

Substitution then yields

$$\vec{v} = -\frac{k}{\mu} \nabla P \qquad (22)$$

Since 1 atm = 1.01325×10^5 N/m^2, we have

$$\vec{v} = -\left(\frac{k}{\mu}\right) \cdot 1.01325 \times 10^5 \nabla P \text{ (atm/m)} \qquad (23)$$

The viscosity of air at 18°C is 182.7 μpoise, which in SI units is 1.827×10^{-5} kg/ms (*22*). This then yields

$$\vec{v} = -5.546 \times 10^9 k \nabla P \text{ (atm/m)} \qquad (24)$$

where k is given in m^2. Gas viscosities are proportional to T^{α} ($\frac{1}{2} < \alpha < 1$) (*23*), so that minor uncertainties in soil temperature will have little effect. Some air viscosity data are given in Table 1. Freeze and Cherry provide ranges for the intrinsic permeabilities of a number of geological media (*21*).

TABLE 1
Viscosity of Air[a]

Temperature (°C)	Viscosity (kg/ms)
0	1.708×10^{-5}
18	1.827
40	1.904

[a] Data from Ref. 22.

RESULTS

Some representative runs with the laboratory column simulator are shown in Fig. 4; in these runs all parameters were held constant except the time constant for diffusion from the blocks of porous medium. The standard parameter set for these runs is given in Table 2. We see that a long time constant (large $1/\lambda$) results in decreased rates of removal, and in extensive exponential tailing in the curves, as one would intuitively expect. One can distinguish between the effects of a small Henry's constant and a long diffusion time constant by carrying out experimental runs at different flow rates. If the assumption of local equilibrium is a good approximation, plots of total residual contaminant versus Qt will be virtually superimposable, as seen in Fig. 5. If vapor stripping is diffusion limited, such plots will tail more to the right (more gas required for removal) for the runs made at the higher flow rates, as seen in the plots shown in Fig. 6.

In Fig. 7 we see the effect of varying the diffusion time constant ($1/\lambda$) on vapor stripping from fractured bedrock by means of a vacuum extraction well. As expected, increasing the diffusion time constant results in reduced removal rates. Note that the initial removal rates for these runs are all very similar; during the initial stages of vapor stripping, contaminant which is already in the vapor phase is being removed, so there is no diffusion-controlled lag. After this material has been removed, diffusion becomes rate limiting, and we see decreases in removal rates. Evidently one cannot count on a short test run at the site to give one information on how long it will take to obtain removal of the bulk of the contaminant if this must diffuse from the interior of blocks of porous medium.

In optimizing soil vapor stripping strategy it is essential to know both the effective Henry's constant of the contaminant and the diffusion constant. If one is dealing with a small Henry's constant but can assume local

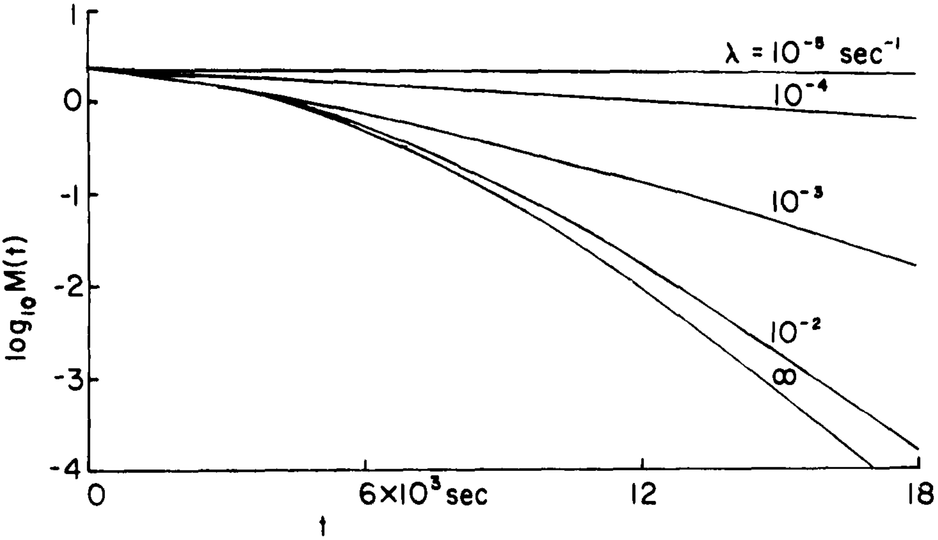

FIG. 4. Plots of $\log_{10}$ (contaminant mass) versus time, vapor stripping in a laboratory column; effects of diffusion time constant λ^{-1}. $\lambda = \infty$, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} s^{-1}. Other parameters as in Table 2.

TABLE 2
Laboratory Column Standard Parameter Set

Column length	50 cm
Column radius	10 cm
Number of volume elements into which the column is partitioned	10
Voids fraction associated with mobile gas	0.2
Voids fraction associated with immobile pore liquid	0.2
Gas flow rate	5 mL/s
Effective Henry's constant	0.1
Soil density	1.6 g/mL
Initial contaminant concentration	100 mg/kg
dt	1 s

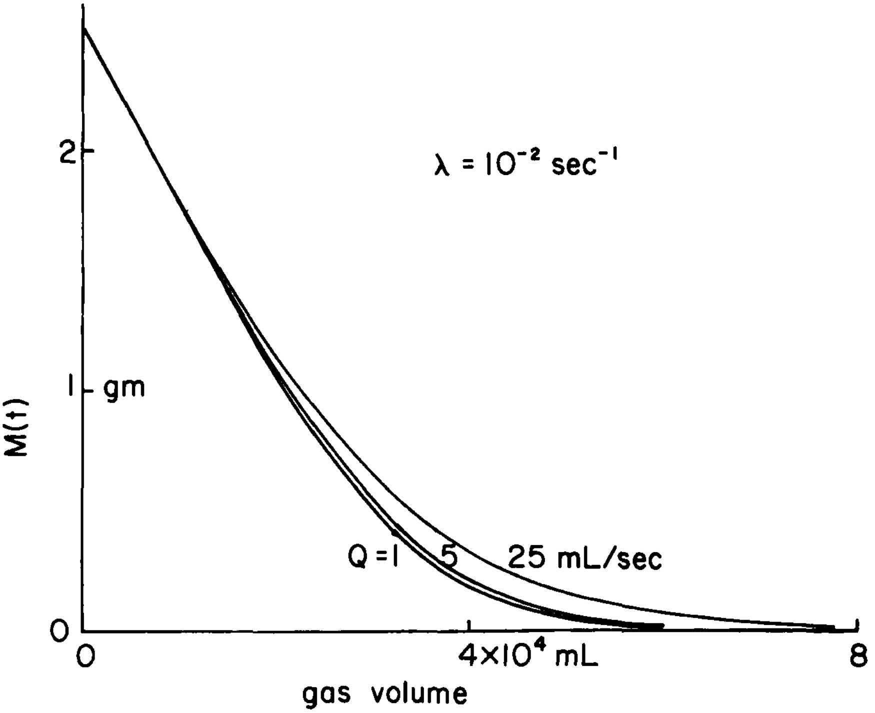

FIG. 5. Plots of contaminant mass versus time, vapor stripping in a laboratory column. In these runs $\lambda = 0.01\ s^{-1}$, and Q = 1, 5, and 25 mL/s (bottom to top); other parameters as in Table 2.

equilibrium, removal rate is proportional to the gas flow rate, and one can therefore decrease cleanup time requirements by designing a well system which will permit maximum gas flow rates. If, on the other hand, diffusion from the porous blocks of medium into the mobile gas stream is rate-limiting, increasing the gas flow rate can very quickly reach the point of diminishing returns; one is spending lots of money to pump lots of air, but the rate of the cleanup process is controlled by the diffusion rate. In such situations, rather long times for clean-up may be required; under these circumstances one can reduce costs by pumping air through the vapor stripping well on a duty cycle of length comparable to the time constant for diffusional mass transfer from the time constant for diffusional mass transfer from the blocks of porous medium.

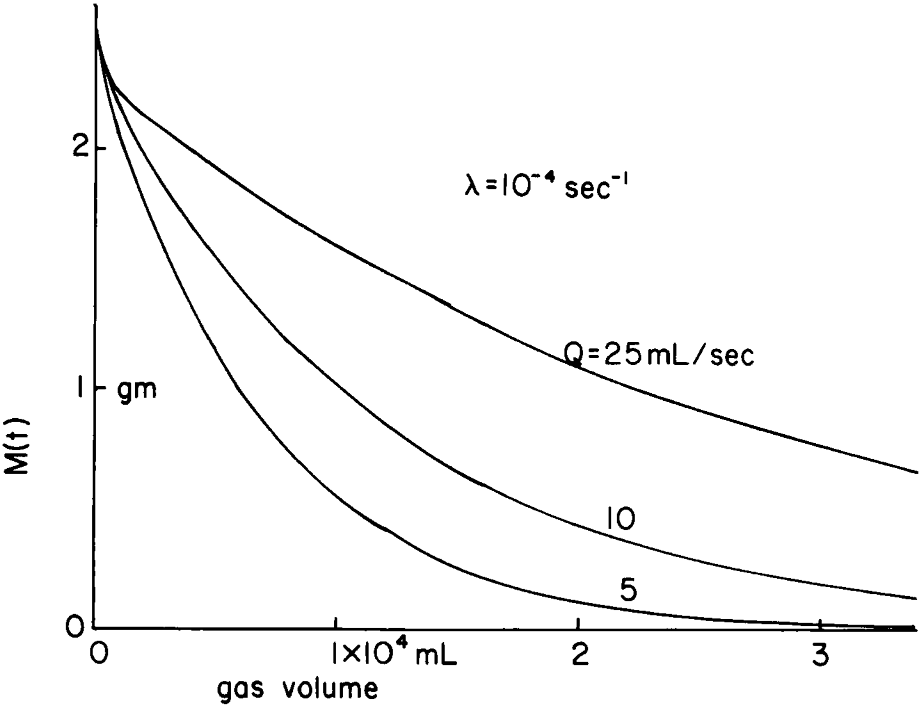

FIG. 6. Plots of contaminant mass versus time, vapor stripping in a laboratory column. In these runs $\lambda = 10^{-4}\ s^{-1}$, and $Q = 5, 10$, and 25 mL/s (bottom to top); other parameter as in Table 2.

In an earlier paper (*4*) we noted that the use of passive vent wells around the periphery of the domain of influence of a soil vapor stripping well resulted in slight decreases in removal rates. We were somewhat skeptical of this rather surprising result, and found, on more detailed examination of the movement of the contaminant during the course of a simulated run, that it was due to the fact that the passive wells provide a short circuit across the bottom of the domain of influence for the soil gas. We still found the result counter-intuitive, so we repeated the computations with a modified and improved procedure for calculating the soil gas velocities. We also explored the effects of impermeable circular caps on the performance of vapor stripping wells with and without passive wells. The results are shown in Figs. 8–11. The system parameters used in making these runs are given in Table 4.

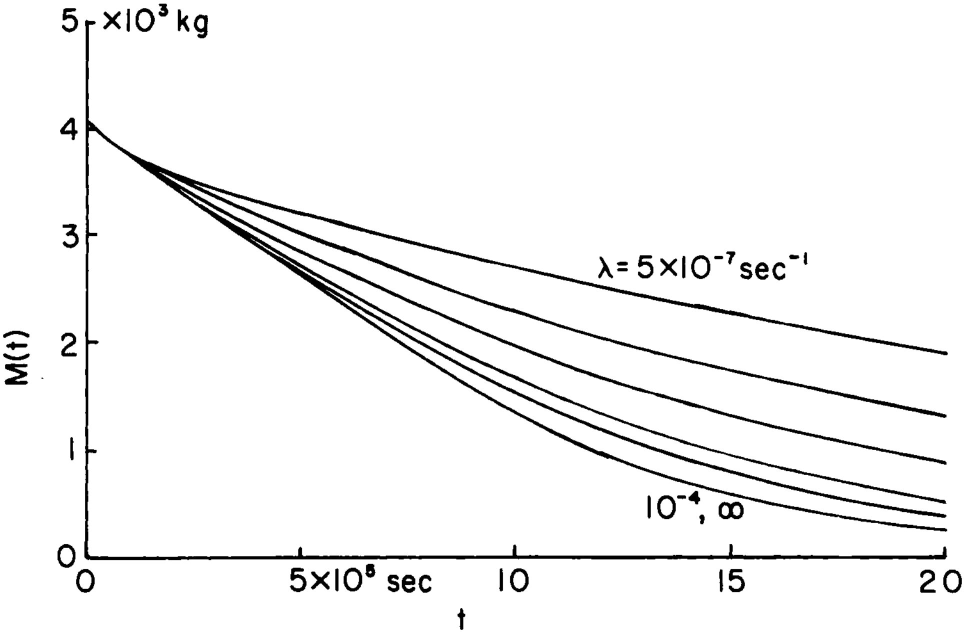

FIG. 7. Plots of contaminant mass versus time, vapor stripping by a vacuum extraction well. In these runs $\lambda = \infty$, 10^{-4} (plots superimposed), 10^{-5}, 5×10^{-6}, 2×10^{-6}, 10^{-6}, and 5×10^{-7} s^{-1}; other parameters are given in Table 3.

TABLE 3
Field Vapor Stripping Well Standard Parameter Set

Radius of domain of influence	30 m
Depth of water table	20 m
Depth of well	17.5 m
Radius of impermeable cap	25 m
Screened radius of well	0.12 m
Well pressure	0.866 atm
Temperature	286 K
Voids fraction associated with mobile gas	0.2
Voids fraction associated with immobile pore liquid	0.2
K_z	1 m^2/atm · s
K_r	1 m^2/atm · s
Effective Henry's constant	0.1
Radius of zone of contamination	20 m
Initial contaminant concentration	100 mg/kg
Soil density	1.6 g/mL
Initial contaminant mass	4018.2 kg
Molar gas flow rate	1.6246 mol/s
Volumetric gas flow rate (1atm)	0.03815 m^3/s
dt	100 s

TABLE 4
Parameters for the Field Vapor Stripping Well Runs Plotted in Figs. 8-11

Radius of domain of influence	30 m
Depth of water table	20 m
Depth of well	17 m
Radius of impermeable cap	0, 5, 10, 15, 20, 25 m
Screened radius of well	0.12 m
Well pressure	0.866 atm
Temperature	286 K
Soil voids fraction	0.2
Soil moisture volumetric fraction	0.2
K_z	0.1 $m^2/atm \cdot s$
K_r	0.1 $m^2/atm \cdot s$
Effective Henry's constant	0.01
Radius of zone of contamination	30 m
Initial contaminant concentration	100 mg/kg
Soil density	1.6 g/mL
Initial contaminant mass	9047.8 kg
Molar gas flow rate	0.17437 mol/s
Volumetric gas flow rate, 286 K, 1 atm	0.0040938 m^3/s

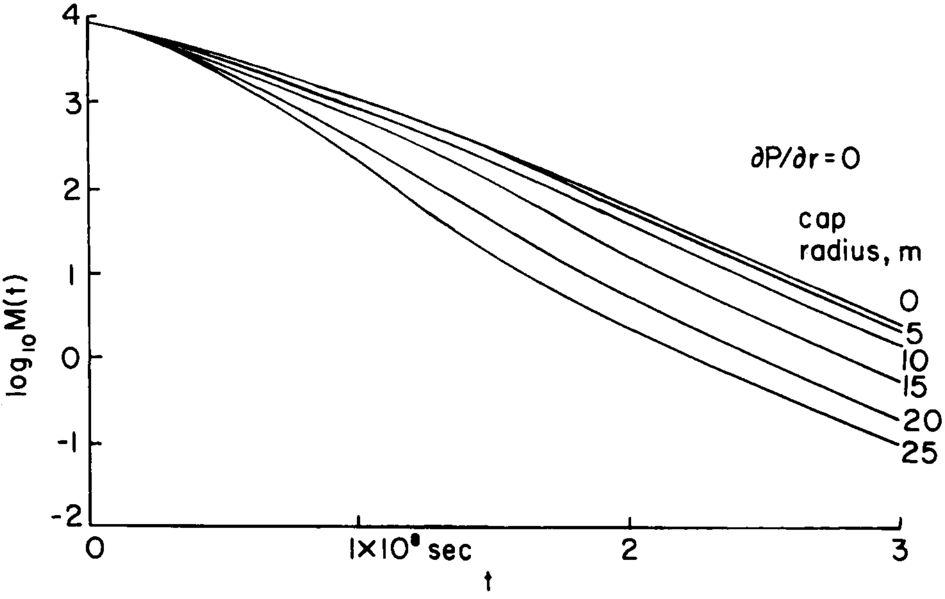

FIG. 8. Log plots of total contaminant mass versus time for a field vapor stripping well. The system parameters are given in Table 4. The boundary condition at the periphery of the domain of influence is $\partial P/\partial r = 0$, a no-flow boundary condition.

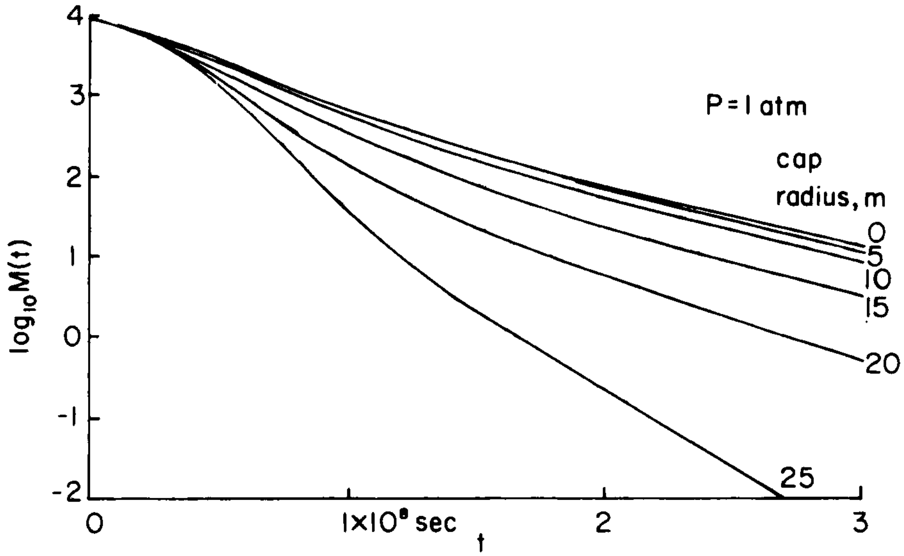

FIG. 9. Log plots of total contaminant mass versus time for a field vapor stripping well. The system parameters are given in Table 4. The boundary condition at the periphery of the domain of influence is $P = 1$ atm, corresponding to the presence of passive vent wells around the periphery.

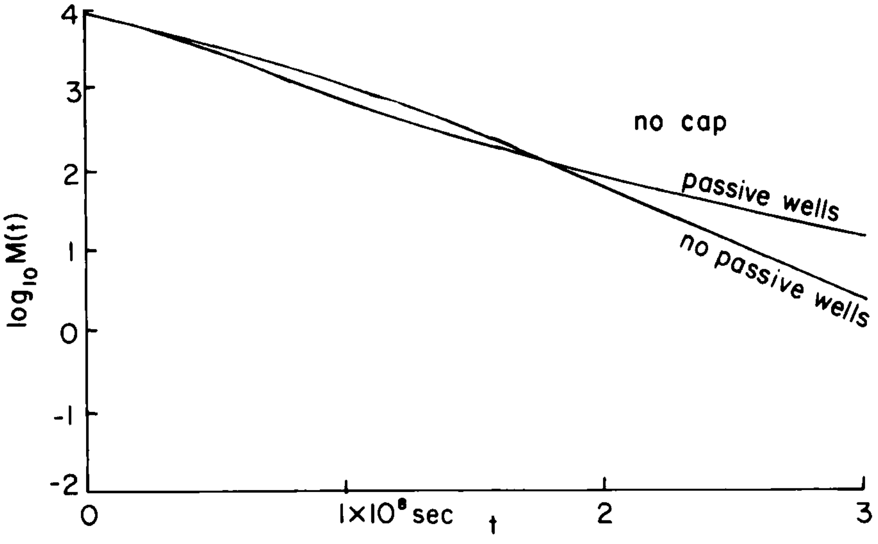

FIG. 10. Comparison of systems with and without passive vent wells. The system parameters are given in Table 4. No impermeable cap is present in these runs.

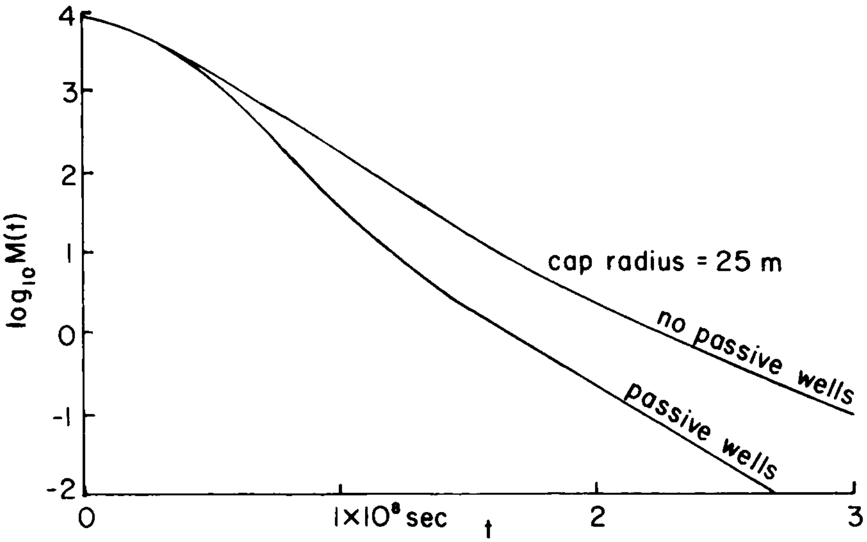

FIG. 11. Comparison of systems with and without passive vent wells. The system parameters are given in Table 4. An impermeable cap of 25 m radius is present in these runs.

In Fig. 8 we see plots of runs made with cap radii ranging from 1 to 25 m; the domain of influence has a radius of 30m and the boundary condition around its periphery is $\partial P/\partial r = 0$, a no-flow boundary condition. We see, as before (*3*), a moderate improvement in contaminant removal rate with increasing cap radius.

Figure 9 shows plots of a similar set of runs for a system which is identical to that used to obtained the results of Fig. 8 except in one respect. The boundary condition around the periphery of the domain of influence is $P = 1$ atm, corresponding to the presence of a fairly closely spaced set of passive wells around the periphery which are screened along their entire length. Again we find that the presence of an impermeable cap increased contaminant removal rate, but here the increase is very dramatic as the cap radius is increased from 20 to 25 m.

Figures 10 and 11 compare removal rates for the two systems (with and without passive wells) in the absence of a cap and in the presence of a 25-m cap. In the absence of a cap the presence of passive wells decreases the contaminant removal rate, as seen before. In the presence of a cap the presence of passive wells increases the removal rate by around 20%. These results suggest that the use of passive wells when one is vapor stripping underneath impermeable surfaces (building floors, parking lots, streets) may be moderately advantageous.

Acknowledgments

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