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Groundwater Cleanup by In-Situ Sparging. IX. Air Channeling Model for Nonaqueous Phase Liquid Removal

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ABSTRACT

A mathematical model is developed to simulate the removal of dissolved and nonaqueous phase liquid (NAPL) volatile organic compounds (VOCs) from contaminated aquifers by sparging. The model assumes that the sparging air moves through the aquifer in persistent channels and that NAPL must dissolve and move to these channels by diffusion and dispersion processes. The dependence of the model results on model parameters is explored, and practical implications for sparging well operation are discussed.

INTRODUCTION

In 1993 EPA indicated (1) that some 25.6 million yd^3 of contaminated soil, sediment, and sludge remains to be cleaned up at sites not yet covered by Records of Decision (RODs). Of those sites covered by RODs (712), 79% have contaminated groundwater which requires treatment and 76% are contaminated with volatile organic compounds (VOCs). Pump and treat operations, in use for many years, have been found to be miserably ineffective at most sites (2), due principally to severely limited mass transport by diffusion from porous domains of low hydraulic permeability, especially if dense nonaqueous phase liquids (DNAPLs) are involved. This has been discussed by a number of authors (3–11, for example).

In-situ air sparging (ISAS) was viewed as a solution to these problems when it was initially introduced (see Ref. 12, for example) and, indeed, results at quite a number of sites were very good. However, as more data on a broader range of sites became available, it was realized that the air flow within the aquifer was taking place through discrete channels rather than as isolated, independent, random bubbles. Mohr's (13) analysis of the mass transfer which could be expected with channeling was both convincing and pessimistic; if the distances between adjacent air channels were appreciable (of the order of a centimeter or more), one would have very severe diffusion-limited mass transport both of contaminant through the aqueous phase to the channels and of oxygen from the channels into the aqueous phase. Dahmani et al. (14) demonstrated the presence of air channels and argued that this implied that mass transfer rates would be limited by the kinetics of interfacial mass transfer (if NAPL is present) or by the rate of transport of contaminants from the bulk water phase to the air/water interface. They suggested the cycling of air sparging operations (pulsed air flow) and the placing of air injection points in identified homogeneous strata.

Johnson, Thomson, and Johnson (15) reported that experimental studies showed virtually no air-induced water circulation during sparging operations except under pulsed conditions; the water was essentially stagnant. Each pulse resulted in water movement of a few centimeters, in agreement with the results of numerical simulations. Payne et al. (16) reported results supporting Broersma's earlier conclusion that there were short-lived periods of water flow at startup and shutdown, with virtually no water flow during periods of steady operation. Their experimental study showed essentially no VOC removal during steady flow operation, but VOC removals of as much as 30% during the first 10 days of pulsed operation.

Chao and Ong (17) noted that "current knowledge on the long-term usefulness [of air sparging] and the understanding of the physical-chemical processes that occur in the subsurface during air sparging are lacking. Therefore, design of air sparging systems is empirical and is generally based on the experience of the engineer." They carried out a lab-scale sparging study of the removal of three chlorinated solvents and found evidence that the removal rate was related to the surface area of the water–air interface of the air channels, with diffusion also being limiting.

Leeson, Hinchee, and Vogel (18) carried out a field study of sparging in sand in shallow standing water, and demonstrated unequivocally that channeling was the mechanism by which the injected air migrated to the top of this quite porous and homogeneous medium. These results invalidate any modeling approach which does not explicitly include the effects of channeling and the associated diffusion/dispersion mass transport of both volatile/biodegradable organics and oxygen.

Wilson, Gómez-Lahoz, and Rodríguez-Maroto (19) published a mathematical model of in-situ air sparging which postulated that the injected air flowed in channels and that diffusion transport in the aqueous phase was necessary for VOC to be removed. They found that the mean distance between channels played a critical role in the rate of VOC removal, with removal rates decreasing drastically as the distance between channels increased. They suggested that pulsed operation be used to increase the effective diffusivities of dissolved solutes.

In the present paper we first discuss the theory of the impact of pulsed sparging on effective diffusivity in ISAS operations. This is followed by the development of a mathematical model for ISAS in which nonaqueous phase liquid (NAPL) droplets are present and in which the sparging air moves in channels through the aquifer. In this model, a straightforward extension of an earlier version (19), the effect of pulsed operation is included by selection of a suitably large effective diffusivity. The model development is followed by a section in which the results of some model calculations are presented and discussed. The paper closes with a summary of conclusions.

EFFECT OF PULSED OPERATION ON DISPERSIVITY

In the course of pulsed sparging, water is displaced away from the air channels as they are formed by the injected air, and then moves toward the air channels as these collapse when the air flow is shut down. We wish to estimate the impact of this on the effective diffusivities of solutes in the water.

Scheidegger (20) gives formulas for the longitudinal and transverse dispersivities in a porous medium; these are

$$D_L = D_{molec} + \alpha_L v \delta \tag{1}$$

$$D_T = D_{molec} + \alpha_T v \delta \tag{2}$$

where D_{molec} = molecular diffusivity, m^2/s
α_L = proportionality constant, about 1.73
α_T = proportionality constant, about 0.07
v = linear velocity of fluid, m/s
δ = grain size parameter, m

Generally, D_{molec} is very much smaller than the second term in Eqs. (1) and (2), and so can be neglected if desired.

Let us examine the movement of water in the vicinity of an air channel as the channel becomes established; the air channel, of radius a_c, and the surrounding saturated domain, of radius b_{ij}, are shown in Fig. 1. Consider a "particle" of water at a distance r_{init} from the axis of the domain at time

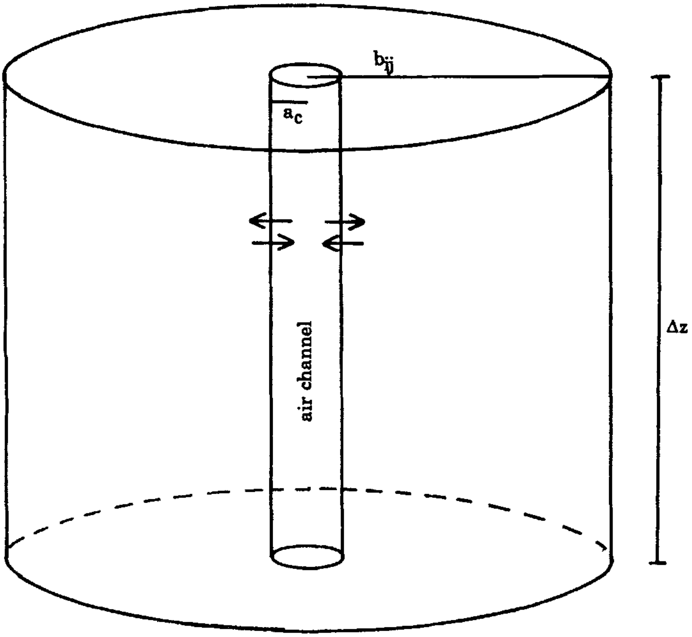

FIG. 1 Schematic of air channel "breathing" as the sparging gas is pulsed.

zero; as the air channel is established, this water is pushed back (away from the axis of the domain) a distance $\Delta r = r_{\text{fin}} - r_{\text{init}}$. Let the height of the domain be Δz. Then we have

$$\pi(r_{\text{init}}^2 + a_c^2)\Delta z = \pi r_{\text{fin}}^2 \Delta z \tag{3}$$

which gives

$$r_{\text{fin}} = (r_{\text{init}}^2 + a_c^2)^{1/2} \tag{4}$$

Generally we will have $r_{\text{init}} \gg a_c$, so Eq. (4) can be approximated as

$$r_{\text{fin}} - r_{\text{init}} = \Delta r = (1/2)a_c^2/r_{\text{init}} \tag{5}$$

which gives the distance the water moves in the time interval $(1/2)t_c$, where t_c is the length of the full duty cycle (on and off) of the sparging pulse. Then the mean velocity of the water normal to the channel axis as it recedes from the forming air channel is given by

$$v = 2\Delta r/t_c \tag{6}$$

Substituting for Δr from Eq. (5) then gives

$$v = a_c^2/r_{\text{init}}t_c \tag{7}$$

We then calculate the longitudinal component of the dispersivity by substituting for v from Eq. (7) into Eq. (1); this yields

$$D_{\text{L}} = D_{\text{molec}} + \frac{\alpha_{\text{L}}\delta a_c^2}{r_{\text{init}}t_c} \tag{8}$$

We do not bother with the transverse dispersivity, since this corresponds to movement parallel to the air channel and therefore does not carry material (oxygen or VOC) to or from the channel.

The initial value of r has a maximum value in any of the annular volume elements in the system; it is the effective radius of the domain surrounding an air channel at that point, denoted in Ref. 19 by b_{ij}. This quantity is shown in Ref. 19 to be given by

$$b_{ij} = (\pi K q_{ij})^{-1/2} \tag{9}$$

Substitution of b_{ij} for r_{init} in Eq. (8) gives the diffusivity which applies to the outermost and largest of the annular subvolume elements surrounding the air channel; the other subvolume elements have smaller values of r_{init} and therefore larger values of D_{L}. The quantity q_{ij} (mol/m^2·s) is the molar air flux and K (s/mol) is a proportionality constant relating the number of air channels per unit area to the molar gas flux.

Thus, the final formula for the aqueous phase dispersivity in the vicinity of an air channel is given by

$$D_{\text{L}} = D_{\text{molec}} + \frac{\alpha_{\text{L}}\delta a_c^2(\pi K q_{ij})^{1/2}}{t_c} = D_{ij} \tag{10}$$

For a given site (for which K and δ are fixed), one can increase the dispersivity by increasing the air flow rate (which increases q_{ij} and/or a_c) and by decreasing t_c, the length of the pulse duty cycle, provided that t_c is not decreased to the point where there is not sufficient time for essentially complete collapse of the air channels. Measurement of the time-dependence of groundwater mounding and collapse should permit one to optimize the durations of the air-on and air-off periods of the duty cycle. The air flow rate should be the maximum which can be achieved without loss of control to obtain maximum radius of influence and minimum t_c.

A number of questions arise in connection with pulsed operation. Some of these permit plausible speculation, while others appear unanswerable at present.

First, is pulsed operation likely to disturb the soil to the extent that air and water flow patterns will be changed? One would expect that pulsed operation might mobilize small quantities of fines, but that the forces involved should not disrupt the structure of the porous medium except perhaps within a few centimeters of the well screen, since these forces would have to be comparable to the force due to the mass of the column of overlying vadose zone soil.

Second, does the air flow used initially affect the number and distribution of persistent, long-term channels? The answer to this is apparently unknown, but could easily be determined experimentally.

Third, do occasional high-flow bursts open new air channels? Certainly they would be expected to do so during the duration of the burst. Whether or not many of these new channels would continue to function under conditions of lower flow rate is problematical, however, although this could readily be determined experimentally. If the answer to this question is affirmative, it would provide a method for rejuvenating a sparging system after the rate of VOC removal has tapered off.

A fourth question involves the extent to which pulsed multiple wells interact; should these be operated in-phase or out-of-phase? Local ground water movement around a system of sparging wells depends in part on the size of the gradients in hydraulic head in the vicinity. This suggests that out-of-phase operation of the pulsed wells would produce the most local ground water movement and therefore increase dispersion the most. Additionally, out-of-phase air injection should itself produce a lateral push-pull effect on the water between two injection wells as water is displaced by the injected air. Eckenfelder, Inc., is currently designing a multiple-well sparging system which will utilize phased pulsing of the wells.

Fifth, what is the effect of pulsed operation on the soil bacteria? The increased dispersion might increase the mobility of bacteria, and the shearing forces should be sufficiently slight at distances more than a meter or so from the well that they cause no damage.

The significant parameters over which the engineer has control in attempting to optimize a sparging operation are 1) well location, and length and depth of well screen with respect to the contaminated zone; 2) air pressure/air flow rate; 3) durations of the on and off phases of the pulse duty cycle; and 4) phases of well duty cycles if one has a multiple-well system. In addition, one may consider the use of nutrients to enhance biodegradation and/or hydrofracturing to improve the permeability of a tight structure.

MODEL FOR ISAS WITH NAPL AND AIR CHANNELING

We next turn to the development of a mathematical model for sparging which assumes that the injected air flows in channels and which includes both dissolved and NAPL VOC. The diffusion-controlled dissolution of NAPL droplets in the aquifer is addressed first. This is followed by development of the description of the transport of dissolved VOC by diffusion/dispersion from the bulk aqueous phase to the channels through which the injected air is moving. Advective transport of VOC in the moving air is then discussed. Finally, these phenomena are merged to form the sparging model. In an earlier model (19) we had included air-induced large-scale water circulation; Johnson et al. (15) have shown that this does not occur, so it is omitted from the present model.

Solution of NAPL Droplets

Solution of NAPL droplets/ganglia trapped interstitially in the aquifer is handled by representing these as spheres which dissolve by steady-state diffusion through a surrounding spherical boundary layer. See Fig. 2. A suitable solution to the steady-state diffusion equation in the boundary layer is given by

$$C(r) = A + B/r \tag{11}$$

where A and B are constants. The boundary conditions are

$$C(a) = C_s = A + B/a \tag{12}$$

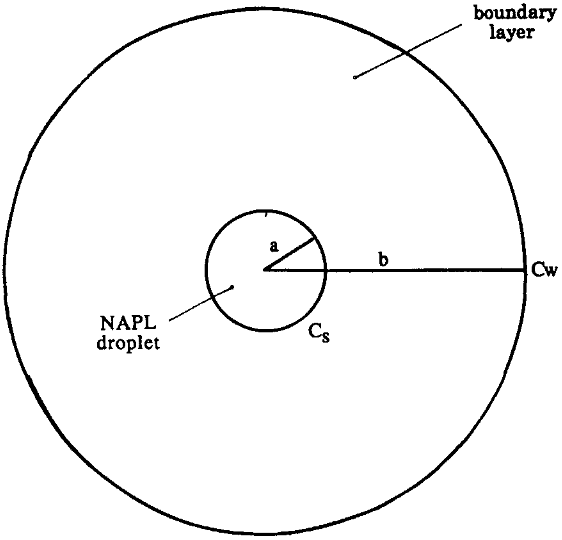

FIG. 2 Dissolving NAPL droplet and surrounding stagnant aqueous boundary layer.

and

$$C(b) = C^w = A + B/b \tag{13}$$

where a = radius of NAPL droplet at time t, m
a_0 = initial radius of NAPL droplet
$b - a$ = thickness of boundary layer, m
C_s = aqueous solubility of NAPL, kg/m^3
C^w = bulk VOC concentration, kg/m^3

It is readily shown that

$$B = (C_s - C^w)ab/(b - a) \tag{14}$$

so that

$$\frac{dC}{dr} = -\frac{(C_s - C^w)ab}{(b - a)r^2} \tag{15}$$

Let

m = mass of droplet at time t, kg
m_0 = initial mass of droplet
ρ_{voc} = density of NAPL

Then

$$m = 4\pi\rho_{\text{voc}}a^3/3 \tag{16}$$

$$m_0 = 4\pi\rho_{\text{voc}}a_0^3/3 \tag{17}$$

and

$$\frac{dm}{dt} = D\cdot 4\pi r^2\frac{dC}{dr} = -D\cdot 4\pi\frac{ab(C_s - C^w)}{b - a} \tag{18}$$

where D = diffusivity of the VOC, m^2/s.

Noting that $a/a_0 = (m/m_0)^{1/3}$ and rearranging Eq. (18) then yields

$$\frac{dm}{dt} = -\frac{4\pi D(C_s - C^w)a_0(m/m_0)^{1/3}}{1 - (a_0/b)(m/m_0)^{1/3}} \tag{19}$$

Let

C_0^N = initial concentration of NAPL, kg/m^3 of bulk porous medium
C^N = concentration of NAPL at time t, kg/m^3

Then the number of droplets per unit volume is given by

$$n = 3C_0^N/(4\pi\rho_{\text{voc}}a_0^3) \tag{20}$$

The rate of change of NAPL concentration is then given by

$$\frac{dC^N}{dt} = n\frac{dm}{dt} = -\frac{3C_0^N D(C_s - C^w)(C^N/C_0^N)^{1/3}}{\rho_{\text{voc}}a_0^2[1 - (a_0/b)(C^N/C_0^N)^{1/3}]} \tag{21}$$

In subsequent computer coding C^N and C^w will be triply subscripted to specify the location of the volume element (i,j) and the annulus within that volume element (k) within the system to which they pertain.

Note that concurrent biodegradation of dissolved VOC will increase the rate of solution of NAPL droplets by decreasing the value of C^w.

Diffusion of VOC to Air Channels

We model a single sparging well in a homogeneous, isotropic aquifer of porosity ν; the well is screened along a short section at the bottom. We use cylindrical coordinates R and z to describe the large-scale geometry, as shown in Fig. 3. The sparging air is assumed to move through the aquifer in persistent channels, with dissolved VOC moving from the surrounding aqueous phase to the border of an air channel by diffusion/dispersion. As indicated earlier, the diffusion/dispersion constant will be strongly affected by the use of pulsed air flow. As with our earlier model, we assume that the number n_{ij} of channels passing through one of the ring-shaped

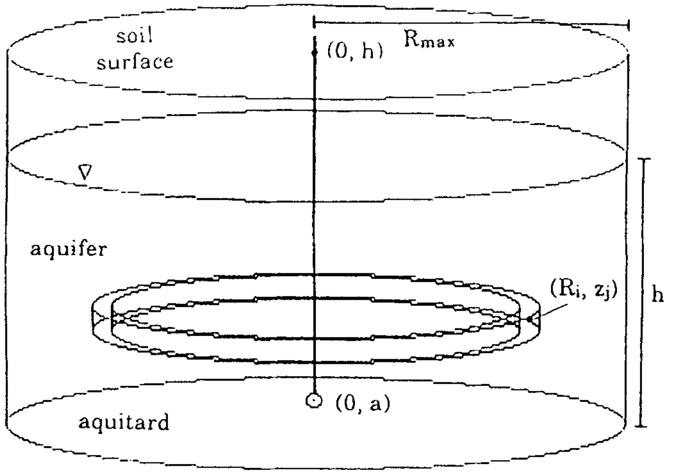

FIG. 3 Large-scale geometry and notation for a simple vertical sparging well screened at the bottom.

volume elements ΔV_{ij} is proportional to $\Delta V_{ij}/\Delta z$ and to the molar air flux in the volume element,

$$q_{ij} = (q_r^2 + q_z^2)^{1/2} \tag{22}$$

with a proportionality constant K, the airflow channel density parameter, that is characteristic of the ease with which channels form in the porous medium.

We consider a single volume element ΔV_{ij} of horizontal cross-sectional area $A_{ij} = \pi(R_{i+1}^2 - R_i^2)$, where $R_i = (i - 1)\Delta R$. The number of air channels passing through this volume element is given by

$$n_{ij} = KA_{ij}q_{ij} \tag{23}$$

We assign to each channel a cylindrical portion of the volume element of volume $\Delta V_{ij}/n_{ij}$ and radius b_{ij} given by

$$n_{ij}\pi b_{ij}^2 = A_{ij} \tag{24}$$

(see Fig. 4) so that

$$b_{ij} = (\pi K q_{ij})^{-1/2} \tag{25}$$

Diffusion/dispersion transport within the cylindrical domain surrounding an air channel is treated as indicated in Fig. 5, which shows one of the air channels and its associated domain. For convenience the subscripts i and j (specifying the volume element ΔV_{ij}) will be dropped for the moment. The water-saturated domain surrounding the air channel is partitioned into n_u annular volume elements as shown in Fig. 5. Δu is given by

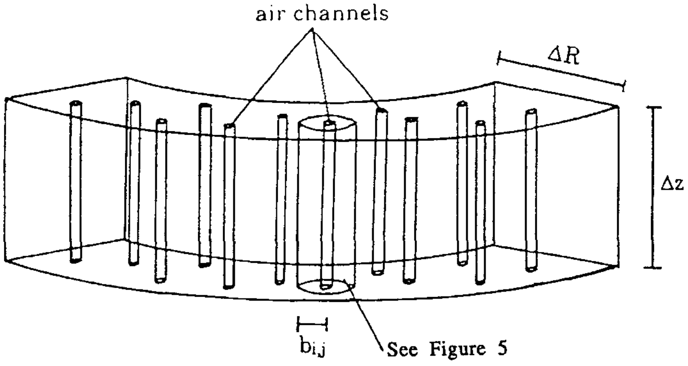

FIG. 4 Representative air channels and an associated domain in the volume element V_{ij}.

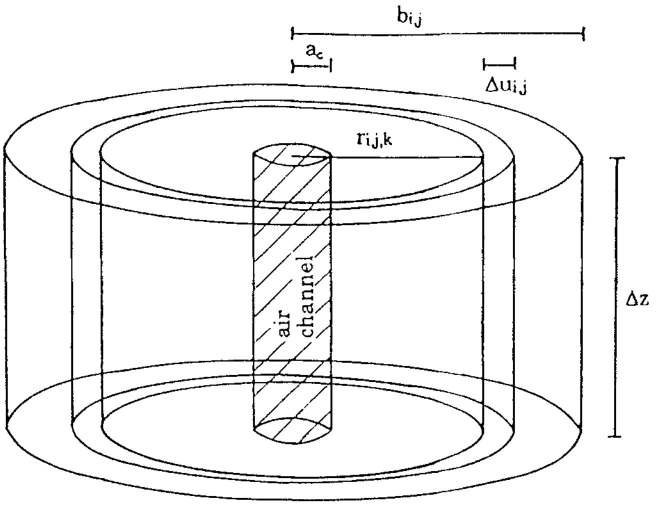

FIG. 5 Partitioning of the domain surrounding a single air channel.

$$\Delta u = \frac{b - a_c}{n_u} \qquad [\text{later, } \Delta u_{ij} = (b_{ij} - a_c)/n_u] \tag{26}$$

where a_c is the radius of the air channel (meters). The inner radius of the kth annular volume element is

$$r_k = a_c + (k - 1)\Delta u \tag{27}$$

and its volume is

$$\Delta v_k = \pi\Delta z(r_{k+1}^2 - r_k^2) = \pi\Delta z[2a_c\Delta u + (2k - 1)(\Delta u)^2] \tag{28}$$

Define

C_k^w = dissolved VOC concentration in the kth annular volume element, kg/m^3

D = diffusivity/dispersivity of VOC in the saturated porous medium, m^2/s (tortuosity included)

Then, after a little rearrangement, we have

$$\frac{dC_k^w}{dt} = \frac{2\pi\Delta zD}{\Delta v_k\Delta u}[r_k(C_{k-1}^w - C_k^w) + r_{k+1}(C_{k+1}^w - C_k^w)] - (1/\nu)\frac{dC_k^N}{dt}, \tag{29}$$
$$k = 2, 3, \ldots, n_u - 1$$

The equation for the outermost shell is

$$\frac{dC^w_{nu}}{dt} = \frac{2\pi \Delta z D}{\Delta v_{nu} \Delta u} r_{nu}(C^w_{nu-1} - C^w_{nu}) - (1/\nu)\frac{dC^N_{nu}}{dt} \tag{30}$$

For the innermost shell we assume that one has equilibrium between the gas phase in the air channel and the aqueous phase immediately bordering it with respect to VOC mass transport, and that this equilibrium is governed by Henry's law. This yields

$$\frac{dC^w_1}{dt} = \frac{2\pi \Delta z D}{\Delta v_1 \Delta u}[2a_c(C^g/K_{\mathrm{H}} - C^w_1) + r_2(C^w_2 - C^w_1)] - (1/\nu)\frac{dC^N_1}{dt} \tag{31}$$

where K_{H} = Henry's constant, dimensionless.

Note that in the computer code implementing the model, C^w and C^N both require triple subscripting (i, j, k)—i and j to specify the volume element ΔV_{ij}, and k to specify the inner and outer radii of the annular domains around the air channels in that volume element.

Advective Transport of VOC in Air

To avoid a difficult problem in multiphasic flow in porous media, we proceed as before (21) and postulate a physically reasonable formula for the z-component of the molar flux of the injected gas,

$$\begin{aligned} q_z(R,z) &= A(a_g^2 - R^2), \qquad R < a_g \\ &= 0, \qquad R > a_g \end{aligned} \tag{32}$$

We take

$$a_g = a_g(z) = a_{g0}(z/h)^{1/2} \tag{33}$$

where h is the depth of the well below the water table and a_{g0} is the radius about the well to which gas is distributed at the surface of the aquifer (the radius of influence, or ROI), estimated by tracer tests or measurements of vadose zone or saturated zone soil gas pressures. Helium tracer and dissolved oxygen measurements both provide unequivocal upper and lower bounds to the ROI.

The requirement that the total molar gas flux through any plane z = constant between $z = 0$ and $z = h$ be constant (Q_a) gives

$$A = \frac{2Q_a h^2}{\pi a_{g0}^4 z^2} \tag{34}$$

Note that this neglects oxygen consumption and carbon dioxide production by biotic and abiotic processes in the soil, which will cause small changes in the total molar gas flow rate as the sparging gas moves up to the water table. The requirement that the molar gas flux be conservative, so that $\nabla \cdot \mathbf{q} = 0$, yields

$$q_r = \frac{Q_a h^2 r}{\pi a_{g0}^4 z^3} [a_{g0}^2(z/h) - R^2] \tag{35}$$

and from Eqs. (32), (33), and (34) we have

$$q_z = \frac{2Q_a h^2}{\pi a_{g0}^4 z^2} [a_{g0}^2(z/h) - R^2] \tag{36}$$

To obtain the volumetric gas flux needed in the model we assume that the gas obeys the ideal gas law and that the gas pressure within the aquifer may be adequately approximated as ambient plus hydrostatic. The volumetric gas flux vector is then given by

$$\mathbf{U} = (U_r, U_z) = [R_g T/P(z)]\mathbf{q} \tag{37}$$

where

$$P(z) = P_{\text{ambient}} + \sigma(h - z) \tag{38}$$

and $\sigma = 1$ atm/10.336 m
T = temperature (K)
$R_g = 8.206 \times 10^{-5}$ m^3 atm/mol·K

Let the volumetric gas fluxes at the Inner, Outer, Bottom, and Top of ΔV_{ij} be U_{ij}^{I}, U_{ij}^{O}, U_{ij}^{B}, and U_{ij}^{T}. Let the areas of the Inner, Outer, Bottom, and Top surfaces of ΔV_{ij} be given by A_{ij}^{I}, A_{ij}^{O}, A_{ij}^{B}, and A_{ij}^{T}. Define

$$\begin{aligned} S(U) &= 1, \quad U > 0 \\ &= 0, \quad U \leq 0 \end{aligned} \tag{39}$$

Then the mass balance for advective transport of VOC in the gas phase is described by

$$\begin{aligned} n_{ij} \nu \pi a_c^2 \Delta z \left[\frac{\partial C_{ij}^g}{\partial t}\right]_{\text{adv}} &= A_{ij}^{\mathrm{I}} U_{ij}^{\mathrm{I}} [S(U^{\mathrm{I}}) C_{i-1,j}^g + S(-U^{\mathrm{I}}) C_{ij}^g] \\ &+ A_{ij}^{\mathrm{O}} U_{ij}^{\mathrm{O}} [-S(-U^{\mathrm{O}}) C_{i+1,j}^g - S(U^{\mathrm{O}}) C_{ij}^g] \\ &+ A_{ij}^{\mathrm{B}} U_{ij}^{\mathrm{B}} \left[S(U^{\mathrm{B}}) \frac{P[(j-1)\Delta z]}{P[(j-3/2)\Delta z]} C_{i,j-1}^g + S(-U^{\mathrm{B}}) \frac{P[(j-1)\Delta z]}{P[(j-1/2)\Delta z]} C_{ij}^g\right] \\ &+ A_{ij}^{\mathrm{T}} U_{ij}^{\mathrm{T}} \left[-S(-U^{\mathrm{T}}) \frac{P[j\Delta z]}{P[(j+1/2)\Delta z]} C_{i,j+1}^g - S(U^{\mathrm{T}}) \frac{P[j\Delta z]}{P[(j-1/2)\Delta z]} C_{ij}^g\right] \end{aligned} \tag{40}$$

So

$$\left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\text{adv}} = \frac{1}{n_{ij}\nu\pi a^2 \Delta z}\Big\{A^{\mathrm{I}}_{ij}U^{\mathrm{I}}_{ij}[S(U^{\mathrm{I}})C^g_{i-1,j} + S(-U^{\mathrm{I}})C^g_{ij}]$$

$$+ A^{\mathrm{O}}_{ij}U^{\mathrm{O}}_{ij}[-S(-U^{\mathrm{O}})C^g_{i+1,j} - S(U^{\mathrm{O}})C^g_{ij}]$$

$$+ A^{\mathrm{B}}_{ij}U^{\mathrm{B}}_{ij}\left[S(U^{\mathrm{B}})\frac{P[(j-1)\Delta z]}{P[(j-3/2)\Delta z]}C^g_{i,j-1} + S(-U^{\mathrm{B}})\frac{P[(j-1)\Delta z]}{P[(j-1/2)\Delta z]}C^g_{ij}\right]$$

$$+ A^{\mathrm{T}}_{ij}U^{\mathrm{T}}_{ij}\left[-S(-U^{\mathrm{T}})\frac{P[j\Delta z]}{P[(j+1/2)\Delta z]}C^g_{i,j+1} - S(U^{\mathrm{T}})\frac{P[j\Delta z]}{P[(j-1/2)\Delta z]}C^g_{ij}\right]\Big\}$$

$$(41)$$

describes the effect of advective transport on the gas-phase VOC concentration in the ijth volume element.

The contribution of diffusion/dispersion transport of VOC from the aqueous phase to C^g_{ij} is obtained similarly to the development of Eq. (31); it is

$$\left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\text{disp}} = -\frac{4D}{\nu a_c \Delta u_{ij}}(C^g_{ij}/K_{\mathrm{H}} - C^w_{ij1}) \tag{42}$$

Lastly, we combine Eqs. (41) and (42) to obtain

$$\frac{dC^g_{ij}}{dt} = \left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\text{disp}} + \left[\frac{\partial C^g_{ij}}{\partial t}\right]_{\text{adv}} \tag{43}$$

as the governing equation set for the gas-phase VOC concentrations.

The Model

The modeling equations are Eq. (21) [NAPL concentrations], Eqs. (29)–(31) [aqueous VOC concentrations], and Eq. (42) [gaseous VOC concentrations]. The total mass of contaminant VOC remaining in the domain of interest at any given time is

$$M_{\text{tot}}(t) = \sum_{i}^{I_R}\sum_{j}^{J_z}\left\{\left[\sum_{k}\Delta v_{ijk}(C^N_{ijk} + \nu C^w_{ijk})\right] + \nu\Delta v_{ij1}C^g_{ij}\right\} \tag{44}$$

The model was implemented in TurboBASIC and the computations were carried out on an MMG 386 DX microcomputer equipped with a math coprocessor and operating at 33 MHz. A typical run required approximately 20 minutes. The differential equations were integrated forward in time by means of the simple Euler method. In one run the integration of the differential equations showed instability (wildly oscillating solutions) when a value of Δt of 2000 seconds was used; reduction of t to 1000 seconds permitted the computation to be made, but this run required 40 minutes. All runs simulated a time period of 50 days.

RESULTS AND DISCUSSION

The effect of variations in K, the airflow channel density parameter (s/m^2·mol), is shown in Fig. 6. Increasing the value of K, which increases the density of the air channels in the medium and decreases the radii of the diffusion/dispersion domains around the air channels, results in increased rates of VOC removal. This is as expected if the system is diffusion-limited, since decreasing the radius of the domain surrounding an air channel decreases the distance across which diffusion/dispersion transport must take place. One expects that K is relatively large for homogeneous porous media and small for heterogeneous media, in which the air channels will tend to follow paths of high permeability. We have assumed that K is constant throughout the domain of influence of the sparging well, but it may well show considerable variation in stratified sites.

Decreasing the air channel diameter decreases the area of the air–water interface at the surface of the channels, so impedes the mass transport of

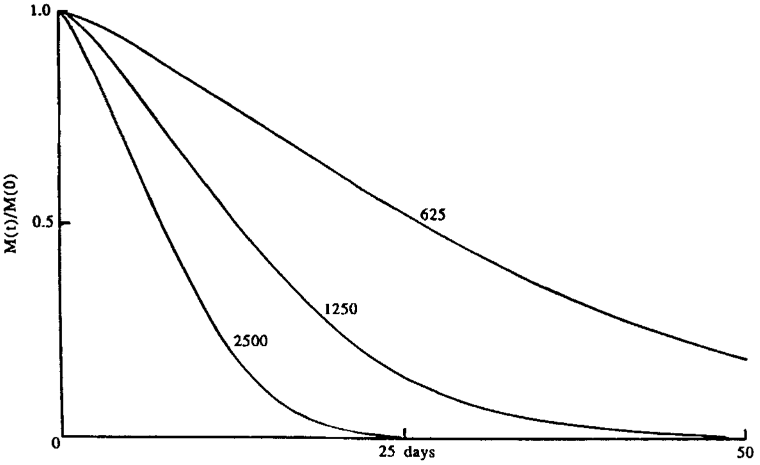

FIG. 6 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of air channeling parameter K. K = 625, 1250, and 2500 s/m^2·mol as indicated; other parameters as in Table 1.

VOC from the surrounding aqueous phase to the air channel. If the system is diffusion-limited, we expect this to lead to reduced removal rates. This is seen in Fig. 7, in which plots are shown for which air channel diameters of 1.0, 0.5, and 0.25 cm were used. One expects that, at least qualitatively, higher air flow rates would result in air channels of larger diameters, associated with faster VOC removal rates. This suggests that the use of short pulses of air at high flow rates might be most efficient, since these would be expected to result in large channels during and immediately after pulsing. The large surface areas of these channels are expected to result in enhanced aqueous-gas VOC mass transport.

The rate of diffusion/dispersion transport of VOC through the water-saturated domain surrounding an air channel is proportional to the large-scale dispersivity. Figure 8 shows the expected increase in VOC removal rate with increasing dispersivity; the dispersivities used here are 1.0, 2.0, and 4.0 × 10^{-7} m^2/s. One has some control over this dispersivity; pulsed operation of the air injection well is expected to increase it quite substantially, as discussed above. The results shown here indicate that one may expect significant increases in VOC removal rate in consequence.

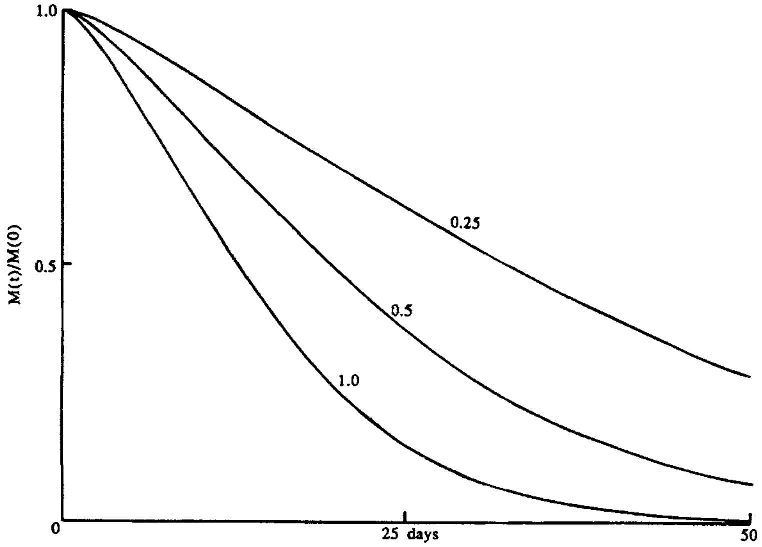

FIG. 7 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of mean air channel diameter a_c. a_c = 0.25, 0.5, and 1.0 cm as indicated; other parameters as in Table 1.

In diffusion-limited operation of a sparging well, one does not expect to find strong dependence of the VOC removal rate on the value of the Henry's constant K_H. This is born out by the plots shown in Fig. 9, in which it is seen that values of K_H of 0.1 and 10^{-3} yield very similar removal rates. Under the conditions of these runs (see Table 1), even a VOC having a Henry's constant of 10^{-4} is removed at what would probably be regarded as an acceptable speed.

The effect of initial NAPL concentration on the contaminant reduced mass $[M(t)/M(0)]$ plots is shown in Fig. 10. Initial NAPL concentrations of 1.0, 2.0, and 4.0 kg/m^3 were used, and the initial total contaminant masses were 208.96, 409.89, and 811.75 kg. The NAPL is assumed initially to be distributed uniformly throughout the domain of interest; the model does not apply to the situation in which dense nonaqueous phase liquid (DNAPL) is pooled on an underlying aquitard, from which it would be removed with great difficulty, if at all. The rates of removal (on an absolute basis—kg/day) increase somewhat with increasing initial NAPL concentration, since the NAPL–water interfacial area is increased very nearly proportionally to the increase in initial contaminant mass. Diffusion/dispersion transport through the aqueous phase to the air channels is not enhanced except by a modest increase in aqueous VOC concentration

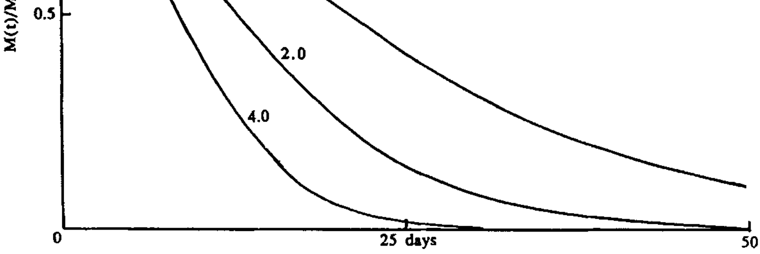

FIG. 8 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of large-scale dispersion coefficient D. D = 1.0, 2.0, and 4.0 × 10^{-7} m^2/s as indicated; other parameters as in Table 1.

TABLE 1
Default Parameters for Model Runs

Radius of domain of interest	10 m
Thickness of aquifer	6 m
Radius of influence of the sparging gas at the top of the aquifer	8 m
Temperature	15°C
Air flow rate in sparging well	25 SCFM
Air channeling parameter	1250 $\mathrm{s/m^2 \cdot mol}$
Mean diameter of air channels	1 cm
Porosity of aquifer medium	0.4
Contaminant simulated	Trichloroethylene
Henry's constant of the VOC (dimensionless)	0.2821
Large-scale dispersivity of VOC in aquifer during sparging	2.0×10^{-7} $\mathrm{m^2/s}$
Initial concentration of VOC in groundwater	100 mg/L
NAPL concentration	1 $\mathrm{kg/m^3}$
NAPL droplet diameter	0.1 cm
NAPL droplet boundary layer thickness	0.5 cm
VOC diffusivity in boundary layer	2.0×10^{-10} $\mathrm{m^2/s}$
Radius of contaminated zone	4 m
Depth of contaminated zone below the water table	4 m
VOC aqueous solubility	1100 mg/L
Density of VOC NAPL	1.46 $\mathrm{g/cm^3}$
Initial total contaminant mass	208.96 kg
Number of points for the R-coordinate	10
Number of points for the z-coordinate	6
Number of points for the u-coordinate	4
Δt	2000 seconds

gradient, however, so the increase in VOC removal rate is less than proportional to the increase in total NAPL. We conclude that distributed NAPL is readily removed by sparging, and also that the technique should also be effective for removing free product from the capillary fringe, through which air moves during sparging.

One should note, however, that NAPL trapped in joints and fractures through which air does not move and in which dispersion may be negligible, on the other hand, will be virtually impossible to remove by sparging. Sites in which substantial amounts of VOC are strongly held by adsorption will also show slow removal and tailing due to the slow release of sorbed VOC to the aqueous phase and to reduced concentration gradients in the aqueous phase.

Increasing the NAPL droplet diameter results in an inversely proportional decrease in NAPL–water interfacial area. In solution/diffusion-lim-

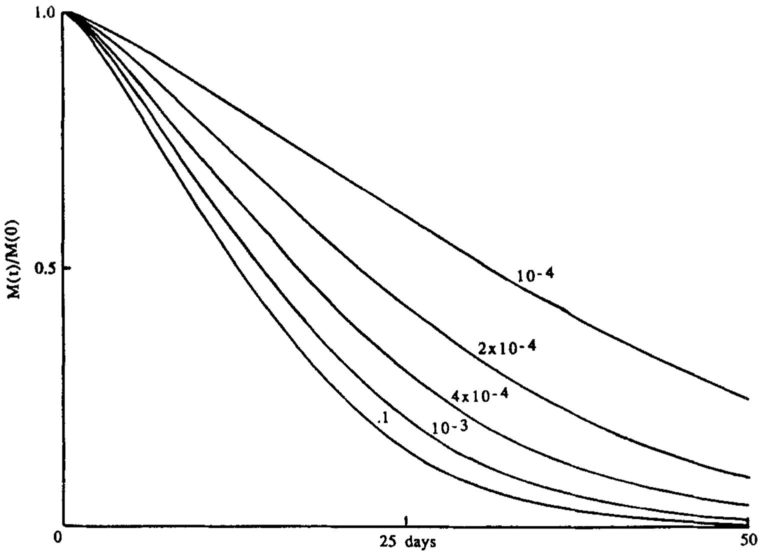

FIG. 9 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of Henry's constant K_H (dimensionless). K_H = 0.1, 1 × 10^{-3}, 4 × 10^{-4}, 2 × 10^{-4}, and 1 × 10^{-4}, as indicated. Other parameters as in Table 1.

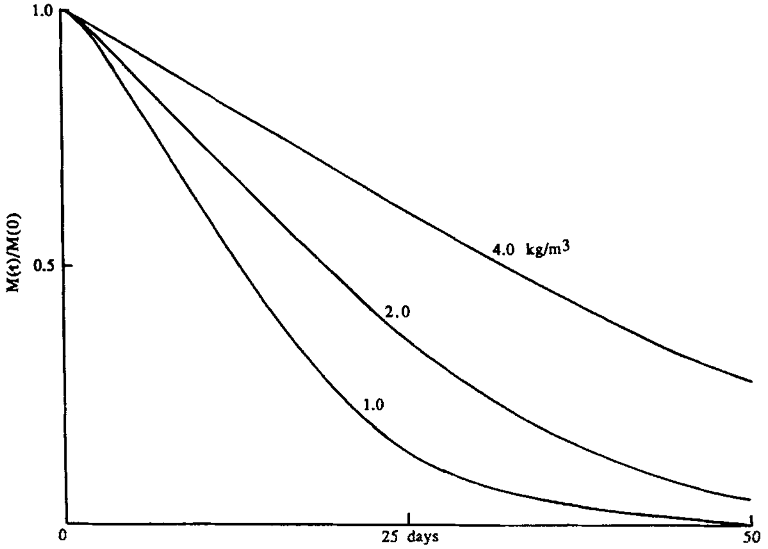

FIG. 10 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of initial NAPL concentration C_0^N. C_0^N = 1.0, 2.0, and 4.0 kg/m^3 of soil as indicated; other parameters as in Table 1. Initial total masses of contaminant are 208.96, 409.89, and 811.75 kg.

ited sparging operation this results in substantial decreases in VOC removal rates, as seen in Fig. 11.

The solubility of the VOC determines the magnitude of the concentration gradients which can be maintained in the aqueous phase and which drive mass transport by solution/diffusion and by dispersion. The runs in Fig. 12 were made for a fictitious VOC having properties as given in Table 1 except for the aqueous solubility. Runs were made corresponding to aqueous solubilities of 1000, 500, and 250 mg/L. The VOC removal rate decreases drastically with decreasing solubility. Since K_H was held constant in these runs, the equilibrium vapor pressure of the VOC decreased proportionally to the decreases in solubility. (K_H is proportional to the equilibrium vapor pressure of the VOC divided by its aqueous solubility.)

Increasing the temperature of the aquifer should increase both VOC solubilities and vapor pressures, which should accelerate remediation by sparging. Addition of surfactant to increase the effective solubility of a VOC by micellar solubilization should also be effective by increasing dispersion transport of VOC, since the dispersivity of the micelles (unlike

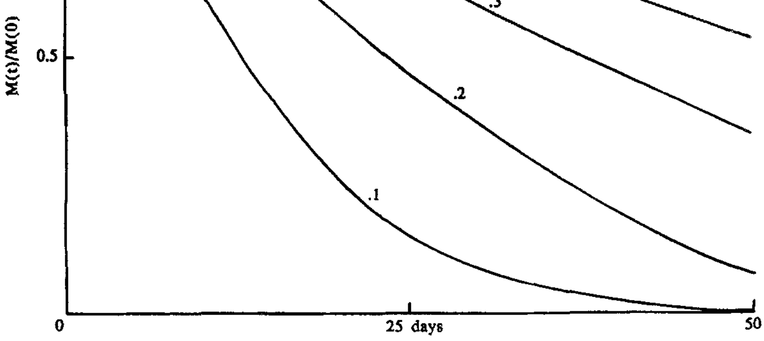

FIG. 11 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of initial NAPL droplet diameter. Droplet diameter = 0.1, 0.2, 0.3, and 0.4 cm as indicated; other parameters as in Table 1.

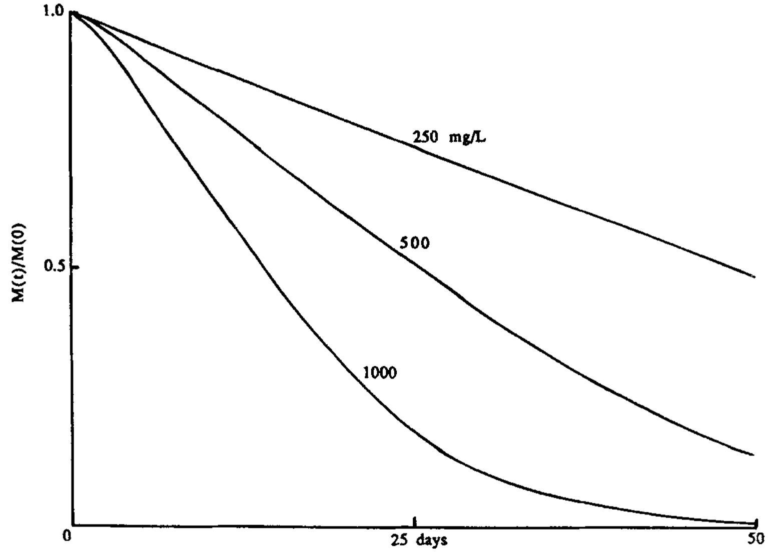

FIG. 12 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of VOC aqueous solubility. Solubility = 1000, 500, and 250 mg/L as indicated; other parameters as in Table 1.

their diffusivity) is not affected by their extremely high effective molecular weights. One would need to address problems of distribution, foaming, and biodegradability with surfactants, however.

In this model one expects a very strong dependence of VOC removal rate on the air flow rate through the well, since the number of air channels per unit area is assumed to be proportional to the molar air flow rate. This effect is illustrated in Fig. 13, in which runs having airflow rates of 25, 15, and 5 SCFM are shown. As will be seen shortly, the dependence of removal rate on air flow rate does not indicate that the system is not diffusion-limited. Diffusion/dispersion is tied to the air flow rate by the fact that the radii of the saturated domains surrounding the air channels are inversely proportional to the square root of the air flow rate. As air flow decreases and these radii increase, diffusion/dispersion of VOC to the air channels becomes slower. These results constitute an argument in support of operating sparging wells under conditions of short pulses at high flow rates.

In Fig. 14 the air flow rate is varied and simultaneously the air channel density parameter K is varied inversely so as to maintain a constant distri-

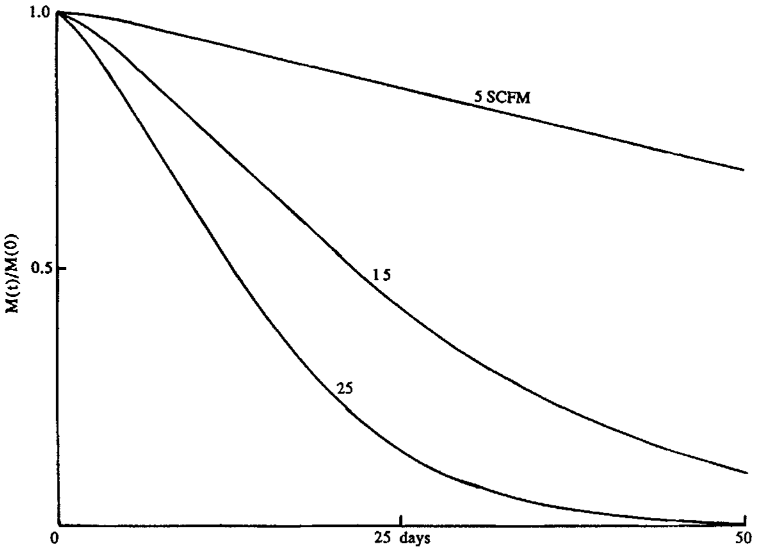

FIG. 13 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of airflow rate. Airflow rate = 25, 15, and 5 SCFM as indicated; other parameters as in Table 1. In these runs the air channel density is proportional to the airflow rate as the airflow channel density parameter K is held constant.

bution of air channels from run to run. Under these conditions the VOC removal rate is nearly independent of air flow rate until one is operating at quite small air flow rates. This indicates that the process is limited by solution/diffusion and/or dispersion until the air flow rate is very small (0.04 SCFM). One should not interpret this as meaning that sparging wells should be operated at such low flow rates, since this would adversely affect the gas distribution pattern around the well and the density of the air channels. These results do, however, indicate that the net reduction in average gas flow resulting from pulsed operation can be expected to have a quite minor deleterious effect, probably swamped out by the beneficial effects of increased dispersion.

One may speculate that sparging might be enhanced by linking it with other techniques such as sonication, heating (rf or electrical resistive), use of surfactants, and electroosmosis. Whether or not any of these will prove useful is an open question at present, however.

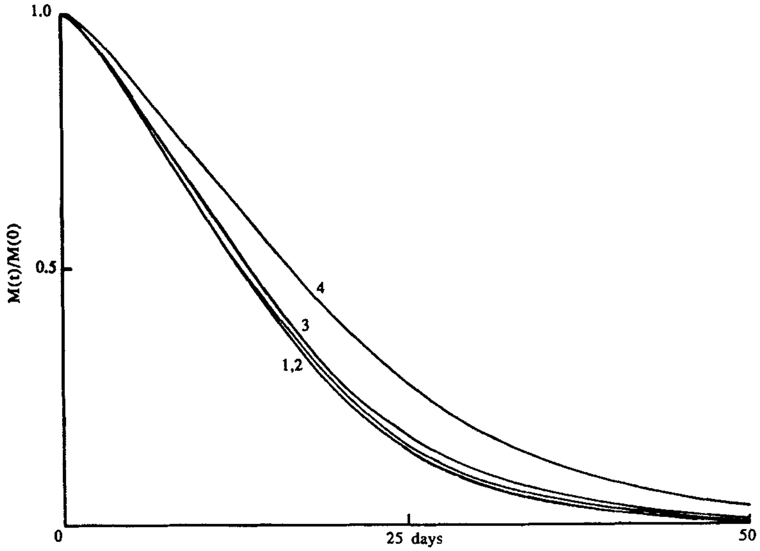

FIG. 14 Plot of contaminant reduced mass $M(t)/M(0)$ versus time; effect of airflow rate. In these runs the airflow channel density parameter K is varied inversely with the airflow rate so that a constant density of airflow channels is maintained in the set. (Airflow rate, K) = (25, 1250), (1, 31,250), (0.2, 156,250), and (0.04, 781,250) in units (SCFM, s/m^2·mol) for Curves 1, 2, 3, and 4, respectively. Other parameters as in Table 1.

CONCLUSIONS

The above results lead to the following set of conclusions:

- Pulsed operation of sparging wells can be expected to result in substantial increases in the dispersivities of contaminant compounds and of dissolved oxygen as well, enhancing VOC removal and biodegradation.
- A decrease in contaminant removal rate with a decrease in air flow rate does not necessarily indicate that the sparging is not limited by dispersion, since the distances over which dispersion must take place are related to the air flow rate.
- Removal of volatile NAPL droplets should be an efficient process free from difficulty. Removal of floating free product should be particularly efficient. However, removal of underlying pooled DNAPL and DNAPL in fractured bedrock is expected to be extremely slow.

- In pilot scale tests of VOC concentration rebound, the time constant which will be measured is that pertaining to diffusion/dispersion unenhanced by pulsed sparging operation, since the sparging well is shut down while the rebound is occurring.
- Even in pulsed operation, gas and water tend to channel around low-permeability heterogeneities, interfering with VOC removal.
- The Henry's constant K_H is important only when VOC volatilization is not diffusion/dispersion controlled.
- Removal rates decrease with decreasing solubility at constant K_H.
- Under conditions of pulsed air flow, high air flow rates are expected to increase the number of air channels and therefore the rate of VOC removal.

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