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Soil Clean Up by *in-situ* Aeration. IX. Diffusion Constants of Volatile Organics and Removal of Underlying Liquid

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Abstract

The removal of volatile organic compounds (VOCs) underlying the vadose zone in a pool of nonaqueous phase liquid (NAPL) in the vicinity of a soil vapor stripping well is modeled mathematically. The diffusivity of the VOC is an important parameter determining the rate of removal of the NAPL; diffusivities of hexane, toluene, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane were determined in fine sand and found to be approximately 2×10^{-6} m^{-2}/s at 25°C. Vapor stripping appears to be a practical method for the removal of NAPL floating on the water table or confined there by capillary pressure, as indicated by mathematical modeling and by bench-scale soil vapor stripping experiments.

INTRODUCTION

The clean up of Superfund and other hazardous waste sites in the United States and elsewhere is proving to be a task of awesome proportions and cost. Many of these sites involve volatile hydrophobic organics (hydrocarbons, chlorinated solvents) which are well adapted to removal by soil vapor stripping (vacuum extraction). This *in-situ* method has proved to be both effective and low in cost at a number of sites, and is coming into fairly common use. This paper continues our work in the development of mathematical models for soil vapor stripping in a variety of situations. Here we address the vapor stripping of nonaqueous phase liquid (NAPL) from pools floating on the water table underlying the vadose zone and the diffusion of some common organic solvents through porous media. Much of the soil

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vapor stripping literature is not conveniently accessible, so we include a review of the literature, focusing particularly on recent developments. This is followed by sections on the diffusion of VOC from an underlying pool into advecting soil gas in the vicinity of a vacuum well, on the measurement of diffusion constants for a number of VOCs in porous media, and on soil vapor stripping with a laboratory-scale apparatus simulating a vapor extraction well.

LITERATURE REVIEW

Much of the early work in soil vapor stripping is discussed in publications of the American Petroleum Institute (API); these are described in a recent listing available from API (*1*). Hutzler, Murphy, and Gierke (*2*) published a fairly recent comprehensive critical review of soil vapor extraction which provides an excellent introduction to the subject.

A pilot-scale vapor stripping operation near Tacoma, Washington, has been described by Woodward-Clyde Consultants (*3*). Anastos et al. (*4*) discussed a pilot study of the removal of trichloroethylene and other compounds at the Twin Cities Army Ammunition Plant, Minnesota, and Bailey and Gervin (*5*) described a pilot study of the vapor stripping of chlorinated solvents. Lord (*6*) 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 (*7*). Mutch et al. (*8*) described pilot vapor stripping work at a site in eastern New Jersey, including an experimental demonstration of the effects of a highly stratified permeability on the soil gas pressure distribution. Baehr, Hoag, and Marley (*9*) described the application of soil vapor stripping to removal of gasoline from a contaminated site, and found that the results supported the quite optimistic assessment provided by lab-scale work and mathematical modeling of the process; we shall have more to say about this paper below.

Dalfonso and Navetta (*10*) discussed the use of biologically enhanced stripping to decontaminate a soil stockpile contaminated with kerosene, bunker oil, and solvents; the presence of an ample oxygen supply facilitates the growth and metabolism of hydrocarbon-consuming microorganisms. A preliminary report by Fall et al. (*11*) on vapor stripping unleaded fuels from soils contaminated by leaking underground storage tanks is of particular interest. Removal rates of gasoline averaged 7.2 gal/h, and the authors have convincingly demonstrated (by reductions in soil gas oxygen levels and increases in soil gas carbon dioxide) that enhanced biological degradation of these hydrocarbons accounted for roughly 30% of the removal rate. These authors also found that they could maintain gasoline vapor concentrations at combustible levels in the effluent soil gas by operating the well intermittently—8 h on and 16 h off. This indicates the importance of diffusive mass transport. Hinchee and collaborators explored the extent to which biodegradation of organics in soils is enhanced by vapor stripping operations (*12*, *13*); this looks very promising in some situations.

At a recent EPA workshop, Sterrett (*14*) presented extensive field results from a vapor stripping operation for the removal of 1,3-dichloropropene (DCP) from a spill site in Arizona. In 6 months of operation some 90,000 lb of DCP were removed and a quite extensive set of data was accumulated. Moisture increased the removal rate markedly, and Sterrett noted that diffusion of DCP from zones of low permeability was an important factor in mass transfer. Also at this workshop, Kreamer (*15*, *16*) described field work on the use of tracer gases for measuring tortuosity and sorption-affected gaseous diffusion transport, both of major importance in soil vacuum extraction. Michaels (*17*) published a technology evaluation report on Terra Vac's *in-situ* soil vacuum extraction operation at Groveland, Massachusetts, and Lyman and Noonan (*18*) discussed soil vacuum extraction in connection with underground storage tank remediation technologies.

Danko and coworkers (*19*, *20*) examined the applicability and limitations of SVE, and published a discussion of an SVE operation at a Superfund site in Michigan (*21*). Trowbridge and Malot (*22*) published a discussion of the use of catalytic oxidation as a means of VOC control in soil vapor stripping operations; Terra Vac's experience indicates that the new base metal oxide catalysts permit the destruction of chlorinated compounds which poison precious metal catalysts. It appears that this represents a quite significant development, given the high costs of VOC control by means of activated carbon.

We next turn to the literature on mathematical modeling. We developed mathematical models for lab column and field-scale soil vapor stripping, and we described the use of lab column data with the lab column model to get effective Henry's constants for the field-scale model. These models were used to interpret preliminary data from a set of pilot-scale wells being operated by Terra Vac at a site near Philadelphia, and were also used to model a worst reasonable case scenario to assess the time which would be required to clean up the site (*23*). The model was also used to explore the effects of well depth, gas flow rate, packed well radius, spacing between the wells, and effective Henry's constant on the progress of clean up. Soil gas velocity fields were calculated by the method of images.

This model was later modified to permit modeling of vapor stripping by a well in the presence of an overlying coaxial impermeable cap; these caps increase the rate of clean up significantly, and the results also indicate the feasibility of vapor stripping underneath buildings, parking lots, streets, etc. The effects of evaporative cooling on vapor stripping were investigated and found generally not to be significant (*24*). Another group of modifications permitted the inclusion of passive vent wells in the model and allowed a rough assessment of the feasibility of vapor stripping underlying nonaqueous phase liquid (NAPL) floating (or confined by capillary pressure) on top of the water table. Passive vent wells were found to be of less than marginal utility for some (but not all) geometries, and the model suggests the feasibility of removing pooled NAPL underlying the vadose zone; the occurrence of such NAPL pools is fairly common at these sites (*25*).

Methods for calculating soil gas pressures in the vicinity of a vapor stripping well when the permeability is anisotropic and varies with depth were described by Mutch and Wilson (*26*). These pressures were then used to calculate soil gas velocity fields and to model soil vapor stripping in such anisotropic and variable media. Mutch et al. (*27*) found that the model provided an excellent fit to the piezometer data obtained at a site in New Jersey at which the top meter of soil was mainly clay; the underlying material was very permeable sand. The effect of the low permeability layer was to greatly extend the lateral range of influence of the vacuum well.

Wilson et al. (*28*, *29*) developed lumped parameter models (lab column and vapor stripping well) for describing the vapor stripping of volatile organics from fractured bedrock and other highly heterogeneous media. [Our previous models have all included the assumption of local equilibrium between the contaminant in the stationary phase(s) and the contaminant in the vapor phase.] In such highly heterogeneous systems the contaminant must be transported by diffusion from the interiors of the blocks of low permeability out into the fracture zones (or other network of high permeability material) before it can be removed by the advecting soil gas. This diffusion process may be rate-limiting; an example of such a situation is provided by Fall's (*11*) data on the effect of an on–off duty cycle on soil gas composition at the Burbank, California, site mentioned above. Rodriguez-Maroto and Wilson later used the steady-state approximation for the vapor phase in the development of a model for diffusion-controlled soil vapor extraction which computes much more rapidly than our earlier model, thereby allowing a more detailed exploration of the effects of model parameters (*30*). Gomez-Lahoz, Rodriguez-Maroto, and Wilson examined the effects of variable permeabilities on soil vapor stripping rates, including the effects of varying soil moisture content and the presence of impermeable clay lenses (*31*). These workers also explored the effects of system geometry on soil vapor extraction efficiency (*32*). Much of the work described above is discussed in conference preceedings (*27*, *33*–*35*).

Baehr, Hoag, and Marley (*9*) published a mathematical model for soil vapor stripping in a lab column and from a single vacuum extraction well. Their model, like most of ours, assumes axial symmetry; it also assumes local equilibrium. They were able to field test their model at the site of a leaky gasoline service station tank; the details of the site were described by Hoag and Cliff (*36*). They noted that the complex composition of gasoline precludes the use of the data obtained for the precise validation of their model, but the success predicted by the model was in fact borne out by the actual recovery of virtually all of the contaminant and by the results of soil gas analyses. They noted that the success of a vapor stripping operation depends primarily on the ability of the system deployed to induce a significant airflow field that intersects the contaminant distributed in the unsaturated zone. Marley and associates at Vapex published on the use of models, particularly for air flow, in the evaluation of soil properties and the design of SVE systems (*37*, *38*). Kuo, Aieta, and Yang (*39*) recently presented a two-dimensional model for estimating the effective radius of influence of a vacuum well in soil vapor extraction.

At the EPA workshop on soil vapor stripping mentioned above, Cho (*40*) presented a model for vapor stripping in a lab soil column, and he also reported on the use of the method of images for calculating pressure distributions and air velocities in the vicinity of multiple well installations. Sykes (*41*, *42*) presented a very detailed and sophisticated model for the transport of volatile organics in variably saturated media; this appears to be an excellent model for the natural evolution of VOC plumes in both the vadose and the unsaturated zone. It does not include the effects of a vapor stripping well. Kemblowski et al. (*43*) presented radial one-dimensional models for screening sites for the feasibility of vapor stripping. These include mass transfer from underlying LNAPL (light nonaqueous phase liquid) and are designed to handle multicomponent mixtures. The models assume local equilibrium and constant soil characteristics.

Johnson et al., (*44*) recently published modeling methods for the clean up of soils contaminated with hydrocarbon mixtures; this paper includes a method for estimating the time required for the gas flow field to achieve a steady state under the influence of a vacuum well, as well as a number of other useful tools. Stephanatos (*45*) also carried out soil vapor extraction modeling. DiGiulio, Cho, Dupont, and Kemblowski (*46*) proposed field tests for the evaluation of soil vapor extraction (SVE). Of particular interest is their scheme for assessing the extent to which an SVE operation may be kinetically controlled by either diffusion or desorption. This involves the isolation of a domain in the vicinity of the vacuum well by means of suitably placed passive vent wells, vapor stripping, and then observing the extent to which soil gas concentrations recover after the vacuum well has been shut down. SVE models including diffusion and/or desorption kinetics are well-suited to extracting the necessary rate parameter(s) from such data. Johnson and coworkers also recently examined the design, operation, and monitoring of *in-situ* SVE systems; they made extensive use of modeling in this analysis (*47*).

We now turn to lab-scale work on soil vapor stripping. Wootan and Voynick described work on the vapor stripping of gasoline from a large-scale simulated sand aquifer (*48*). Clarke reported on the vapor stripping of a number of hydrocarbon and chlorinated solvents in lab columns (*49*). This work is of particular interest because the matrix, which was very wet and contained large quantities of old septic tank waste in addition to the organic solvents, was particularly unfavorable for vapor stripping. Nevertheless, Clarke was able to demonstrate successful vapor stripping of these compounds. The work of Baehr, Hoag, and Marley (*9*) mentioned above is of particular interest in that it combines lab column work with mathematical modeling and a successfully completed field application.

Eckenfelder, Inc., carried out a number of lab column vapor stripping tests at several sites in connection with vapor stripping feasibility studies (*50*). Davies (*51*) showed that dehydrated soils are powerful adsorbents for VOCs; water, however, tends to displace these from sorption sites on mineral soils—the so-called wet dog effect. He presented extensive data on the sorption of chlorobenzene in soils of varying moisture content. Bouchard (*52*) reviewed the role of sorption in contaminant transport during vapor stripping. Subsoils are generally very low in natural organic carbon, in contrast to topsoils. Column breakthrough curves often exhibit the tailing expected with diffusion mass transfer limited behavior, so the assumption of local equilibrium is often less than perfect. He noted the possible damaging impact of anthropogenic immobile organic carbon. Reible (*53*) reported that the BET isotherm was a good representation for vapor adsorption on subsoils; this was supported by data on chlorinated benzenes and dieldrin. He concurred that very significant reduction in soil sorption of VOCs is observed as the soil moisture content increases.

Hutzler and his group (*54*) carried out mathematical modeling of the movement of VOCs in unsaturated soil columns. The model includes advection in air and water, dispersion in air and water, air–water mass transfer and equilibrium, diffusion in immobile water, mass transfer between mobile and immobile water, and sorption. The model was tested against column experiments with trichloroethylene; columns were packed with sand or uniformly sized clay aggregates.

Recent work by Thibodeaux and collaborators (*55*) deals with the adsorption of five VOCs (benzene, dichloropropane, methylcyclohexane, ethyl ether, and methanol) on four types of dry soils. They concluded that adsorption of VOCs by dry soils is quite considerable and is dominated by mineral adsorption. Their adsorption isotherms were markedly nonlinear and could be fit by the BET isotherm equation. Valsaraj and Thibodeaux also reviewed the equilibrium adsorption of chemical vapors on soils (*56*); they found that adsorbed nonpolar VOCs tend to be displaced by moisture and that an extended BET isotherm provides an adequate description of the adsorption process in dry, damp, and wet soils.

Diffusivities and dispersivities are important parameters in modeling vapor stripping from highly inhomogeneous media (such as fractured bedrock) and in modeling vapor stripping of underlying NAPL. Scheidegger's (*57*) formulas for calculating longitudinal and transverse dispersivities seem to be well established; these are

$$D_{\text{long}} = D_{\text{mol}} + 1.75\delta v \tag{1}$$

$$D_{\text{trans}} = D_{\text{mol}} + 0.055\delta v \tag{2}$$

Here D_{mol} = molecular diffusivity in the porous medium, m^2/s
δ = grain size parameter, m
v = linear gas velocity, m/s

Methods for estimating diffusivities in porous media have been developed; Jury and Valentine (*58*) regard the tortuosity model of Millington and Quirk (*59*) as probably the most satisfactory. This relates the diffusivity of a volatile chemical in the soil to its diffusivity in air.

$$D_{\text{soil}} = \frac{(\nu - \theta)^{10/3}}{\nu^2} D_{\text{air}} \tag{3}$$

where ν = total soil porosity, dimensionless
θ = specific moisture content, dimensionless

Thibodeaux and coworkers (*60*) used this expression in modeling chemical vapor losses from landfills.

Jury (*61*) noted that there is a high degree of vertical and lateral variability in virtually all the parameters characterizing soil transport processes. This requires that any vapor stripping model be used with a rather detailed sensitivity analysis. We note that random variations in the permeability can be included in the form of Fourier series; this allows one to obtain appropriate spatial correlation. Another approach is to introduce domains into the region of interest in which the permeability is higher and/or lower than in the general matrix. Permeability measurements typically show a log normal distribution (*62*). Sets of permeability data typically show correlation lengths which depend rather strongly on the measurement spacing. This suggests that there is a rather wide range of wavelengths contributing to the Fourier series used to represent the random component of the variation in the permeability.

VAPOR STRIPPING OF UNDERLYING NAPL

Theoretical

We consider the evaporation of NAPL from a plane surface underlying the vadose zone into the vadose zone. The evaporated VOC is then swept away by a constant, uniform flow of soil gas, such as would be generated in the vicinity of a vapor stripping well. We wish to estimate the rate of removal of the NAPL. The geometry and boundary conditions are indicated in Fig. 1. The equilibrium vapor concentration C_0 (kg/m^3) is given in terms of the vapor pressure by

$$C_0 = [0.01603(\mathrm{MW})/T]P_0(T) \tag{4}$$

where (MW) = molecular weight, g/mol
T = temperature, °K
$P_0(T)$ = equilibrium vapor pressure at temperature T, torr

Let

v = soil voids fraction
b = thickness of vadose zone, m
v_x = soil gas linear velocity, m/s
D_x = longitudinal dispersivity, m^2/s
D_y = transverse dispersivity, m^2/s

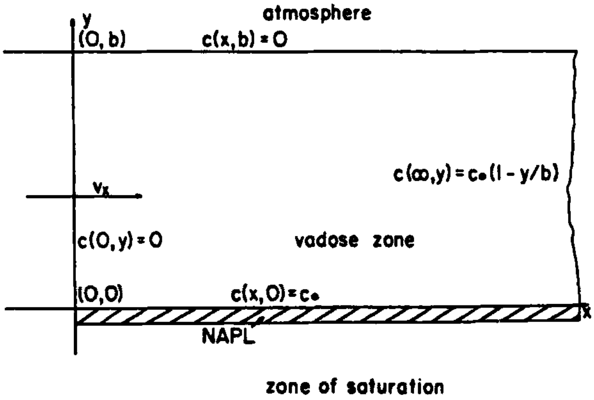

FIG. 1. Model for vapor stripping of LNAPL underlying the vadose zone.

The steady-state advection-dispersion equation for the system is

$$D_x \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} + D_y \frac{\partial^2 c}{\partial y^2} = 0 \tag{5}$$

with boundary conditions (from Fig. 1)

$$c(x,b) = 0 \tag{6}$$

$$c(0,y) = 0 \tag{7}$$

$$c(x,0) = C_0 \tag{8}$$

$$\lim_{x \to \infty} c(x,y) = C_0(b - y)/b \tag{9}$$

Equation (5) is solved by separation of variables; one assumes that

$$c(x,y) = C_0(b - y)/b + \sum_{\lambda} X_\lambda(x)Y_\lambda(y) \tag{10}$$

This gives

$$0 = D_x \frac{X_\lambda''}{X_\lambda} - v_x \frac{X_\lambda'}{X_\lambda} + D_y \frac{Y_\lambda''}{Y_\lambda} \tag{11}$$

which splits to yield

$$Y_\lambda'' + \frac{\lambda}{D_y} Y_\lambda = 0 \tag{12}$$

and

$$D_x X_\lambda'' - v_x X_\lambda' - \lambda X_\lambda = 0 \tag{13}$$

The solution to Eq. (12) is

$$Y_\lambda = A_\lambda \sin\sqrt{\frac{\lambda}{D_y}}y + B_\lambda \cos\sqrt{\frac{\lambda}{D_y}}y \tag{14}$$

Equation (8) requires that the $B\lambda$ vanish, and Eq. (6) requires that

$$\sin\sqrt{\frac{\lambda}{D_y}}b = 0$$

which yields

$$\lambda = \lambda_n = D_y\left(\frac{n\pi}{b}\right)^2, \qquad n = 1, 2, \ldots \tag{15}$$

so

$$Y_\lambda = Y_n = A_n \sin(n\pi y/b) \tag{16}$$

Equation (13) is solved by the usual exponential substitution; the characteristic equation is

$$D_x m^2 - v_x m - \lambda_n = 0 \tag{17}$$

which yields

$$m_n^{\pm} = \frac{v_x \pm [v_x^2 + 4D_xD_y(n\pi/b)^2]^{1/2}}{2D_x} \tag{18}$$

We see that $m_n^+ > 0$ and $m_n^- < 0$ for all $n = 1, 2, 3, \ldots$; to avoid exponentially increasing solutions, we must drop the solutions $\exp(m_n^+ x)$. Our solution is therefore

$$c(x,y) = C_0(b - y)/b + \sum_{n=1}^{\infty} A_n \exp(-m_n x) \sin(n\pi y/b) \tag{19}$$

where

$$m_n = \frac{v_x}{2D_x}\left[\left(1 + 4D_xD_y\left(\frac{n\pi}{v_x b}\right)^2\right)^{1/2} - 1\right]$$

We must choose the A_n to satisfy Eq. (7), which yields

$$-C_0(b - y)/b = \sum_{n=1}^{\infty} A_n \sin(n\pi y/b) \tag{20}$$

Multiplying by sin $(m\pi y/b)$ and integrating from 0 to b yields

$$A_m = -2C_0/m\pi \tag{21}$$

so finally we have

$$c(x,y) = C_0(b - y)/b - \frac{2C_0}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\exp(-m_n x)\sin(n\pi y/b) \tag{22}$$

for the concentration distribution above the pool of NAPL.

We next calculate $F(x)$, the total contaminant flux through a vertical surface normal to the direction of gas flow, extending from $y = 0$ to $y = b$, and 1 m wide. This is given by

$$F(x) = \int_0^b \nu v_x c(x,y)dy \tag{23}$$

Substitution of Eq. (22) into Eq. (23) and integration then yields

$$F(x) = \frac{\nu v_x C_0 b}{2}\left[1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2i+1)^2}\exp(-m_{2i+1}x)\right] \tag{24}$$

where

$$m_{2i+1} = \frac{v_x}{2D_x}\left\{\left[1 + 4D_xD_y\left(\frac{(2i+1)\pi}{v_x b}\right)^2\right]^{1/2} - 1\right\} \tag{25}$$

One can modify the model by requiring that there be an impermeable barrier at the top of the vadose zone. In this second case, Eq. (6) is replaced by

$$\frac{\partial}{\partial y}c(x,b) = 0 \tag{26}$$

and the problem is solved very much as before. Under these conditions Eq. (9) must be replaced by

$$\lim_{x\to\infty} c(x,y) = C_0 \tag{27}$$

The trial form of the solution is then

$$c(x,y) = C_0 + \sum_{\lambda} X_\lambda(x) Y_\lambda(y) \tag{28}$$

which eventually gives

$$c(x,y) = C_0 + \sum_{n=1}^{\infty} A_n \sin\left[\frac{(2n-1)\pi y}{2b}\right] \exp(-M_n x) \tag{29}$$

where

$$M_n = \frac{v_x}{2D_x}\left\{\left[1 + 4D_x D_y\left(\frac{(2n-1)\pi}{2bv_x}\right)^2\right]^{1/2} - 1\right\} \tag{30}$$

The Fourier coefficients A_n are calculated from the requirement that

$$-C_0 = \sum_{n=1}^{\infty} A_n \sin\left(\frac{(2n-1)\pi y}{2b}\right) \tag{31}$$

which yields

$$c(x,y) = C_0 - \frac{4C_0}{\pi}\sum_{n=1}^{\infty}\frac{1}{2n-1}\sin\left(\frac{(2n-1)\pi y}{2b}\right)\exp(-M_n x) \tag{32}$$

The flux is calculated as before; the result is

$$F(x) = \nu v_x C_0 b\left[1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\exp(-M_n x)\right] \tag{33}$$

The equilibrium vapor pressures P_0 of liquids depend strongly on the temperature, while their solubilities in water vary much more slowly. A commonly used equation for the variation of P_0 with temperature is

$$\log_e P_0(T) = A - \Delta H/RT \tag{34}$$

Values of A and ΔH for a number of VOCs are given in Table 1. Equation (4) can then be used to calculate vapor concentrations C_0 (kg/m^3) for these VOCs at various temperatures. These are shown in Table 2. If the soil temperature in the vadose zone is known, one can interpolate in this table to get the desired value of C_0.

TABLE 1
Vapor Pressure Parameters for Some Common Organic Solvents[a]

$$\log_e P_0(T)\ (\text{torr}) = A - \frac{\Delta H}{R} \cdot \frac{1}{T}$$

Solvent	A	ΔH (J/mol)
Benzene	18.05	33,500
Toluene	18.60	38,000
p-Xylene	18.70	41,100
n-Hexane	18.55	33,600
n-Heptane	18.68	37,000
n-Octane	19.01	40,700
C_2HCl_3	18.32	34,800
C_2Cl_4	18.50	38,700
CH_3CCl_3	18.32	33,600
CCl_4	18.33	33,900
C_6H_5Cl	18.57	40,000

[a]Calculated from data taken from Ref. *63*.

Results

Preliminary measurements of the rate of loss of hexane by evaporation through fine sand gave a value for the molecular diffusivity of hexane in this medium of $2.6 \times 10^{-6}\ m^2/s$. (Diffusivity measurements will be discussed in detail later in this paper.) If one assumes a soil grain size δ of 0.1 cm and a soil gas velocity of 0.1 m/s, Scheidegger's formulas (Eqs. 1

TABLE 2
Equilibrium Concentration for the Vapors of some Common Organic Solvents

	C_0 (kg/m^3)			
Solvent	10°C	15°C	20°C	25°C
Benzene	.201	.253	.316	.391
Toluene	.0610	.0793	.102	.130
p-Xylene	.0208	.0276	.0364	.0475
n-Hexane	.351	.442	.550	.666
n-Heptane	.110	.141	.181	.230
n-Octane	.0361	.0479	.0630	.0815
C_2HCl_3	.256	.325	.409	.511
C_2Cl_4	.0737	.0960	.125	.161
CH_3CCl_3	.432	.544	.679	.839
CCl_4	.443	.559	.700	.869
C_6H_5Cl	.0309	.0408	.0533	.0690

TABLE 3
Model Parameters Used for Vapor Stripping Underlying NAPL

Soil thickness, b	0.5 m
Soil gas velocity, v_x	0.1 m/s
Longitudinal dispersion coefficient	1.78×10^{-4} m^2/s
Transverse dispersion coefficient	8.1×10^{-6} m^2/s
Number of terms in Fourier series	100
C_0	0.666 kg/m^3
Porosity, ν	0.2

and 2) yield for the longitudinal dispersivity D_x a value of 1.78×10^{-4} m^2/s and for the transverse dispersivity D_y a value of 8.1×10^{-6} m^2/s. Values of these and other parameters required by the models for vapor stripping of underlying NAPL are given in Table 3.

It was found that the values of $c(x,y)$ obtained by the models were markedly dependent on the number of terms used in the series, exhibited oscillatory behavior, and were sometimes negative if large values of b (the vadose zone thickness) were used, particularly if the values of x were small. On the other hand, values of $c(x,y)$ were essentially independent of b as long as the values of x used were small enough that $c(x,y) \rightarrow 0$ for values of y significantly smaller than b. In most of our calculations we used a value of b of 0.5 m, with values of $x \leq 20$ m. Under these conditions the first model $[c(x,b) = 0]$ and the second model $[\partial c(x,b)/\partial y = 0]$ yield results which are virtually identical and which are independent of the exact value of b selected (0.35, 0.5, 1.0 m). Using large values of b and small values of y necessitates the evaluation of a Fourier series near a discontinuity, convergence of which is slow or (at the discontinuity) may fail altogether. This problem is avoided by using artificially small values of b which are still large enough that $c(x,b/2) = 0$ over the range of x of interest.

Plots of $c(x,y)/C_0$ versus y for $x = 1, 2, 5, 10$, and 20 m were calculated with the first model; these are shown in Fig. 2. Since $c(20,y) \rightarrow 0$ as $y \rightarrow 0.20$ m, a value of 0.5 m for b is sufficient. From these plots one can estimate the flux of contaminant being carried in the moving gas stream at a distance x downwind of the edge of the NAPL pool. We estimate this as follows. Take the boundary layer thickness $l(x)$ as the value of y for which $c/C_0 = 1/2$, and approximate the curve $c(x,y)$ as linear in y. Then the flux per meter is given approximately by

$$F(x) = v_x \nu l/(x) C_0 \qquad (35)$$

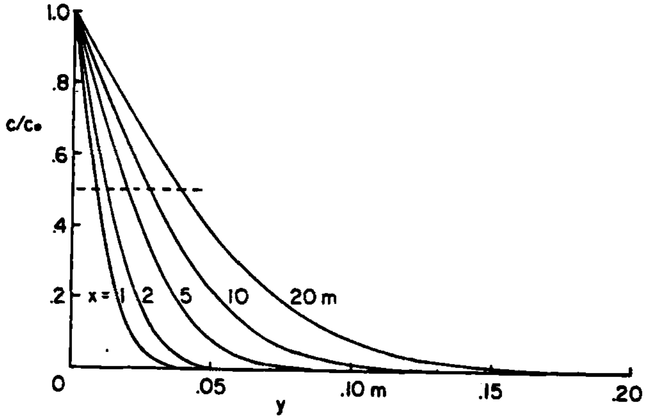

FIG. 2. Concentration profiles in the vadose zone the first 20 cm above the LNAPL pool at various distances x downwind from the edge of the pool. The boundary condition $c(x,b) = 0$ was used in this run. The parameters for the run are given in Table 3. Hexane at 25°C is being modeled in Figs. 2–5.

For hexane as 25°C, $C_0 = 0.666$ kg/m^3. From Table 3, $v_x = 0.1$ m/s and $\nu = 0.2$. From the plots in Fig. 2 we see that $l(5\text{ m}) = 1.87$ cm, $l(10\text{ m}) = 2.68$ cm, and $l(20\text{ m}) = 3.75$ cm. Substitution into Eq. (35) then yields

$$F(5\text{ m}) = 21.6\text{ kg/m day}$$

$$F(10\text{ m}) = 30.8$$

$$F(20\text{ m}) = 43.2$$

We can also calculate the flux exactly from Eq. (24). This is done by using the parameters in Table 3, and the result is plotted in Fig. 3. From Eq. (24) we obtain

$$F(5\text{ m}) = 26.11\text{ kg/m day}$$

$$F(10\text{ m}) = 36.92$$

$$F(20\text{ m}) = 52.19$$

indicating fairly good agreement between the estimate and the exact calculation.

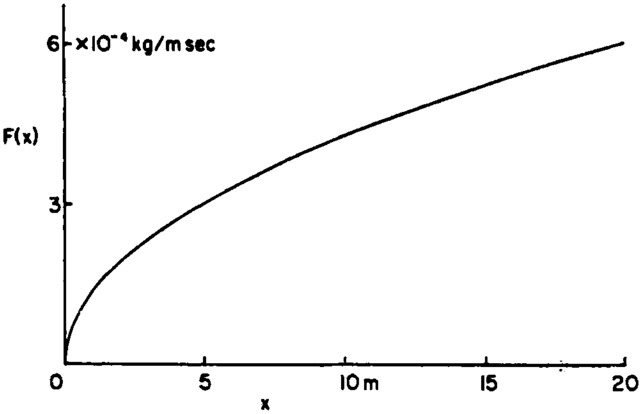

FIG. 3. Flux $F(x)$ of LNAPL evaporated from a pool of length x. Note: 10^{-4} kg/m·s = 8.64 kg/m·day. See Table 3 for the run parameters. $c(x,b) = 0$.

The second model, for which $\partial c(x,b)/\partial y = 0$, was used to calculate plots of $c(x,y)$ and $F(x)$ using the parameters given in Table 3. Plots of $c(x,y)/C_0$ versus y for $x = 1, 2, 5, 10$, and 20 m are shown in Fig. 4; a plot of $F(x)$ is given in Fig. 5. These curves are indistinguishable from those in Figs. 2 and 3, indicating the irrelevance of the boundary condition at the surface of the soil until solute has migrated up to that surface.

These fluxes are large enough to demonstrate the feasibility of vapor stripping underlying NAPL pools, provided that the vapor pressure of the

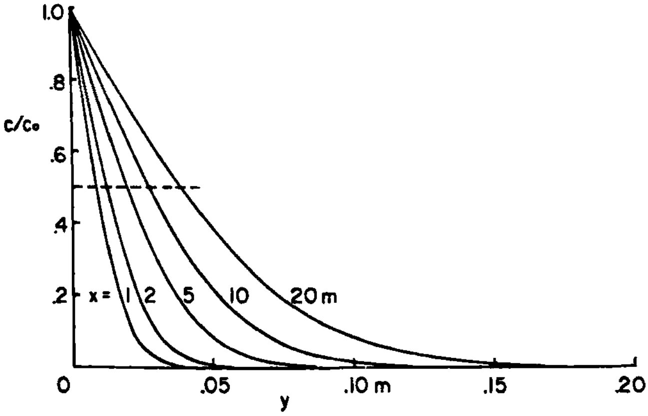

FIG. 4. Concentration profiles in the vadose zone in the first 20 cm above the LNAPL pool at various distances x downwind from the edge of the pool. The boundary condition $\partial c(x,b)/\partial x = 0$ was used here. Run parameters are given in Table 3.

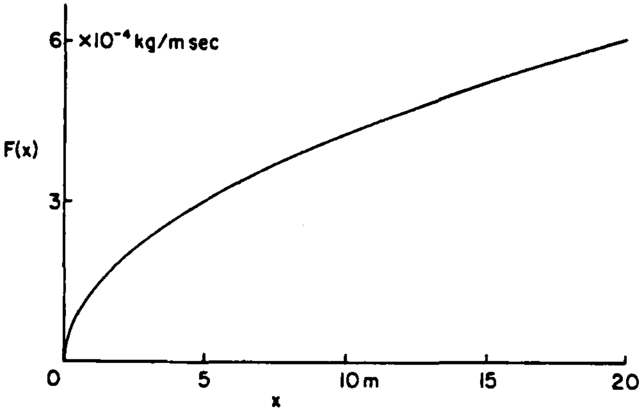

FIG. 5. Flux $F(x)$ of LNAPL evaporated from a pool of width x. The boundary condition $\partial c(x,b)/\partial x = 0$ was used. Run parameters as in Table 1.

VOC at the ambient temperature is high enough. In Eqs. (24) and (25), or Eqs. (30) and (33), one would not expect the dispersivities D_x and D_y to depend to any great extent on the identity of the NAPL being stripped. The only other term in these equations which depends on the identity of the NAPL is C_0, the equilibrium vapor concentration, given by Eq. (4). Table 2 lists these for 12 solvents over the temperature range 10 to 25°C. The lowest is that for *p*-xylene at 10°C, which is 0.0208 kg/m^3. This generates a worst case for the soil vapor stripping of these NAPLs. For *p*-xylene, we multiply the fluxes found for hexane by C_0(xylene, 10°C)/C_0(hexane, 25°C) = 0.0312 to get

$$F(5\text{ m}) = 0.81\text{ kg/m day}$$

$$F(10\text{ m}) = 1.15$$

$$F(20\text{ m}) = 1.63$$

Evidently even a solvent with as low a vapor pressure as *p*-xylene can be evaporated at a reasonable rate from a pool of NAPL underlying the vadose zone. Vapor stripping of the other 11 solvents will be more rapid than that of *p*-xylene. Fluxes for these can be calculated by the formula

$$F_M(x,T) = [C_{0M}(T)/C_{0\text{hexane}}(25°\text{C})]F_{\text{hexane}}(x,25°\text{C}) \tag{36}$$

DIFFUSIVITIES

Theory

The apparatus for measuring diffusivities in porous media is simply a tube with a reservoir at the bottom for the VOC and a screen and filter paper to support the porous medium above the liquid. See Fig. 6. Several tubes of inside diameter 1.9 cm and lengths ranging from 9.4 to 14.5 cm were used. All work was done at room temperature, about 25°C. The porous medium used usually was Fisher fine washed sea sand; in some runs this was sieved and various fractions were used.

The diffusivity of a VOC in a porous medium is determined with this apparatus as follows. Let $m(t)$ be the mass of liquid VOC contained in the tube at time t. Then

$$l_2(t) = l_3 - m(t)/\pi r^2 \rho \tag{37}$$

where ρ is the density of the VOC. We assume steady-state diffusion, so the total flux from the tube is given by

$$F = -dm/dt = \pi r^2 D_1 c_1 / l_1 \tag{38}$$

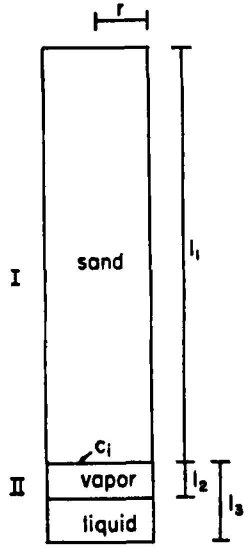

FIG. 6. Sketch of diffusion tube apparatus with notation. A wire screen and filter paper support the sand at the boundary between the porous medium and the underlying vapor.

Also,

$$-dm/dt = \pi r^2 D_2(C_0 - c_i)/l_2 \tag{39}$$

Here, c_i is the VOC concentration (g/mL) at the interface between Regions I and II, and C_0 is the equilibrium vapor concentration.

From Eq. (38):

$$c_i = Fl_1/\pi r^2 D_1 \tag{40}$$

which is substituted into Eq. (39) to yield, after rearrangement,

$$-\frac{dm}{dt}\left(\frac{l_1}{D_1} + \frac{l_2}{D_2}\right) = C_0\pi r^2 \tag{41}$$

Use of Eq. (37) then gives

$$-\frac{dm}{dt}\left(\frac{l_1}{D_1} + \frac{l_3}{D_2} - \frac{m}{\pi r^2 \rho D_2}\right) = C_0\pi r^2 \tag{42}$$

This can be integrated to give

$$\left(\frac{l_1}{D_1} + \frac{l_3}{D_2}\right)[m(t) - m_0] - \frac{m^2(t) - m_0^2}{2\pi r^2 \rho D_2} = -C_0\pi r^2 t \tag{43}$$

which can be used to calculate D_1. A somewhat simpler approach involves the replacement of m in Eq. (42) by $m_0/2$, which gives

$$\frac{l_1}{D_1} + \frac{1}{D_2}\left(l_3 - \frac{m_0}{2\pi r^2 \rho}\right) = -\frac{C_0\pi r^2}{(dm/dt)} \tag{44}$$

A plot of $-C_0\pi r^2/(dm/dt)$ versus l_1 then yields a straight line to a quite good approximation; the slope of the line is $1/D_1$. Equation (44) was used to interpret our diffusion tube data.

Experimental

The diffusion tubes were open-ended 19 mm (i.d.) tubes which were modified by making four small indentations around the circumference of each tube approximately 4.0 cm from the bottom. These indentations supported wire gauze screens upon which filter paper circles (Whatman #1) were placed to prevent the porous medium from falling into the neat test liquid below. Tubes varied in length from 9.5 to 14.5 cm, allowing depths of approximately 4.5 to 10.0 cm of porous medium to be used.

Fisher washed sea sand (Catalog #S25-500) was used as-is in most of the runs. Some runs were made with sieved sand to investigate the effects of pore size, and one run was made with a fine-grained air-dried soil consisting mainly of silica particles with some clay. Five common organic solvents (hexane, toluene, trichloroethylene, 1,1,1-trichloroethane, and tetrachloroethylene) were investigated. A top-loading electronic balance was used for all weighings; this was calibrated prior to each set of weighings.

Each experimental run was made with a set of six sample tubes ranging in length from 9.5 to 14.5 cm. Each contained 7 mL of pure neat liquid, which left an air space of about 0.5 cm between the surface of the sample liquid and the wire gauze/filter paper, and this air space prevented wicking of the liquid into the porous medium. Test liquid was pipetted into each tube through the wire screen. The filter paper was then placed on top of the screen and the porous medium was poured into the tube with continuous tapping in an effort to achieve uniform, reproducible compaction. The tubes were filled to the top with porous medium.

The weight losses of the tubes were then measured at 12- or 24-h intervals, at which times the ambient temperature was recorded. After completion of the run, the weight of each tube was plotted against time and the slope of the resulting line (d/mdt) was calculated by linear regression analysis of the data. The six calculated slopes were then substituted into Eq. (44) and plotted against the depth of the porous medium in the six tubes. The slope of the resultant linear plot was calculated by linear regression analysis; the diffusion constant in the porous medium is the inverse of this slope.

The effect of pore size on diffusion constant was studied by screening the Fisher sea sand into three grain size ranges; >420, 246–297, and 149–210 μm, and then making runs with these screened media. Hexane was used as the test liquid in these runs.

Bulk densities were measured by determining the weight of a 25-mL portion of sand packed in a 25-mL graduated cylinder by the same procedure used to pack the diffusion tubes. The resultant bulk densities were used to calculate the porosities of the sea sand and soil media by using the following relation:

$$\nu = 1 - \rho_B/\rho_G \qquad (45)$$

where ν is the porosity, ρ_B is the bulk density of the porous medium, and ρ_G is the density of the solid substance making up the porous medium, mainly quartz. The density of quartz was taken as 2.66 g/cm^3 (*63*). The porosities determined by this method ranged from 0.41 for the coarse- and medium-grained sands to 0.44 for the fine sand. The porosities for the mixed sand and the fine-grained silty soil were found to be 0.41 and 0.48, respectively.

Direct porosity measurements on the sand were made by determining the volume of the pores in a measured bulk volume of dry sample. A measured volume of distilled water, V_W, is added to a measured bulk volume of dry sand, V_B, in a 25-mL graduated cylinder, which was then stirred and compacted with a tamping rod to insure complete filling of all the pores by water. The volume of the water and sand, V_{W+S} was then read and the volume of the water subtracted from this total to give the volume of the sand, V_S. The fraction of the bulk volume occupied by the solid sand grains is then given by

$$F_S = (V_{W+S} - V_W)/V_B \tag{46}$$

and the porosity is given by

$$\nu = 1 - F_S \tag{47}$$

The porosities obtained in this way were 0.42 and 0.41 for the coarse- and medium-grained sands, respectively. The mixed and fine-grain sands were found to have equal porosities of 0.43. This technique could not be used on the fine-grained silty soil.

The porosities obtained by the two methods are given in Table 4.

Results

Regression analysis of the weight versus time plots yielded linear regression coefficients (r) of 0.999 or better for all five compounds. See Fig. 7.

TABLE 4
Porosities of Media Used in Diffusion Tube Experiments

Porous medium	Bulk density method	Direct method
Coarse-grained sand (>420 μm)	0.41	0.42
Medium-grained sand (246–297 μm)	0.41	0.42
Fine-grained sand (149–210 μm)	0.44	0.43
Mixed sand (<149 to >420 μm)	0.41	0.43
Fine-grained silty soil (<5 to >420 μm)	0.48	[a]

[a] Not determined by this method.

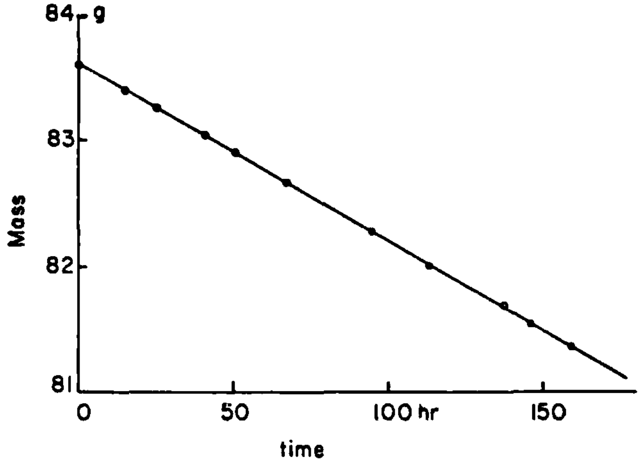

FIG. 7. Variation of diffusion tube mass with time. Diffusion tube porous medium length = 9.95 cm; VOC is hexane; the porous medium is coarse sand. r for this run = .99988.

The linear regression coefficients for the weight loss rate versus depth of porous medium were only slightly poorer (0.99 or better), probably due to the difficulty in obtaining an accurate measurement of l_1, the depth of the porous medium, and the variability of compaction from tube to tube. See Fig. 8.

Diffusivities of hexane (a mixture of isomers), toluene, tetrachloroethy-

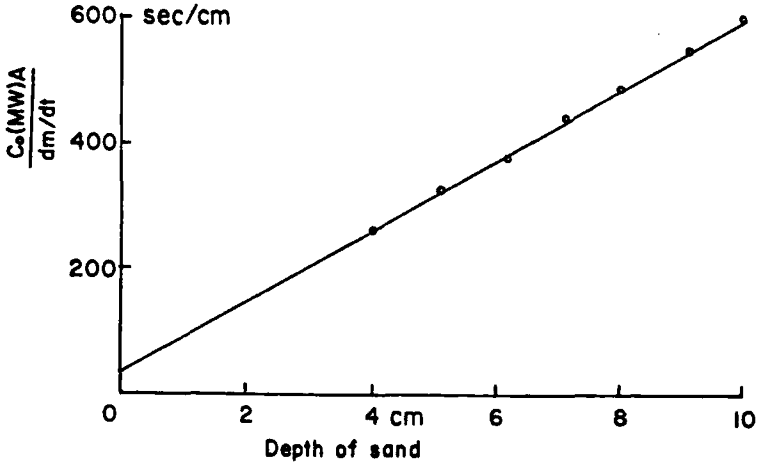

FIG. 8. Plot of $C_0(\mathrm{MW})A/(dm/dt)$ versus depth of sand column for toluene at 26.6°C. The slope of this line is the reciprocal of the diffusivity of toluene in this medium.

TABLE 5
Measured Diffusivities of VOCs in Unscreened Washed Sea Sand

Compound	Diffusion constant ($\times 10^{-6}$ m^2/s)	Temperature (°C)	Percent error
CH_3CCl_3	1.78	22.1	1.3
Toluene	1.93	26.6	1.6
Hexane	2.18	26.8	2.5
C_2Cl_4	2.42	26.6	3.1
C_2HCl_3	2.44	22.1	4.5

lene, trichloroethylene, and 1,1,1-trichloroethane were determined by the procedure just described. The results are given in Table 5. The percent error in the diffusion constants ranged between 1.28 and 4.47%. The effects of pore size (grain size) and porosity on diffusion constant are seen in Table 6. The hexane data do not indicate any substantial variation of diffusivity with sand grain size in the size range examined, in agreement with Millington and Quirk's formula. We note that the mean free paths of the solvent molecules are orders of magnitude smaller than the grain sizes and interstitial spacings in these media. The results indicate that one could use a value of the diffusivity of a nonadsorbing solvent of 2×10^{-6} m^2/s in sands and coarse media of similar porosity as a quite reasonable approximation.

Table 7 gives diffusivities for these compounds in nitrogen in porous media as calculated from the kinetic theory of gases and Millington and Quirk's formula (Eq. 3); Levine (*64*). These theoretical values are compared with our experimental results. Effective radii of the molecules were calculated from the densities of the liquids, assuming that the molecules approximate close-packed spheres. Millington and Quirk's formula (Eq. 3) was then used to calculate diffusivities; a porosity of 0.42 and a specific

TABLE 6
Effects of Medium Grain Size and Porosity on Diffusivity

Compound	Grain size (μm)	Temperature (°C)	Porosity	Diffusivity ($\times 10^{-6}$ m^2/s)
Hexane	>420	25.6	0.40	1.90
	246–297	25.6	0.41	1.99
	149–210	25.6	0.43	2.20
CH_3CCl_3	210–246	22.1	0.42	1.78
	<5 to >420	21.8	0.48	2.28

TABLE 7
Comparison of Experimental Diffusivities with Theoretical Values[a]

Compound	D, theoretical[c] ($\times 10^{-6}$ m^2/s)	D, experimental ($\times 10^{-6}$ m^2/s)	Difference (%)
CH_3CCl_3	2.24	1.78	−20.5
	2.59[b]	2.28	−12.0
Toluene	2.34	1.93	−17.5
Hexane	2.16	2.18	+0.9
C_2Cl_4	2.23	2.42	+8.5
C_2HCl_3	2.34	2.44	+5.6

[a] Experimental values for gaseous VOC in unscreened sea sand, porosity 0.43, moisture content assumed to be zero. Theoretical values calculated using gas-phase diffusivities of the VOCs in nitrogen, Millington and Quirk's formula [Eq. (3)], and a porosity of 0.43 unless otherwise noted.

[b] Experimental value for gaseous VOC in fine-grained silty soil. Theoretical value calculated as in Footnote *a* but using a measured porosity of 0.487 for the soil.

[c] Molecular weights and radii used in calculating theoretical diffusivities were as follows:

Compound	Molecular weight (g/mol)	Molecular radius ($\times 10^{-10}$ m)
Air	29	2.20
Hexane	86	3.37
Toluene	92	3.14
C_2HCl_3	131.4	2.98
C_2Cl_4	165.8	3.11
CH_3CCl_3	133.4	3.09

moisture content of the dry sand of zero were used. The results calculated from Eq. (3) are, on the average, 5.8% larger than the measured diffusivities. The agreement is certainly not perfect, but it is adequate to give one confidence in using either our experimental results or Eq. (3) for making estimates of diffusion rates in vapor stripping operations.

DETERMINATION OF LNAPL REMOVAL RATE BY LAB-SCALE SOIL VAPOR STRIPPING

Experimental

The apparatus used for lab-scale simulation of soil vapor stripping in the presence of underlying LNAPL (light nonaqueous phase liquid) was constructed as follows. A cylindrical Pyrex jar, 17.2 cm in diameter and 28.9 cm in height, was modified to provide it with a small collar about 3.7 cm above the bottom of the jar. A hardware cloth screen was placed on this collar, and an 18.5-cm circle of Whatman #1 filter paper was pressed down on top of the hardware cloth support. A thistle tube was inserted through the filter paper and the wire mesh screen to allow easy addition of liquid VOC to the lower (LNAPL pool) compartment of the apparatus. Air was withdrawn from the apparatus through a coarse frit airstone approximately 2.5 cm in length which was attached to a 29-cm piece of 8-mm glass tubing; the airstone could be placed at any desired level in the porous medium contained in the upper section of the jar.

An aquarium air pump (Whisper Model 1000, Willinger Bros., Inc., 49 Smith St., Englewood, New Jersey) was converted into a vacuum pump by sealing its case with Permatex clear RTV silicone adhesive so that the air pump's only air intake opening was the small hole in the rubber base. The silicone polymer valve of this air pump is resistant to attack by the VOCs to be used in this work. Airflow was regulated by means of a micrometer valve placed between the stripping well and the air pump. Airflow measurements were made with a soap-film flowmeter and a stopwatch. Flow rates used ranged from 25 to 500 mL/min.

The porous medium employed was a commercially available sand-gravel mixture (Quikrete all purpose sand) with particle sizes varying from fine dust to small pebbles over 1 cm in diameter. It was used as-is to fill the jar to a depth of approximately 18.7 cm. No shaking, settling, or compaction was employed. A diagram of the apparatus is given in Fig. 9.

The jar and its contents were placed on the pan of a Fisher Model XD-12K top-loading electronic balance, and the liquid VOC was introduced through the thistle tube to the LNAPL poor reservoir below the medium. Hexane was used in this study as the VOC. The thistle tube was then closed off with a small stopper.

A determination of the rate of VOC mass loss due to simple diffusion of VOC vapor through the medium was carried out first. For this, the vapor stripping well was clamped off just above the junction of the flexible tubing to the pump and the glass stripping well casing. The total weight of the apparatus and the hexane was determined immediately after addition of the liquid VOC and at intervals thereafter for 192 h.

In the vapor stripping runs the mass loss of the apparatus was monitored for shorter periods (<72 h) since the mass loss rate was greatly increased. The ambient temperature was recorded each time a weight measurement was made, and the average temperature during each run was calculated. Removal rates were calculated from the slope of linear regression fits of the weight versus time plots of the experimental data.

The porosity of the sand/gravel mixture was determined by the direct porosity method outlined previously. Since the mixture was quite hetero-

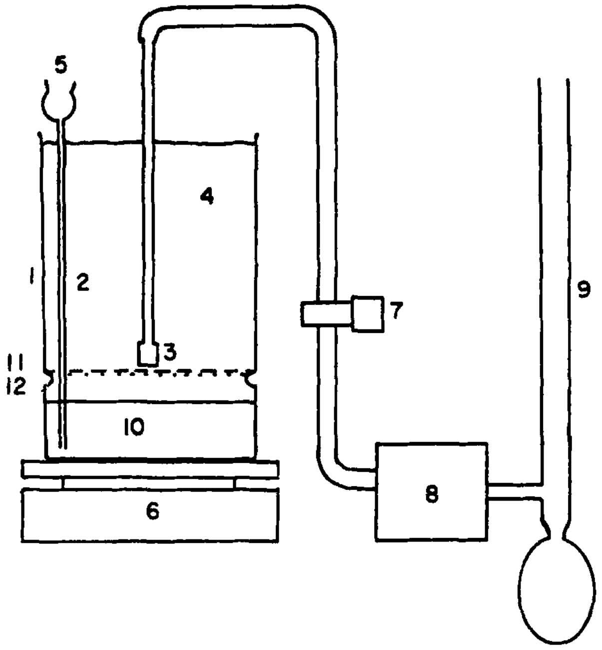

FIG. 9. Schematic of the lab scale soil vapor stripping apparatus. 1, Pyrex jar; 2, porous medium; 3, air stone; 4, vacuum well, clamped at the desired depth; 5, thistle tube for introducing VOC; 6, top-loading balance; 7, micrometer valve; 8, vacuum pump; 9, soap film flowmeter; 10, liquid VOC pool; 11, filter paper; 12, hardware cloth screen.

geneous, the bulk density method could not be used. The porosity was found to be 0.30, somewhat smaller than the values found for the more homogeneous sea sand. The presence of fine dust particles which fill the interstices between the larger sand particles and the presence of nonporous gravel components of the mixture make this result reasonable.

Wicking was observed in the porous medium overlying the liquid pool. When the apparatus was covered with aluminum foil and allowed to equilibrate, liquid phase was observed as high as 7.7 cm above the bottom of the porous medium. One can use this observation and the Kelvin equation to estimate an effective pore size for the dusty sand/gravel mixture. The Kelvin equation is

$$\log_e \frac{P(r)}{P_0} = -\frac{2\gamma \bar{V}}{rRT}$$

where P_0 = equilibrium vapor pressure of the VOC, dyn/cm
$\overline{V}$ = molar volume of VOC, cm^3
γ = VOC surface tension of VOC, dyn/cm
R = gas constant, 8.3145 × 10^7 ergs/mol·deg
T = temperature, °K
$P(r)$ = vapor pressure of VOC above a wetted capillary of radius r (cm), dyn/cm^2

The *CRC Handbook of Chemistry and Physics* gives for hexane λ = 18.43 dyn/cm, P_0 = 146.8 torr, density = 0.65937 g/mL (which yields a molar volume for hexane of 130.7 cm^3/mol). The capillary rise (wicking) can be used to determine the pressure decrease; this gives

$$\Delta P = \rho_{\text{hexane}} g h$$

where h = height to which wicking occurs, cm.

If one approximates

$$\log_e \frac{P(r)}{P_0} = -\frac{\Delta P}{P_0}$$

and substitutes into the Kelvin equation, solution for r gives

$$r = \frac{2\gamma \overline{V} P_0}{RT\rho g h}$$

Substituting h = 7.7 cm then yields a pore radius of 7.65 × 10^{-5} cm and an effective pore diameter of 1.53 × 10^{-4} cm.

Results

For the passive diffusion experiment, the observed removal rate after steady-state conditions were reached was 1.02 g/h, with a standard error of 0.01 g/h. A theoretical calculation of the removal rate at the average ambient temperature yielded a value of only 0.64 g/h if wicking was neglected. Including wicking results in a markedly increased VOC concentration gradient in the porous medium and thereby increases the calculated removal rate to 1.03 g/h, in good agreement with the experimental results.

A total of 11 soil vapor stripping runs were made; in these the air flow rate and the well inlet height above the bottom of the porous medium were varied. The results of these runs are given in Table 8. Linear regressions of plots of mass versus time yielded very good fits, with regression coef-

TABLE 8

Removal Rates of Underlying Hexane by Soil Vapor Extraction in the Laboratory-Scale Apparatus at Room Temperature

Air flow rate (mL/min)	Well inlet height above base of porous medium (cm)	Observed removal rate (g/h)	Calculated removal rate (g/h)
0	0	1.02	—
25	0	1.08[a,b]	1.48
50	0	1.90	2.22
100	0	2.55	2.79
285	0	4.21	4.58
500	0	5.96	6.32
100	2	1.86	1.56
300	2	3.29	2.78
100	4	1.84[a]	0.82
300	4	2.50	1.54
100	6	1.36[a]	0.46
300	6	1.85	0.93

[a] Formation of a saturated capillary fringe at the bottom of the porous medium due to the Kelvin effect. Removal rate calculated on the basis of the depth of unsaturated medium remaining.

[b] Possible nonsteady-state conditions during this run.

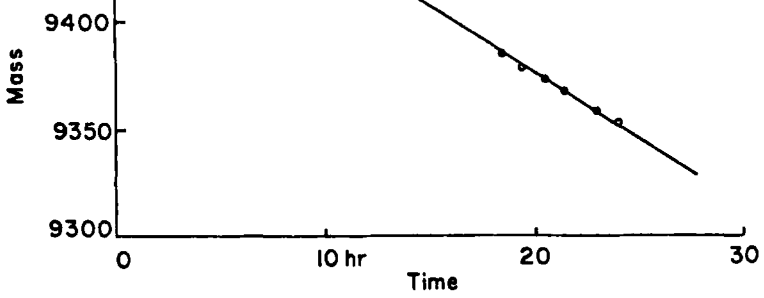

FIG. 10. Plot of mass loss of soil vapor stripping apparatus versus time. Gas flow rate = 500 mL/min; temperature = 22.2°C; VOC is hexane; the bottom of the air is just above the filter paper at the bottom of the porous medium.

ficients of 0.997 or better in all cases. Figure 10 shows a typical mass–time plot for an experimental run.

Maximum removal rate was achieved by the placement of the well inlet as close to the bottom of the porous medium as possible and by use of high volumetric airflow rates. Removal rates decrease considerably as the distance between the well inlet and the surface of the underlying LNAPL increases, by increasingly larger amounts as the volumetric air flow rate increases, as seen in Fig. 11.

The hexane concentration of the effluent soil gas was calculated from the observed VOC removal rate and the volumetric air flow rate. The ratios of this concentration to the saturation concentration (the concentration when the VOC is present at its equilibrium vapor pressure) are plotted against flow rate in Fig. 12. The results indicate that the hexane concentration in the effluent soil gas decreases from the equilibrium vapor concentration at low flow rates in a nonlinear fashion as the soil gas flow rate increases.

A comparison of the observed removal rates for hexane versus those predicted by use of the two-dimensional model developed earlier in this paper is shown in Table 8; agreement appears to be fairly good. When the placement of the well is such that the conditions of the model for soil gas movement (i.e., horizontally across the surface of the LNAPL pool) are

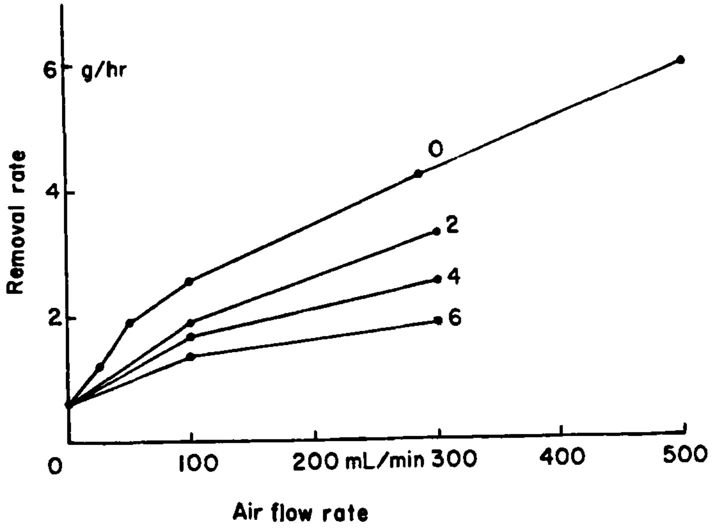

FIG. 11. Plots of VOC (hexane) removal rate versus air flow rate for various heights of the air stone above the bottom of the porous medium. The numbers by the plots are the distances between the bottom of the porous medium and the bottom of the air stone.

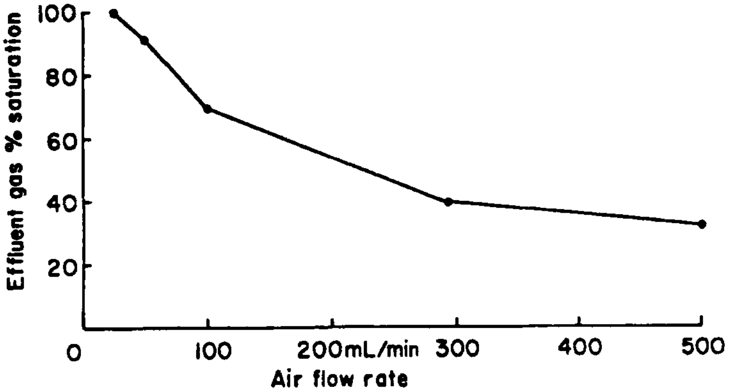

FIG. 12. Plot of effluent gas percent saturation (hexane) versus air flow rate. The bottom of the air stone is located immediately above the bottom of the porous medium.

nearly realized and the gas flow is sufficiently high to prevent the formation of liquid phase contaminant in the porous medium itself, the model overpredicts the observed removal rate by less than 10%. This should be quite adequate for feasibility studies and engineering design calculations. However, placement of the well inlet further above the saturated layer alters the streamlines and soil-gas flow across the LNAPL pool, reducing the accuracy of the model predictions, as evidenced by the comparisons between theoretical and observed results at well inlet heights of 2.0, 4.0, and 6.0 cm above the LNAPL reservoir.

CONCLUSIONS

The data and calculations presented here indicate that the removal of NAPL underlying the vadose zone by soil vapor stripping is feasible if the organic compounds are of sufficient volatility to make vapor stripping of the vadose zone itself a viable option. Wells should be placed so as to maintain the highest practicable soil gas velocity over the NAPL pool; this means that the wells should be drilled nearly to the water table and screened only near the bottom. Millington and Quirk's formula for estimating diffusivities in porous media gives results which range from 20.5% smaller to 8.5% larger than results obtained by diffusion tube experiments. The removal of DNAPL underlying a layer of water by vapor stripping is not practical because of the extremely slow rates of diffusion of the VOCs through the aqueous phase layer.

Vapor stripping experiments carried out in a small bench-scale soil vapor stripping apparatus with hexane yielded results which were in agreement with the theoretical model, provided that capillary wicking of the VOC is not taking place in the porous medium. If such wicking is occurring, the concentration gradient of VOC in the vicinity of the underlying pool is increased, and increased removal rates are typically observed.

Acknowledgments

We are indebted to Eckenfelder, Inc., and to the Water Resources Research Institute of the University of Tennessee for support of this work.

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