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Groundwater Cleanup by In-Situ Sparging. VI. A Solution/Distributed Diffusion Model for Nonaqueous Phase Liquid Removal

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ABSTRACT

A microcomputer model for the sparging of aquifers contaminated with volatile organic compounds (VOCs) is presented which includes the kinetics of solution of nonaqueous phase liquid (NAPL) droplets and of diffusion from low-permeability porous layers. The well configuration modeled is a horizontal slotted pipe. Modeling results lead to the following conclusions. 1) The presence of low-permeability porous lenses of clay, till, silt, etc. results in marked increases in cleanup times. The extent of the increases depends strongly on the thickness of the structures. NAPL droplets of large size also result in marked increases in cleanup time. 2) Increases in air flow rate do not yield corresponding decreases in cleanup time if the system is limited by solution/diffusion kinetics. 3) The rate of induced water circulation plays a minor role in determining cleanup time. 4) Wells should be sufficiently deep and operated at an air flow rate such that air is delivered to the entire zone of contamination. 5) The spatial distribution of the VOC has little effect on the cleanup time as long as air is delivered to the entire contaminated zone. 6) Cleanup times increase roughly proportionally to increasing initial VOC concentration. 7) The terminal phase of cleanup typically shows substantial tailing as water containing VOC must circulate into the zone of aeration for the VOC to be stripped. 8) VOCs having Henry's constants of 0.05 or larger can readily be removed by sparging.

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INTRODUCTION

Sparging is basically the injection of air into groundwater in situ for the purpose of removing contaminating volatile organic compounds (VOCs). The technique is distinguished from air stripping above-ground by trickle columns, by fine-bubble aeration, or by aeration in basins. The equilibrium and mass transport principles in sparging are basically the same as in these other water treatment techniques. Sparging is carried out at present in three configurations. These are 1) vacuum-vaporizer wells, 2) aeration curtains, and 3) simple sparging wells.

In all cases one desires to remove dissolved VOCs [and possibly nonaqueous phase liquids (NAPLs)] from a contaminated aquifer. Soil vapor extraction, while useful for the removal of VOCs above the water table, is ineffective below the water table. The equilibria and mass transport processes involved in sparging are as follows. First, if NAPL is present, it will also be dissolved into the aqueous phase. This equilibrium is governed by the solubility of the VOC, and the mass transport is controlled by the aqueous-phase diffusion constant in the porous medium, by the boundary layer thickness around the NAPL blobs or droplets which are trapped interstitially in the porous medium, and perhaps by the existence of both mobile (advecting) and immobile aqueous phase. The latter may be water in the porosity of low-permeability structures such as clay or silt lenses, etc. The VOC will also be distributed between the slowly moving aqueous phase and the much more mobile vapor phase which is present in the aquifer as a result of the injection of air via the sparging well. This equilibrium is governed by Henry's law, and here the approach to equilibrium is governed by turbulence, diffusion, and dispersion.

Sparging is a technique which is directed toward VOCs of low water solubility. As such it is in direct competition with the pump and treat technique, the oldest and most widely used of the various in-situ technologies. Problems arise with this technology; many pump and treat operations have been started but very few have been successfully closed, particularly if dense nonaqueous phase liquids (DNAPLs) in the aquifer were involved. There are some excellent physical chemical reasons for this which have been discussed in depth by Feenstra and Cherry (1–3), Mackay et al. (4), Powers et al. (5, 6), Miller et al. (7), Mutch et al. (8), and Schwille (9) (among many others). Paramount is the fact that molecular diffusion constants of VOCs in the aqueous phase are extremely small, so diffusion transport of VOC out of nonmobile water or away from a blob of NAPL through a quiescent aqueous boundary layer of appreciable thickness to the slowly moving mobile groundwater is quite slow. This bottleneck then limits the entire remediation process.

In sparging, one is introducing a good deal of energy into the aquifer as one injects compressed air. As this air expands and rises, energy is dissipated as local turbulence, which reduces the thickness of the quiescent boundary layers around the NAPL blobs and thereby increases their rate of solution, which is inversely proportional to the square of the boundary layer thickness. If air actually comes in contact with the NAPL blobs, so much the better for mass transport to the vapor phase. The principal potential advantage in sparging is improved mass transport between NAPL and the aqueous phase and between relatively quiescent aqueous phase and the freely flowing fluid (in this case air) which moves the contaminant from the aquifer to an agency for its capture or destruction. Angell (10), Brown (11), and Middleton and Hiller (12) have provided good overviews of the sparging technology.

Herrling and his coworkers in Germany have been quite active in the development of sparging techniques. In the United States they have collaborated with IEG Technologies, of Charlotte, North Carolina. They have specialized in the vacuum-vaporizer-well configuration, which permits simultaneous sparging below the water table and soil vapor extraction above it, with a single rather complex well. In a recent EPA report they described use of this technique for the remediation of a site in the Rhine-Main area of Germany which was contaminated with chlorinated hydrocarbons, principally tetrachloroethylene. This report also presents results of Herrling's elegant three-dimensional mathematical modeling of the flow patterns in the vicinities of these wells (13–15).

In the United States, Groundwater Technology, Inc., has done quite a lot of work in the field of sparging. Brown and Fraxedas, in the EPA report mentioned above, described the case history of a site that is the former location of a dry-cleaning establishment, at which both soil and groundwater contamination resulted from leaking underground storage tanks (16). Contaminants were tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylene, and some petroleum hydrocarbons associated with heating oil. PCE was the major contaminant of concern. Brown and Fraxedas gave a description of the operation, including chlorinated hydrocarbon levels in groundwater initially, after 54 days of sparging, and after 125 days of sparging. The results showed impressive amounts of VOC removal.

A sparging well treatability study was conducted by Eckenfelder, Inc., at an industrial site in California. Sparging resulted in an average 49%

decrease in the total VOC concentration in the groundwater at two test locations. The TCE present in the groundwater showed a 48% reduction (23 to 12 mg/L) at one location and a 25% reduction (10 to 7.5 mg/L) at the other after only 3 hours of sparging, which looked quite promising (17).

Johnson et al. (18) described a combination SVE/sparging/pump-and-treat operation for the remediation of a gasoline service station site in Costa Mesa, California. An estimated 4000 kg of gasoline was present near the water table, and free product was floating on the groundwater. The system used four vapor extraction wells, two air sparging wells, and one groundwater pumping well. After the first year it was felt that vapor extraction well flow rates were too low, so dual vapor extraction/groundwater recovery wells were installed. These increased the total air flow rate to 30–40 scfm; when the report was written, a total of 2700 kg of product had been recovered.

Radecki, Matson, and Brenoel (19) reported on the use of sparging and pre-aerated infiltration water in enhancing the biodegradation of hydrocarbons at a site in northern Michigan. The site is a shallow, unconfined sand and sandy loam aquifer contaminated with a dissolved fraction from a gasoline spill in 1984. Twelve weeks of operation was reported to yield a reduction of more than 100 gallons of gasoline; the authors estimated that to remove that quantity of contaminant by pump and treat alone would have required years.

Horizontal wells have been installed and tested for in-situ remediation of groundwater and soils at the DOE Savannah River Site (20, 21). One deep horizontal well, installed below the water table, was used for air injection to strip VOCs from the groundwater, while a shallow horizontal well in the vadose zone recovered the vapor-phase VOCs. This concept is based on directional drilling technology developed for the oil industry (22).

We have developed models for sparging dissolved VOCs by means of an aeration curtain (23) and by a simple air injection well (24). We also have modeled the removal of DNAPL by means of a vacuum-vaporizer well and by an aeration curtain (25), as well as by means of a sparging well configured as a single vertical pipe screened at the bottom or as a single buried horizontal slotted pipe (26). Most recently we included the circulation of water induced by the aeration and the use of a lumped parameter approximation to handle mass transport kinetics between the aqueous phase and the gas phase (27). This work is also summarized elsewhere (28–30).

The modeling of sparging is complicated by the presence of two mobile phases (aqueous and vapor) and the extreme complexity of modeling two-phase flows in porous media. In our earlier work (27) we circumvented this problem by postulating gas and water flow fields which were intuitively reasonable. Here we present what we think is a somewhat more reasonable water flow field than that used previously. We also include the presence of low-permeability porous clay or silt lenses in which VOC and possibly DNAPL can be stored and from which such contaminant must diffuse before it can be removed by advection in the gas and/or mobile aqueous phase. Some aspects of this model have been used previously in modeling pump-and-treat operations (31), and we have also used this approach in describing soil vapor extraction (32).

In the following sections we first present the rather lengthy analysis leading to the equations of the model. This is followed by presentation of results showing the dependence of cleanup rates on the various parameters of the model. The paper closes with a discussion of the conclusions which can be drawn from the results.

ANALYSIS

The Physical Picture

We consider the sparging of a contaminated aquifer by means of a buried horizontal slotted pipe; the configuration is shown in Fig. 1. Air is injected through the pipe and then rises and spreads as it moves up through the

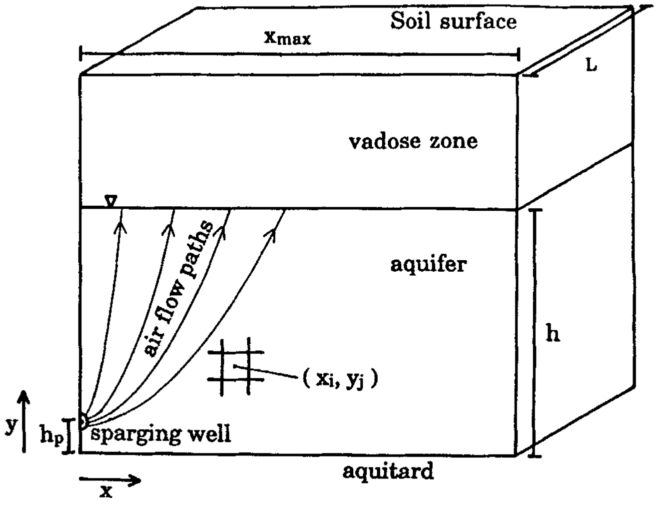

FIG. 1 Geometry and notation for modeling a sparging well, buried horizontal slotted pipe configuration.

aquifer. This, in turn, induces a circulation of the mobile groundwater, with upwelling in the near vicinity of the well and a corresponding downward movement of water farther away laterally from the well.

The contaminant is assumed to be present as dissolved VOC in the mobile groundwater and also in virtually immobile groundwater contained in the porosity of low-permeability clay, till, or silt lenses or layers present in the aquifer. See Fig. 2. The contaminant may also be present as nonaqueous phase liquid (NAPL). Before the VOC can be removed, it must be dissolved if present as NAPL, and it may have to diffuse through a length of immobile groundwater before it reaches the mobile water. See Fig. 3 for a schematic of this process. The VOC in the mobile water is assumed to be in local equilibrium with that in the air injected by the sparging well in those portions of the domain of interest through which air is moving. This equilibrium is governed by Henry's law. The VOC dissolved in mobile water in regions through which air is not flowing must move by advection into a region which is being aerated before it can be removed.

The construction of a model for sparging therefore breaks down into 1) determination of the air flow in the vicinity of the sparging well; 2) determination of the water circulation in the vicinity of the sparging well; 3) modeling of the solution of NAPL droplets, if these are present; 4) modeling of the diffusion of dissolved VOC through the immobile water

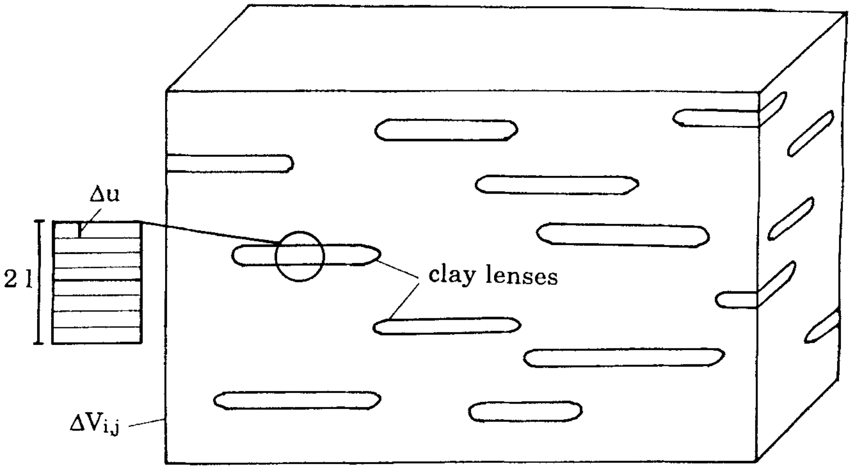

FIG. 2 Distribution of low-permeability porous lenses in a volume element, and partitioning of a lens into slabs for mathematical analysis.

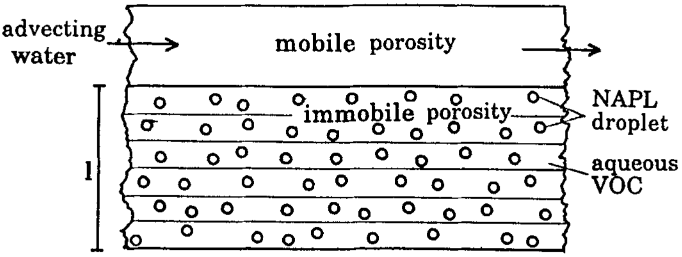

FIG. 3 Partitioning of a clay lens into slabs, distribution of NAPL droplets within the slabs, and relationship of the lens to the mobile porosity.

in the clay lenses to the mobile water; and 5) combination of the results of the first four steps to yield the equations modeling the sparging process.

Air Flow

We follow Burchfield's (26) treatment. Assume that the molar gas flux in the vertical (y) direction is given by

$$\begin{aligned} q_y(x, y) &= A(y)[a^2(y) - x^2], \qquad x < a(y) \\ &= 0, \qquad x \geqslant a(y) \end{aligned} \tag{1}$$

where

$$\begin{aligned} a(y) &= a_0 \left[\frac{y - y_p}{h - h_p}\right]^{1/2}, \qquad y - h_p > 0 \\ &= 0, \qquad y - h_p < 0 \end{aligned} \tag{2}$$

Here: x = horizontal coordinate at right angles to the direction of the horizontal slotted pipe, m
h = thickness of aquifer, m
h_p = height of pipe above the underlying aquitard, m

So

$$\begin{aligned} q_y &= A(y)\left[a_0^2 \frac{y - h_p}{h - h_p} - x^2\right], \qquad x < a_0 \left[\frac{y - h_p}{h - h_p}\right]^{1/2} \\ &= 0, \qquad x > a_0 \left[\frac{y - h_p}{h - h_p}\right]^{1/2} \end{aligned} \tag{3}$$

To calculate $A(y)$ we note that

$$\frac{Q}{2} = L \int_0^\infty q_y(x, y)\, dx, \qquad h_p < y < h \tag{4}$$

Define

$$h' = h - h_p$$
$$y' = y - h_p$$

Then

$$\frac{Q}{2L} = A(y) \int_0^{a_0(y'/h')^{1/2}} [a_0^2(y'/h') - x^2]\, dx \tag{5}$$

This readily yields

$$\begin{aligned} A(y) &= \frac{3Q}{4La_0^3}\left[\frac{h - h_p}{y - h_p}\right]^{3/2}, \qquad y > h_p \\ &= 0, \qquad y < h_p \end{aligned} \tag{6}$$

and

$$\begin{aligned} q_y &= \frac{3Q}{4La_0^3}\left[\frac{h - h_p}{y - h_p}\right]^{3/2} \left\{a_0^2\left[\frac{y - h_p}{h - h_p}\right] - x^2\right\} \\ &= 0, \qquad y - h_p < 0 \text{ and/or } x > a_0\left[\frac{y - h_p}{h - h_p}\right]^{1/2} \end{aligned} \tag{7}$$

To obtain the x-component of the molar gas flux, q_x, note that

$$\nabla \cdot \mathbf{q} = 0 \tag{8}$$

so that

$$\frac{\partial q_x}{\partial x} = -\frac{\partial q_y}{\partial y} \tag{9}$$

Use of Eq. (7) then yields

$$-\frac{\partial q_y}{\partial y} = \frac{\partial q_x}{\partial x} = -\frac{3Q}{8La_0^3}[-a_0^2 h'^{1/2} y'^{-3/2} + 3x^2 h'^{3/2} y'^{-5/2}] \tag{10}$$

Integration with respect to x gives

$$\int_0^x \frac{\partial q_x}{\partial x'}\, dx' = q_x(x, y') - q_x(0, y') = q_x(x, y') \tag{11}$$

since $q_x(0, y') = 0$ from the symmetry of the problem. So

$$q_x(x, y') = \frac{3Q}{8La_0^3}\int_0^x [a_0^2 h'^{1/2} y'^{-3/2} - 3h'^{3/2} y'^{-5/2} x'^2]\, dx' \tag{12}$$

This in turn yields

$$q_x = \frac{3Qx}{8La_0^3}\frac{(h - h_p)^{3/2}}{(y - h_p)^{5/2}}\left[a_0^2 \frac{y - h_p}{h - h_p} - x^2\right] \tag{13}$$

Recall that

$$q_y = \frac{3Q}{4La_0^3}\left[\frac{h - h_p}{y - h_p}\right]^{3/2}\left[a_0^2\left(\frac{y - h_p}{h - h_p}\right) - x^2\right] \tag{7'}$$

This completes the calculation of the components of the molar gas flux. What we shall need, however, is the volumetric gas flux U, given (if we assume the gas is ideal) by

$$U = qRT/P \tag{14}$$

where R = gas constant, 8.206×10^{-5} m^3·atm/mol·deg
T = temperature, °K
P = pressure, atm

We assume that the pressure can be approximated as the ambient pressure P_a plus that due to the hydrostatic head, so

$$P = P(y) = P_a + \eta(h - y) \tag{15}$$

where $\eta = 0.09675$ atm/m. Then

$$U_x = q_x \frac{RT}{P_a + \eta(h - y)} \tag{16}$$

and

$$U_y = q_y \frac{RT}{P_a + \eta(h - y)} \tag{17}$$

A representative set of streamlines for the molar gas flux q is shown in Fig. 4.

Water Circulation

In the water circulation function used previously (27), the water disappeared into a fictitious sink at the bottom of the aquifer under the well, only to reappear coming from a fictitious source at the top of the aquifer

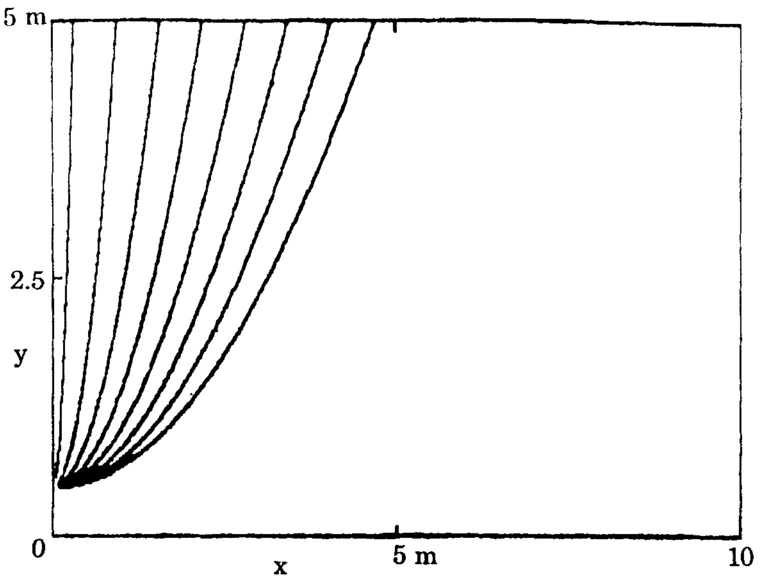

FIG. 4 Streamlines calculated from the molar air flux function q.

above the well. Obviously this water circulation function could not be even qualitatively correct in the near vicinity of the well. We therefore propose the water superficial velocity field **v** (m^3/m^2 s) developed in this section.

Let us postulate

$$v_y = By(h - y)(b - x)\exp(-cx) \tag{18}$$

Here B, b, and c are constants to be determined. Note that $v_y(x, 0) = v_y(x, h) = 0$, that v_y is positive for small values of x ($<b$) and negative for large values, and that v_y approaches zero as x approaches ∞. These are all requirements which must be satisfied by any physically acceptable function v_y.

The downward total flux of water must equal the upward total flux of water, which gives the requirement that

$$\int_0^\infty v_y(x, y)\,dx = 0 \tag{19}$$

Substitution of Eq. (18) in Eq. (19) and the change of variable $u = cx$ then gives

$$\frac{1}{c}\int_0^{\infty} (b - u/c)\exp(-u)\,du = 0 \tag{20}$$

or

$$b/c - 1/c^2 = 0$$

from which we obtain the requirement that $c = 1/b$. The vertical component of the superficial water velocity is therefore given by

$$v_y = By(h - y)(b - x)\exp(-x/b) \tag{21}$$

The water flow is conservative, so

$$\nabla\cdot\mathbf{v} = 0 \tag{22}$$

which gives

$$-\frac{\partial v_y}{\partial y} = \frac{\partial v_x}{\partial x} = -B(h - 2y)(b - x)\exp(-x/b) \tag{23}$$

We have boundary conditions $v_x(0, y) = v_x(\infty, y) = 0$; we use the second, and so obtain

$$\int_x^{\infty} \frac{\partial v_x}{\partial x'}\,dx' = -v_x(x, y) \tag{24}$$

$$= -B(h - 2y)\int_x^{\infty} [b - x']\exp(-x'/b)\,dx' \tag{25}$$

which finally yields

$$v_x = -Bbx(h - 2y)\exp(-x/b) \tag{26}$$

for the x-component of the superficial velocity of the mobile water in the vicinity of the sparging well. Figure 5 shows a representative set of streamlines together with water transit times around the loops. These transit times are inversely proportional to the scale factor B, which could be estimated by doing tracer tests at the sparging well. This would be time-consuming and difficult, so it is fortunate that we shall find that sparging cleanup rates depend only quite weakly on the size of the scale factor B.

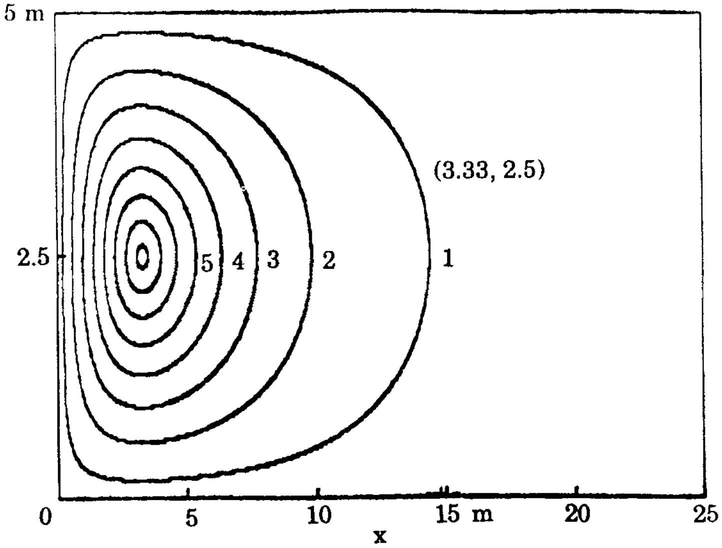

FIG. 5 Streamlines calculated for the water circulation function **v**. Note that the scale of the x-axis is different from that used in Fig. 4. The scale factor B is 0.1. The times required for the water to traverse a complete loop are as follows:

Trajectory number	Transit time (days)
1	12.35
2	5.53
3	4.11
4	3.51
5	3.20
6	3.03
7	2.94
8	2.90

Transit times are inversely proportional to B.

Mass Transport of VOC

Mobile Water-Gas

For the mass transport of VOC between the gas phase and the mobile aqueous phase, we assume local equilibrium and Henry's law, so

$$C^g = K_H C^w \tag{27}$$

in all regions within the domain in which gas phase is present.

Solution of DNAPL Droplets

Here we examine the dissolution of VOC from a NAPL droplet into a quiescent aqueous phase, perhaps distributed in the porosity of a clay, silt, or till lens. The steady-state diffusion equation is

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dC^w}{dr}\right] = 0 \tag{28}$$

with boundary conditions

$$C^w(a') = C_{\text{sat}} \tag{29}$$

and

$$C^w(d) = C_0 \tag{30}$$

where C_{sat} is the solubility of the VOC in water and C_0 is the VOC concentration at the outer surface ($r = d$) of the aqueous boundary layer surrounding the drop. From Eqs. (28)–(30) one readily obtains

$$\frac{dC^w}{dr} = -\frac{a'd}{d - a'}(C_{\text{sat}} - C_0)/r^2 \tag{31}$$

Fick's first law and Eq. (31) then give for the rate of change of mass of the droplet

$$\frac{dm}{dt} = -\frac{4\pi Da'(C_{\text{sat}} - C_0)}{1 - a'/d} \tag{32}$$

where D is the diffusivity of the VOC in the aqueous phase (including the tortuosity factor) and m is the mass of the droplet. Evidently

$$a'(t) = a_0'[m(t)/m_d]^{1/3} \tag{33}$$

where m_d is the initial mass of the droplet and a_0' is its initial radius. This gives

$$\frac{dm}{dt} = -\frac{4\pi Da_0'(C_{\text{sat}} - C_0)(m/m_d)^{1/3}}{1 - (a_0'/d)(m/m_d)^{1/3}} \tag{34}$$

Rewriting this in terms of the notation for the kth slab in the ijth volume element of the system then gives

$$\frac{dm_{ijk}}{dt} = -\frac{4\pi Da_0'(C_{\text{sat}} - C_{ijk}^i)(m_{ijk}/m_d)^{1/3}}{1 - (a_0'/d)(m_{ijk}/m_d)^{1/3}} \tag{35}$$

where C_{ijk}^i = concentration of VOC in the immobile water in the kth slab of the ijth volume element, kg/m^3

m_{ijk} = mass of NAPL in the kth slab of the ijth volume element, kg

A reasonable estimate for d, the boundary layer thickness around the droplet, is half the mean distance between droplets. This is calculated as follows. Let n be the number of NAPL droplets in a volume element $L\Delta x\Delta y$. Then

$$n\,\frac{4\pi a_0'^3\rho_{\text{voc}}}{3} = L\Delta x\Delta y C_0^N \tag{36}$$

where ρ_{voc} = NAPL density, kg/m^3
C_0^N = initial NAPL concentration, kg/m^3

From this we obtain

$$n = \frac{3L\Delta x\Delta y C_0^N}{4\pi a_0'^3\rho_{\text{voc}}} \tag{37}$$

These droplets are contained in a volume of water $\omega L\Delta x\Delta y$, where ω is the water-filled porosity, so the volume of water per droplet is

$$V' = \frac{4\pi a_0'^3\omega\rho_{\text{voc}}}{3C_0^N} \tag{38}$$

the mean distance between the droplets is

$$2d = a_0'\left[\frac{4\pi\omega\rho_{\text{voc}}}{3C_0^N}\right]^{1/3} \tag{39}$$

and finally

$$d = a_0'\left[\frac{\pi\omega\rho_{\text{voc}}}{6C_0^N}\right]^{1/3} \tag{40}$$

is the thickness of the boundary layer.

Initial Distribution of VOC among the Phases

We assume that the initial concentrations of VOC in the mobile and immobile aqueous phases and the NAPL phase are constant from volume element to volume element within the contaminated region of the domain of interest, and that these concentrations are constant from slab to slab within the slabs used to represent the low-permeability clay lenses (see Fig. 3). We also assume that the phases are initially at equilibrium with respect to VOC and that the volume of the gas phase is sufficiently small that the amount of VOC present in it can be neglected in doing a mass balance. Then

$$C_{\text{tot}} = (\omega^i + \omega^m)C_0^w + C_0^N \tag{41}$$

We assume that $C_0^N = 0$, which yields

$$C_0^w = \frac{C_{\text{tot}}}{\omega^i + \omega^m} \tag{42}$$

If $C_0^w < C_{\text{sat}}$, this is the correct value of C_0^w, and $C_0^N = 0$. If, however, $C_0^w > C_{\text{sat}}$, then the correct values are

$$C_0^w = C_{\text{sat}} \tag{43}$$

$$C_0^N = C_{\text{tot}} - (\omega^i + \omega^m)C_{\text{sat}} \tag{44}$$

Mass Balance of VOC in the Slabs of Immobile Water

We assume that the clay (silt, till) lenses from which diffusion of VOC is taking place are of thickness $2l$, and that they contain all the immobile water. Then the volume of immobile water in a volume element can be written as

$$\Delta V^i = \omega^i L \Delta x \Delta y = 2lA'\nu_{\text{clay}} \tag{45}$$

where A' = total cross-sectional area of saturated clay lenses in the volume element, m^2

ν_{clay} = porosity of the clay

Then

$$A' = \frac{\omega^i L \Delta x \Delta y}{2l\nu_{\text{clay}}} \tag{46}$$

and the total area of lenses from which VOC may diffuse is

$$2A' = \frac{\omega^i L \Delta x \Delta y}{l\nu_{\text{clay}}} \tag{47}$$

where we have counted the top and bottom halves of the lenses separately. This is also the area of interface between any two adjacent slabs within the volume element into which the immobile aqueous phase is partitioned and between which diffusion of VOC is possible.

We do a mass balance on the VOC in the immobile aqueous phase in the kth slab of the ijth volume element; this yields

$$\frac{\omega^i L \Delta x \Delta y}{n_u}\frac{dC_{ijk}^i}{dt} = \frac{\omega^i L\ \Delta x\ \Delta y}{l\nu_{\text{clay}}}\frac{D}{\Delta u}(C_{ijk+1}^i - 2C_{ijk}^i + C_{ijk-1}^i) - \frac{dm_{ijk}}{dt},$$

$$k = 2, 3, \ldots, n_u - 1 \tag{48}$$

which in turn gives

$$\frac{dC^i_{ijk}}{dt} = \frac{D}{(\Delta u)^2 \nu_{\text{clay}}}(C^i_{ijk+1} - 2C^i_{ijk} + C^i_{ijk-1}) - \frac{n_u}{\omega^i L \Delta x \Delta y}\frac{dm_{ijk}}{dt} \tag{49}$$

For the innermost slab ($k = n_u$, on either side of the center plane of the lenses), we have

$$\frac{dC^i_{ijnu}}{dt} = \frac{D}{(\Delta u)^2 \nu_{\text{clay}}}(-C^i_{ijnu} + C^i_{ijnu-1}) - \frac{n_u}{\omega^i L \Delta x \Delta y}\frac{dm_{ijnu}}{dt} \tag{50}$$

For the slab adjacent to the advecting mobile water,

$$\frac{dC^i_{ij1}}{dt} = \frac{D}{(\Delta u)^2 \nu_{\text{clay}}}[C^i_{ij2} - C^i_{ij1} + 2(C^m_{ij} - C^i_{ij1})] - \frac{n_u}{\omega^i L \Delta x \Delta y}\frac{dm_{ij1}}{dt} \tag{51}$$

The Advection Equations. Completion of the Model

In this section we develop the equations describing advective transport of VOC by means of gas flow and water circulation. These are then used, together with the results of previous sections, to construct the differential equations which constitute the model. The section closes with the calculation of the total mass of residual VOC as a function of time.

Advective Transport by Gas Flow

We consider the *ij*th volume element, with Left, Right, Top, and Bottom surfaces through which VOC may be transported in the gas phase. The mass flow of VOC into ΔV_{ij} by gas-phase advection is given by

$$\begin{aligned} M^g_{ij} = {} & U^L_{ij} L \Delta y[S(U^L)C^g_{i-1,j} + S(-U^L)C^g_{ij}] \\ & + U^R_{ij} L \Delta y[-S(-U^R)C^g_{i+1,j} - S(U^R)C^g_{ij}] \\ & + U^B_{ij} L \Delta x[S(U^B)C^g_{i,j-1} + S(-U^B)C^g_{ij}] \\ & + U^T_{ij} L \Delta x[-S(-U^T)C^g_{i,j+1} - S(U^T)C^g_{ij}] \end{aligned} \tag{52}$$

where

C^g_{pq} = gas phase concentration of VOC in ΔV_{pq}

$$\begin{aligned} S(U) &= 1, \quad U > 0 \\ &= 0, \quad U \leqslant 0 \end{aligned} \tag{53}$$

$$U_{ij}^{\mathrm{L}} = U_x[(i - 1)\Delta x, (j - 0.5)\Delta y] \tag{54}$$

$$U_{ij}^{\mathrm{R}} = U_x[i\Delta x, (j - 0.5)\Delta y] \tag{55}$$

$$U_{ij}^{\mathrm{B}} = U_y[(i - 0.5)\Delta x, (j - 1)\Delta y] \tag{56}$$

$$U_{ij}^{\mathrm{T}} = U_y[(i - 0.5)\Delta x, j\Delta y] \tag{57}$$

Now we must correct the concentrations in the gas phase for the pressure changes which occur as the gas rises and expands. This gives

$$C^g(y) = \frac{P(y)}{P(y')} C^g(y') \tag{58}$$

where we are assuming that the gas is ideal, and shall use Eq. (15) to calculate the pressures. Recall

$$P = P(y) = P_a + \eta(h - y) \tag{15'}$$

These corrections yield for the mass flow of VOC into ΔV_{ij} by gas-phase advection

$$\begin{aligned} M_{ij}^g = {} & U_{ij}^{\mathrm{L}} L \Delta y[S(U^{\mathrm{L}})C_{i-1,j}^g + S(-U^{\mathrm{L}})C_{ij}^g] \\ & + U_{ij}^{\mathrm{R}} L \Delta y[-S(-U^{\mathrm{R}})C_{i+1,j}^g - S(U^{\mathrm{R}})C_{ij}^g] \\ & + U_{ij}^{\mathrm{B}} L \Delta x\left[S(U^{\mathrm{B}}) \frac{P[(j-1)\Delta y]}{P[(j-1.5)\Delta y]} C_{i,j-1}^g \right. \\ & \left. + S(-U^{\mathrm{B}}) \frac{P[(j-1)\Delta y]}{P[(j-0.5)\Delta y]} C_{ij}^g \right] \\ & + U_{ij}^{\mathrm{T}} L \Delta x\left[-S(-U^{\mathrm{T}}) \frac{P[j\Delta y]}{P[(j+0.5)\Delta y]} C_{i,j+1}^g \right. \\ & \left. - S(U^{\mathrm{T}}) \frac{P[j\Delta y]}{P[(j-0.5)\Delta y]} C_{ij}^g \right] \end{aligned} \tag{59}$$

Note that the gas phase VOC concentrations are calculated from

$$C_{pq}^g = K_{\mathrm{H}} C_{pq}^m \tag{60}$$

since we are assuming local equilibrium between the gas and mobile aqueous phases.

Advective Transport by Water Circulation

A mass balance for advective transport by circulation of the mobile water gives

$$\begin{aligned}\omega^m \Delta V_{ij}\left[\frac{dC_{ij}^m}{dt}\right]_{\text{water adv}} &= v_{ij}^{\mathrm{L}} L\Delta y[S(v^{\mathrm{L}})C_{i-1,j}^m + S(-v^{\mathrm{L}})C_{ij}^m] \\ &\quad + v_{ij}^{\mathrm{R}} L\Delta y[-S(v^{\mathrm{R}})C_{i+1,j}^m - S(v^{\mathrm{R}})C_{ij}^m] \\ &\quad + v_{ij}^{\mathrm{B}} L\Delta x[S(v^{\mathrm{B}})C_{i,j-1}^m + S(-v^{\mathrm{B}})C_{ij}^m] \\ &\quad + v_{ij}^{\mathrm{T}} L\Delta x[-S(-v^{\mathrm{T}})C_{i,j+1}^m - S(v^{\mathrm{T}})C_{ij}^m] \end{aligned} \tag{61}$$

where

$$v_{ij}^{\mathrm{L}} = v_x[(i - 1)\Delta x, (j - 0.5)\Delta y] \tag{62}$$

$$v_{ij}^{\mathrm{R}} = v_x[i\Delta x, (j - 0.5)\Delta y] \tag{63}$$

$$v_{ij}^{\mathrm{B}} = v_y[(i - 0.5)\Delta x, (j - 1)\Delta y] \tag{64}$$

$$v_{ij}^{\mathrm{T}} = v_y[(i - 0.5)\Delta x, j\Delta y] \tag{65}$$

Completion of the Mobile Liquid Phase VOC Material Balance

We require 1) the mobile liquid-phase advection terms just derived, 2) the gas-phase advection terms (since local equilibrium is assumed between mobile liquid and gas and the volume of the gas phase is neglected, this is simple), and 3) a term corresponding to diffusion mass transport of VOC from the outermost slab of immobile water. This last is given by

$$\omega^m \Delta x \Delta y L\left[\frac{dC_{ij}^m}{dt}\right]_{\text{diff}} = \frac{\omega^i \Delta x \Delta y L}{l\nu_{\text{clay}}}\,\frac{D}{(\Delta u/2)}\,(C_{ij1}^i - C_{ij}^m) \tag{66}$$

or

$$\left[\frac{dC_{ij}^m}{dt}\right]_{\text{diff}} = \frac{\omega^i D}{\omega^m l\nu_{\text{clay}}(\Delta u/2)}\,(C_{ij1}^i - C_{ij}^m) \tag{67}$$

The gas advection terms (see Eqs. 59 and 60) yield

$$\begin{aligned}\left[\frac{dC_{ij}^m}{dt}\right]_{\text{gas adv}} &= \frac{K_{\mathrm{H}} U_{ij}^{\mathrm{L}}}{\omega^m \Delta x}[S(U^{\mathrm{L}})C_{i-1,j}^m + S(-U^{\mathrm{L}})C_{ij}^m] \\ &\quad + \frac{K_{\mathrm{H}} U_{ij}^{\mathrm{R}}}{\omega^m \Delta x}[-S(-U^{\mathrm{R}})C_{i+1,j}^m - S(U^{\mathrm{R}})C_{ij}^m]\end{aligned}$$

$$+ \frac{K_{\mathrm{H}}U^{\mathrm{B}}_{ij}}{\omega^m \Delta y}\left[S(U^{\mathrm{B}})\frac{P[(j-1)\Delta y]}{P[(j-1.5)\Delta y]}C^m_{i,j-1} + S(-U^{\mathrm{B}})\frac{P[(j-1)\Delta y]}{P[(j-0.5)\Delta y]}C^m_{ij}\right] \tag{68}$$

$$+ \frac{K_{\mathrm{H}}U^{\mathrm{T}}_{ij}}{\omega^m \Delta y}\left[-S(U^{\mathrm{T}})\frac{P[j\Delta y]}{P[(j+0.5)\Delta y]}C^m_{i,j+1} - S(U^{\mathrm{T}})\frac{P[j\Delta y]}{P[(j-0.5)\Delta y]}C^m_{ij}\right]$$

The advection of mobile water (Eq. 61) gives

$$\begin{aligned}\left[\frac{dC^m_{ij}}{dt}\right]_{\text{water adv}} &= \frac{v^{\mathrm{L}}_{ij}}{\omega^m \Delta x}[S(v^{\mathrm{L}})C^m_{i-1,j} + S(-v^{\mathrm{L}})C^m_{ij}] \\ &+ \frac{v^{\mathrm{R}}_{ij}}{\omega^m \Delta x}[-S(-v^{\mathrm{R}})C^m_{i+1,j} - S(v^{\mathrm{R}})C^m_{ij}] \\ &+ \frac{v^{\mathrm{B}}_{ij}}{\omega^m \Delta y}[S(v^{\mathrm{B}})C^m_{i,j-1} + S(-v^{\mathrm{B}})C^m_{ij}] \\ &+ \frac{v^{\mathrm{T}}_{ij}}{\omega^m \Delta y}[-S(-v^{\mathrm{T}})C^m_{i,j+1} - S(v^{\mathrm{T}})C^m_{ij}]\end{aligned} \tag{69}$$

Finally, then,

$$\frac{dC^m_{ij}}{dt} = \left[\frac{dC^m_{ij}}{dt}\right]_{\text{water adv}} + \left[\frac{dC^m_{ij}}{dt}\right]_{\text{gas adv}} + \left[\frac{dC^m_{ij}}{dt}\right]_{\text{diff}} \tag{70}$$

The model then consists of Eq. (70) for the time dependence of the C^m_{ij}, Eq. (35) for that of the m_{ijk}, and Eqs. (49)–(51) for that of the C^i_{ijk}. Initialization consists of reading in the model parameters, and specifying the initial zone of contamination and the value of C_{tot} in that zone. The differential equations are then integrated forward in time to simulate the run. RAM limitations dictated that we use the simple Euler formula for this. The total mass of contaminant at any time t during the run is then given by

$$M_{\text{tot}}(t) = \sum_{i=1}^{n_x}\sum_{j=1}^{n_y}\left\{\Delta V\omega^m C^m_{ij} + \sum_{k=1}^{n_u}\left[m_{ijk} + \frac{\omega^i \Delta V}{n_u}C^i_{ijk}\right]\right\} \tag{71}$$

RESULTS

Computational Statistics and Default Parameters

The model was implemented in TurboBASIC on a 486-DX microcomputer with a clock speed of 50 MHz. The runs presented below required almost exactly 7 minutes of machine time. Default parameters for these runs are given in Table 1; when other values were used, this is noted in the caption to the figure. In most of the runs (with the exception of Fig. 16), the sparging of trichloroethylene (TCE) is modeled. Parameters for TCE were obtained from Montgomery and Welkom's compilation (33).

TABLE 1

Default Parameters for Sparging Runs, Horizontal Slotted Aeration Pipe Configuration

Thickness of aquifer, h	5 m
Height of sparging pipe above aquitard, h_p	0.5 m
Length of sparging pipe, L	10 m
Molar air flow rate to well, Q	1 mol/s
(Volumetric air flow rate to well	51.8 SCFM)
Radius of influence of air at top of aquifer, a_0	5 m
Distance from median plane to center of circulation, b	3.333 m
Half-width of domain of interest, $x_{\max}$	25 m
Velocity scale factor for water circulation, B	0.05
Temperature, T	298 K
Mobile water-filled porosity, ω^m	0.2
Immobile water-filled porosity, ω^i	0.2
Soil density	1.7 g/cm^3
Identity of VOC	Trichloroethylene
Density of VOC, ρ_{voc}	1.46 g/cm^3
Aqueous solubility of VOC, C_{sat}	1100 mg/L
Henry's constant of VOC, K_{H} (dimensionless)	0.2821
Diffusivity of VOC in water in porous medium, D	2×10^{-10} m^2/s
n_x	25
n_y	5
Thickness of clay lenses containing immobile water, $2l$	1 cm
Porosity of clay in the lenses, ν_{clay}	0.4
Number of slabs into which the immobile water is subdivided, n_u	5
Initial total VOC concentration, C_{tot}	2000 mg/kg
Initial NAPL droplet diameter, $2a_0'$	0.1 cm
Lateral distance to which contamination extends away from median plane	4 m
Depth to which contamination extends in aquifer	4 m
Δt	450 seconds

Effects of Model Parameters on Cleanup Rates

The results of the calculations are presented as plots of $M'(t) = M_{tot}(t)/M_{tot}(0)$ versus time over a period of 30 days.

One question which had to be answered before the bulk of the modeling runs could be made was to what extent would the water circulation wash contaminant out of the domain being modeled. This would result in a spurious appearance of cleanup when in fact contaminant was being pushed out to large distances from the sparging well, rather than being removed. Figure 6 explores this point, and indicates that, if $x_{max} = 25$ m, reasonable values of the water circulation scale parameter B result in relatively minor wash-out. In these runs the air flow rate was set equal to zero, and B was set equal to 0.025, 0.05, and 0.1. For this most unfavorable case (with no VOC being removed by air sparging), a value of B of 0.05 resulted in only about 7% of the VOC being lost by wash-out. This value was therefore selected as the default value. It yields circulation periods of about 4 days for most of the water stream lines.

It was mentioned earlier that the determination of the water circulation scale parameter B would be rather difficult in practice, and that it was

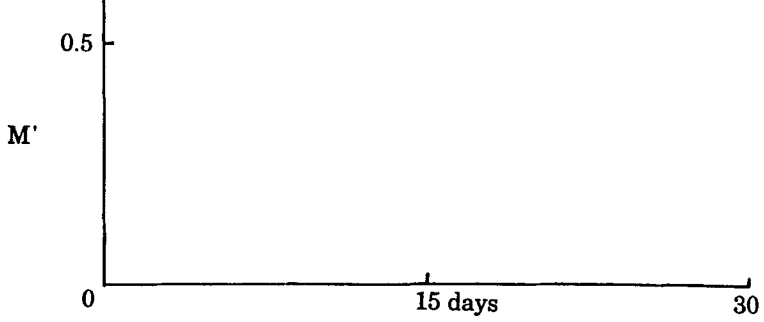

FIG. 6 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; "wash-out" effect. The air flow rate $Q = 0$ here. The water circulation rate parameter $B = 0.025$, 0.05, and 0.1, top to bottom. Other parameters in this and all following figures are as given in Table 1.

therefore fortunate that the modeling results depend only weakly on B. This is shown in Fig. 7, where values of B of 0, 0.5, 0.1, and 0.2 were used. The run for which $B = 0$ shows a nonzero residual VOC mass that is not being removed because a portion of the zone of contamination lies outside the parabolic domain being aerated and there is no mechanism for its removal, since for this run there is no water circulation. The other runs show essentially identical results, indicating that an accurate estimation of B is not necessary in using the model. A run (not shown) for which $B = 0.025$ gave results virtually superimposed on the plot for $B = 0.05$.

The effect of variations in air flow rate is shown in Fig. 8. Air flow rates of 0.25, 0.5, 1, and 2 mol/s yield the results shown. As one would intuitively expect, increased air flow rates result in increased rates of cleanup. Since the system is solution/diffusion limited, however, the rate of cleanup is not proportional to the air flow rate. As with our other sparging and soil vapor extraction models, increasing air flow rate can be quite ineffective, as well as quite costly, if the process is mass-transport-limited.

One expects that the water circulation rate would be at least roughly proportional to the air flow rate. The runs shown in Fig. 8 do not reflect this dependence, since B is being held constant in those calculations. In Fig. 9, however, a set of runs is presented in which the water circulation rate is taken as proportional to the air flow rate. As in Fig. 8, we find that

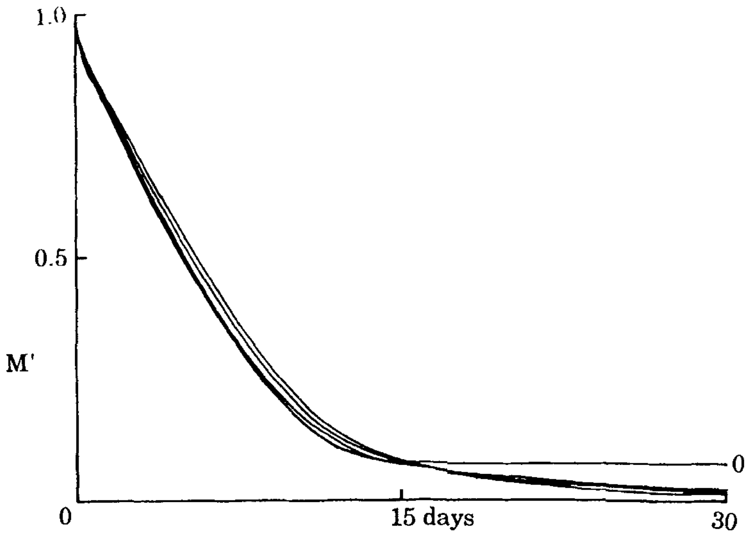

FIG. 7 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; effect of water circulation rate parameter B. $B = 0$ (indicated curve), 0.05, 0.1, and 0.2.

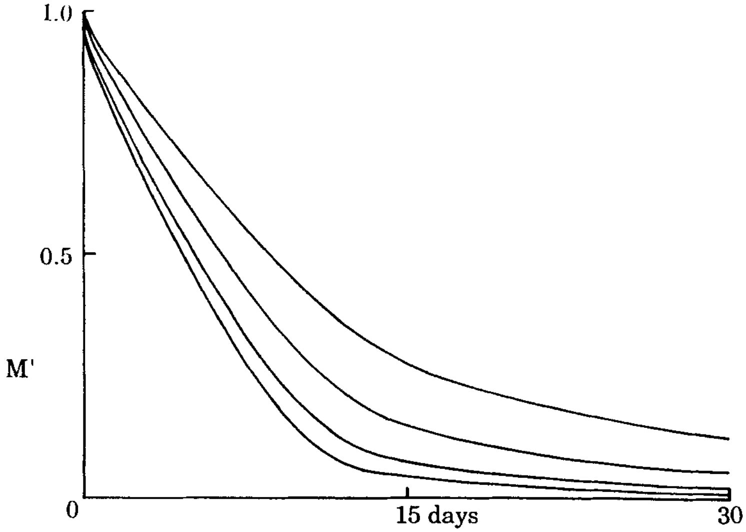

FIG. 8 Plots of M' [$M_{tot}(t)/M_{tot}(0)$] versus time; effect of air flow rate Q. Q = 0.25, 0.5, 1, and 2 mol/s from the top down (12.95, 25.9, 51.8, and 103.6 SCFM).

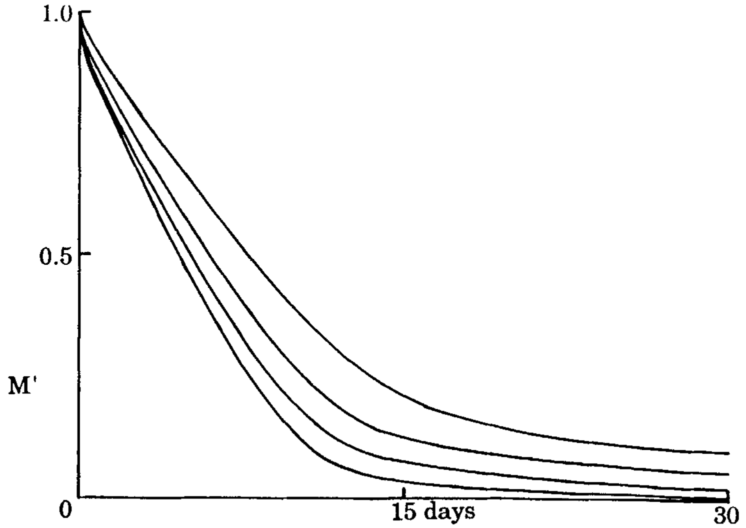

FIG. 9 Plots of M' [$M_{tot}(t)/M_{tot}(0)$] versus time; effect of joint molar air flow rate Q (mol/s) and water circulation parameter B. Values of (Q, B) are (0.25, 0.0125), (0.5, 0.025), (1, 0.05), and (2, 0.1) from the top down.

increased air flow rates result in increased rates of VOC removal, but that the process here is evidently rather limited by mass-transport kinetics. As one might have expected from the results shown in Fig. 7, the differences between Fig. 8 and Fig. 9 are not large.

The effect of the distance of the sparging pipe above the bottom of the aquifer being treated is shown in Fig. 10. The closer to the bottom of the aquifer the sparging well is located, the more rapid is the cleanup, a conclusion identical to that found in the course of modeling soil vapor extraction. Evidently the effect of water circulation is not sufficient to compensate for the inefficiency resulting from a shallow sparging well.

The effect of the half-width of the aeration zone at the top of the aquifer, a_0, is shown in Fig. 11. We find that if the value of a_0 is sufficiently small that air is not delivered to an appreciable fraction of the contaminated zone, cleanup is slow. On the other hand, an increase in the value of a_0 beyond that necessary to deliver air to most of the contaminated zone appears to have relatively little effect. In practice, values of a_0 can be estimated by making soil gas pressure measurements in the vadose zone near the water table at various distances from the sparging well when it is in operation (23). Note that the value of a_0 obtained is dependent on the gas flow rate being used.

The thickness of the clay lenses, $2l$, has a profound effect on the rate of cleanup by sparging, as seen in Fig. 12. Values of $2l$ ranging from 0.5

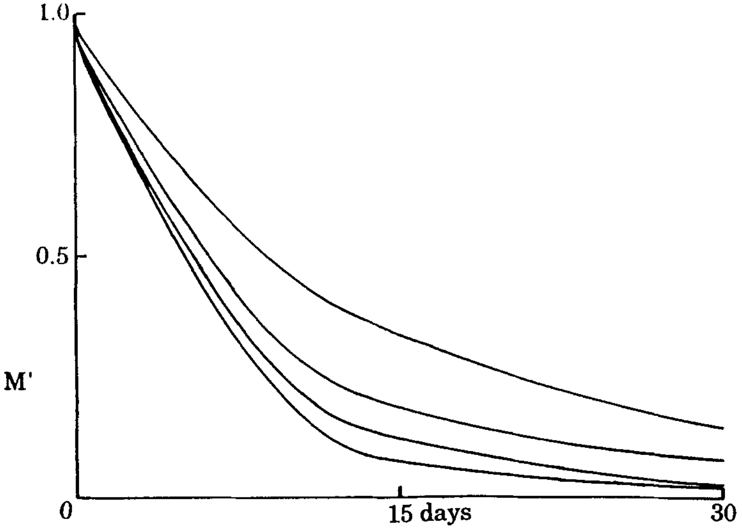

FIG. 10 Plots of M' $[M_{\rm tot}(t)/M_{\rm tot}(0)]$ versus time; effect of sparging well height above the bottom of the aquifer, h_p. Values of h_p are 3, 2, 1, and 0 m from the top down.

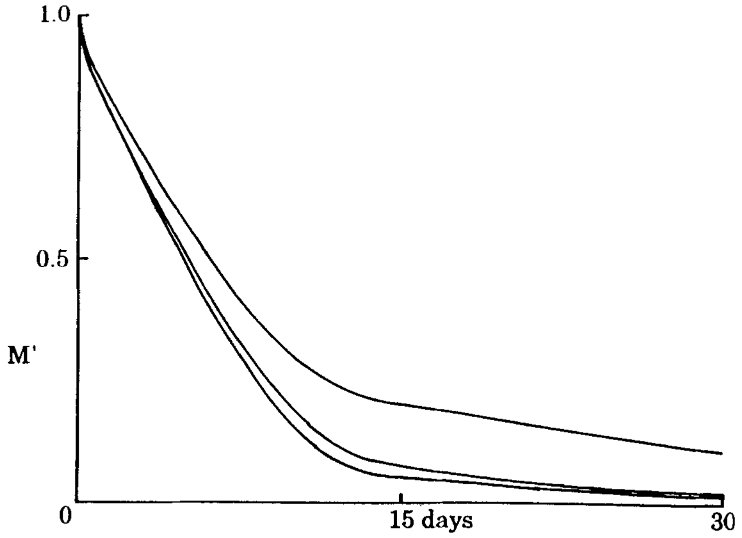

FIG. 11 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; effect of the width parameter for the air distribution, a_0. a_0 = 4, 5, and 7 m from the top down.

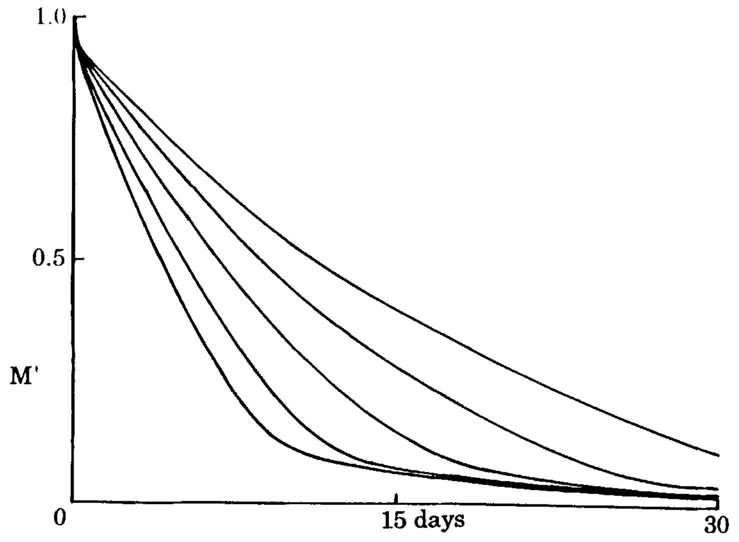

FIG. 12 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; effect of the thickness of the clay lenses, $2l$. $2l$ = 0.5, 1.0, 1.5, 2.0, and 2.5 cm from the bottom up.

to 2.5 cm were used in making these runs, and it is seen that cleanup rates are severely diffusion-limited for the larger values of $2l$. If well logs indicate that low-permeability lenses of significant thickness are present in a contaminated aquifer, one expects that sparging will indeed show rather rapid reduction in the VOC concentration in the mobile groundwater, but that there will be severe tailing and troublesome rebounds in VOC concentration after the operation has been shut down. This indicates the importance of a post-cleanup monitoring period of duration sufficient to determine if rebound is occurring.

Figure 13 shows the effects of NAPL droplet size on the rate of cleanup. Small droplets give a larger total water–NAPL surface than larger droplets for a given total mass of VOC. One therefore expects that remediation should be more rapid if the droplets are small than if they are large; this is what is observed in these results, and the effect is large. The remarks made about tailing and VOC concentration rebound in the last paragraph apply equally here.

We note that several of the runs shown in Figs. 11, 12, and 13 show substantial tailing toward the end of the cleanup. This is associated with the time required to circulate all the water through the zone of aeration so that it can be cleaned up by aeration. With our model parameters this

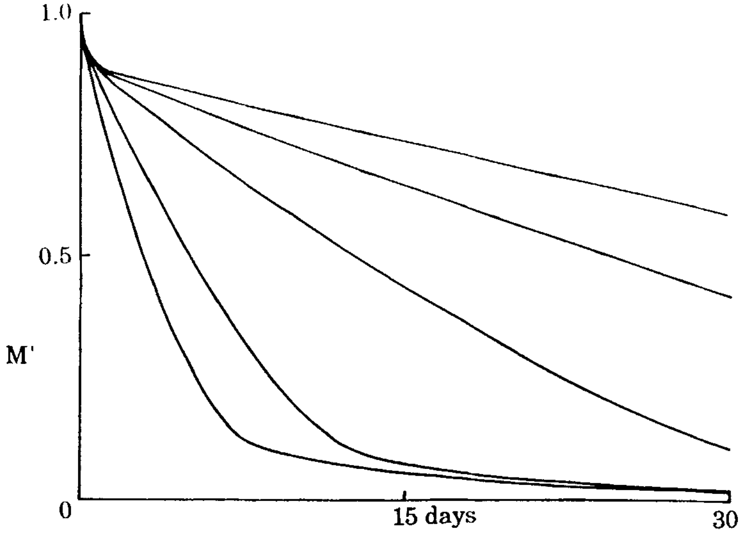

FIG. 13 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; effect of the initial NAPL droplet diameter, $2a_0'$. $2a_0'$ = 0.05, 0.1, 0.2, 0.3, and 0.4 cm from the bottom up.

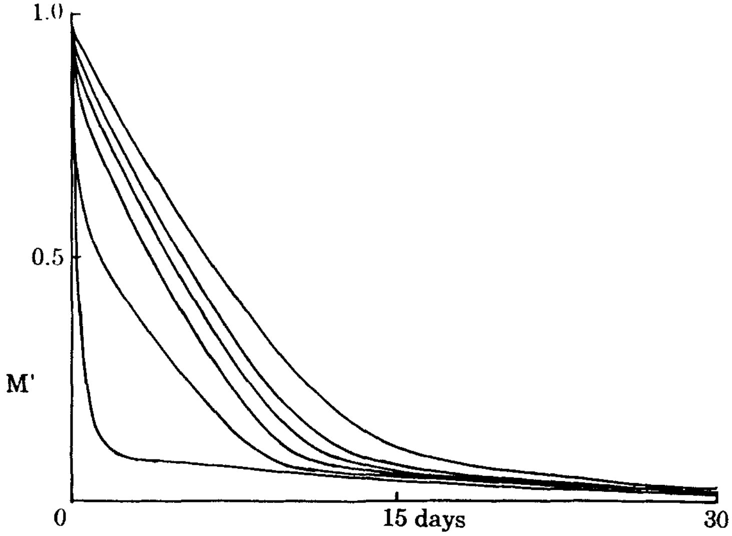

FIG. 14 Plots of M' $[M_{\text{tot}}(t)/M_{\text{tot}}(0)]$ versus time; effect of initial VOC concentration C_{tot}. $C_{\text{tot}} = 250, 500, 1000, 1500, 2000$, and 3000 mg/kg from the bottom up.

is a relatively slow process, so one finds this tailing after all of the NAPL has been removed.

The effect of initial total VOC concentration is seen in Fig. 14. The higher the initial total VOC concentration, the longer it takes to remove the bulk of the VOC, as expected. In all cases, however, one finds fairly prolonged tailing as a result of the slow circulation of water containing dissolved VOC through the zone of aeration.

Figure 15 shows the effect of the depth of the distribution of a given mass of contaminant—how far it has distributed itself down into the aquifer. Interestingly enough, the effect is not particularly large, especially when one takes the tailing mentioned above into account. One actually finds that the shallowest distribution (penetration only 1 m down into the aquifer) cleans up slightly more slowly than the others, perhaps because the sparging air has a longer contact time with the contaminated zone when the distribution is thicker (2, 3, or 5 m).

The effect of Henry's constant K_H on the rate of cleanup is seen in the results given in Fig. 16. Values of K_H of 0.025, 0.05, 0.1, 0.2, 0.4, and 0.8 are shown here; the Henry's constant for TCE in water at 25°C is 0.2821 for comparison. For the smaller values of K_H the sparging is evidently controlled by the equilibrium of VOC between the mobile water and the gas phase. For larger values, this becomes less important as the process

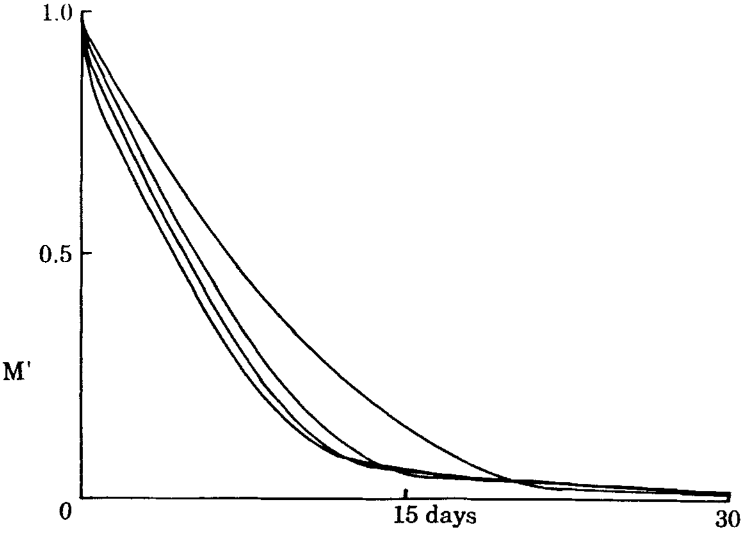

FIG. 15 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; effect of initial spatial distribution of 816 kg of trichloroethylene. In all cases the half-width of the initial distribution is 4 m. The initial depth of the distribution is 1, 2, 3, and 5 m from right to left.

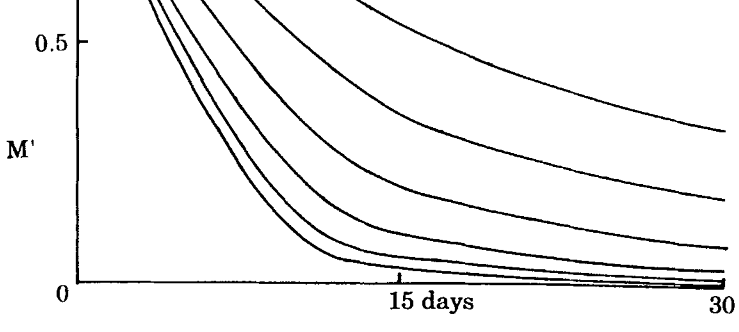

FIG. 16 Plots of M' $[M_{tot}(t)/M_{tot}(0)]$ versus time; effect of Henry's constant K_H. K_H = 0.025, 0.05, 0.1, 0.2, 0.4, and 0.8 (dimensionless) from the top down.

becomes mass-transport-limited. One concludes that most of the common organic solvents can readily be removed by sparging, notable exceptions being such oxygenated solvents as alcohols and ketones. The tailing effect mentioned earlier is also seen here.

CONCLUSIONS

A model for the sparging of aquifers contaminated with VOCs has been developed which permits inclusion of the kinetics of solution of NAPL droplets and of diffusion from low-permeability porous layers. The sparging well configuration modeled is that of a buried horizontal slotted pipe. The model runs readily on currently available microcomputers, requiring less than 10 minutes on a machine equipped with a 80486 microprocessor and running at 50 MHz. The conclusions which can be drawn from the modeling results are as follows.

- The presence of low-permeability porous structures (lenses or intermittent layers of clay, till, silt, etc.) results in very marked increases in the times required for cleanup. The presence of such structures can be ascertained from the drilling logs obtained in the course of investigation of the site. The extent of the increase in cleanup time depends strongly on the thickness of the structures. The presence of NAPL droplets of large size also results in a marked increase in cleanup time.
- As with soil vapor extraction, increases in air flow rate do not result in corresponding decreases in cleanup time if the system is limited by solution/diffusion kinetics. One must note, however, that cleanup times can be expected to decrease if the air pressure gradients are sufficient to force air through the low-permeability domains.
- The magnitude of the rate of induced water circulation plays a rather minor role in determining the cleanup time. It does not appear to be necessary to go to great effort and expense to determine an accurate value for this parameter.
- Wells should be sufficiently deep and operated at an air flow rate such that air is delivered to the entire zone of contamination. Depending on water circulation to move VOC from a contaminated region to a region through which air is moving results in markedly increased cleanup times.
- The spatial distribution of the VOC does not appear to be of particular importance in determining the cleanup time, as long as air is delivered to the entire region containing contaminant.
- Cleanup times increase roughly proportionally to increasing initial VOC concentration if NAPL is present.

- The terminal phase of cleanup with a horizontal slotted pipe sparging well typically shows substantial tailing as water which contains VOC must circulate into the zone of aeration before the VOC can be stripped. This effect might be reduced by the judicious placement of recovery wells to reduce the size of the region through which water containing dissolved VOC circulates.
- The runs reported here indicate that VOCs having Henry's constants of 0.05 or larger can quite readily be removed by sparging.

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