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# Groundwater Cleanup by *in-situ* Sparging. III. Modeling of Dense Nonaqueous Phase Liquid Droplet Removal

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## Abstract

Microcomputer models for describing the removal of dispersed DNAPL (dense nonaqueous phase liquid) droplets from contaminated aquifers by air sparging are presented, and the dependence of cleanup times on the model parameters is explored. Diffusion transport is assumed to take place from spherical DNAPL droplets through a thick stagnant water layer in a porous medium to the advecting mobile water. Single sparging wells and single sparging curtains are modeled.

## INTRODUCTION

One of the most challenging problems in hazardous waste site remediation is the removal of dense nonaqueous phase liquids (DNAPLs) from below the water table. These materials, many of them common chlorinated hydrocarbon solvents, typically have relatively low solubilities in water (of the order of 1000 mg/L or less), and their diffusion constants in water are quite small, as is the case with all diffusion constants in condensed phases. Kinetic limitations on the rates of solution of these compounds are therefore rather severe, resulting in very long drawn-out remediations if pump-and-treat methods are used.

An introduction to DNAPLs in groundwater has been provided by Feenstra and Cherry (*1*). Schwille's (*2*) elegant experimental work with chlorinated hydrocarbons demonstrated that these compounds quickly move down through most aquifers, leaving a substantial trail of DNAPL droplets/ganglia trapped interstitially in the porous aquifer medium. This DNAPL residue may amount to 5–50 L/m$^3$, which may be the major part of the material to be removed.

Powers et al. (*3*) investigated the nonequilibrium factors involved with the solution of "blobs" of NAPL held interstitially in water-saturated porous media. They concluded that the low rates of mass transfer were due to 1) rate limited mass transport between the nonaqueous and aqueous phases (the solution process itself), 2) the tendency of advecting aqueous phase to bypass contaminated regions of low aqueous permeability, and 3) nonuniform flow resulting from aquifer heterogeneities. These workers noted that mass transport of volatile organic compounds (VOCs) from trapped "blobs" is very much slower than it is in highly regular media such as the glass beads used by Miller et al. (*4*).

One of the techniques which it is hoped will speed up the remediation of sites contaminated with DNAPL is air sparging. Herrling and Stamm (*5*) discussed the use of vacuum-vaporizer wells in Germany for the sparging of VOCs in the vadose and saturated zones. Brown (*6*) described a somewhat simpler sparging technique which Ground Water Technology, Inc., has used in the United States for *in-situ* removal of VOCs from groundwater. We published a model for the sparging of dissolved VOCs from groundwater by means of an aeration curtain (*7*), and also developed a model for sparging dissolved VOCs with a simple air injection well (*8*).

We published several models for the flushing of DNAPL droplets/ganglia by pump-and-treat operations (*9*); these include the effects of mass transport kinetics, and are simple enough to run on microcomputers. They should be helpful in giving insight into the impact of solution/diffusion limitations in pump-and-treat cleanups. They also bear on the problem of DNAPL removal from the zone of saturation by sparging, since one expects that the dissolution of the DNAPL ganglia in pump-and-treat and in sparging will be governed by the same mechanism.

In the following we combine the advective flow field developed earlier for sparging dissolved VOCs (*8*) with the mass transport kinetics developed for the flushing of DNAPLs present as trapped droplets (*9*) to construct a model for the sparging of DNAPL droplets from the zone of saturation.

## ANALYSIS

### Simple Sparging Well

The scheme used for the DNAPL sparging model and the notation are shown in Figs. 1 and 2. Figure 1 shows the overall layout. Air is injected near the bottom of the aquifer, and is assumed to rise rather close to the pipe. The rising air may be confined within a larger pipe coaxial with the air injection pipe and perhaps packed with crushed rock to provide a longer transit time for the rising air bubbles. In any case, it is assumed that the rising air induces a flow of water into the axis of the system at the bottom of the aquifer, and that this water is sparged and then discharged at the

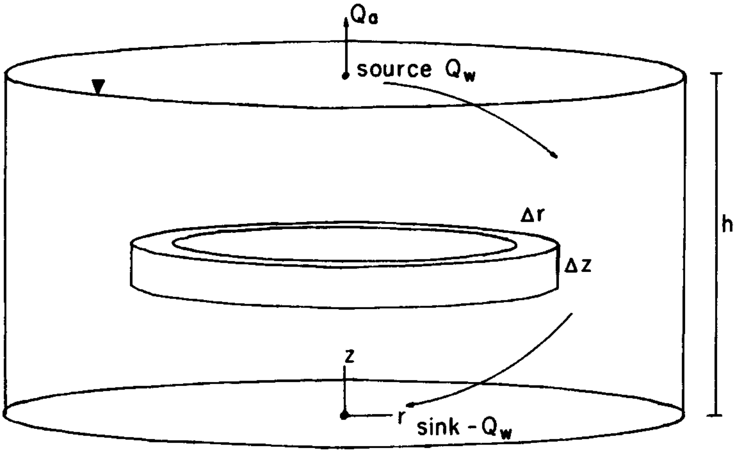

FIG. 1. Sparging well geometry and notation.

top of the aquifer. Thus, as in our previous work, we require a water flow field which provides a sink of magnitude $-Q_w$ at (0, 0) and a source of magnitude $Q_w$ at (0, $h$). We also require that there be no flow through either the top or the bottom of the aquifer. We further assume that the aquifer is of constant and isotropic permeability, so our system is axially symmetric. It was shown earlier (*8*) that the method of images can be used to construct a solution to Laplace's equation which serves as a velocity potential function for this system, and that the resulting velocities are given by

$$v_r = \frac{Q_w}{2\pi\nu} \sum_{n=-\infty}^{\infty} \left[ \frac{r}{\{r^2 + [z - (2n + 1)h]^2\}^{3/2}} - \frac{r}{\{r^2 + [z - 2nh]^2\}^{3/2}} \right] \tag{1}$$

and

$$v_z = \frac{Q_w}{2\pi\nu} \sum_{n=-\infty}^{\infty} \left[ \frac{z - (2n + 1)h}{\{r^2 + [z - (2n + 1)h]^2\}^{3/2}} - \frac{z - 2nh}{\{r^2 + [z - 2nh]^2\}^{3/2}} \right] \tag{2}$$

We define

$$r_i = (i - \tfrac{1}{2})\Delta r \tag{3}$$

$$z_j = (j - \tfrac{1}{2})\Delta z \tag{4}$$

and

$$v^{\mathrm{L}}_{ij} = v_r[(i - 1)\Delta r, (j - \tfrac{1}{2})\Delta z] \tag{5}$$

$$v^{\mathrm{R}}_{ij} = v_r[i\Delta r, (j - \tfrac{1}{2})\Delta z] \tag{6}$$

$$v^{\mathrm{B}}_{ij} = v_r[(i - \tfrac{1}{2})\Delta r, (j - 1)\Delta z] \tag{7}$$

$$v^{\mathrm{T}}_{ij} = v_r\{(i - \tfrac{1}{2})\Delta r, j\Delta z] \tag{8}$$

Also, the $ij$th annular volume element is given by

$$V_{ij} = (2i - 1)\pi(\Delta r)^2\Delta z \tag{9}$$

Let

$c_{ij}$ = concentration of dissolved VOC in $V_{ij}$, kg/m$^3$ of water
$C_{ij}$ = concentration of DNAPL in $V_{ij}$, kg/m$^3$ of medium
$v$ = porosity of the aquifer, dimensionless

and define

$$\begin{aligned} S(x) &= 0, \qquad x \leq 0 \\ &= 1, \qquad 0 < x \end{aligned} \tag{10}$$

We then carry out a material balance on dissolved VOC in the $ij$th volume element. This yields

$$\begin{aligned} \frac{dc_{ij}}{dt} = {} & \frac{2\pi(i - 1)\Delta r\Delta z}{V_{ij}} v^{\mathrm{L}}_{ij}[S(v^{\mathrm{L}})c_{i-1,j} + S(-v^{\mathrm{L}})c_{ij}] \\ & - \frac{2\pi i\Delta r\Delta z}{V_{ij}} v^{\mathrm{R}}_{ij}[S(-v^{\mathrm{R}})c_{i+1,j} + S(v^{\mathrm{R}})c_{ij}] \\ & + \frac{\pi(2i - 1)(\Delta r)^2}{V_{ij}} v^{\mathrm{B}}_{ij}[S(v^{\mathrm{B}})c_{i,j-1} + S(-v^{\mathrm{B}})c_{ij}] \\ & - \frac{\pi(2i - 1)(\Delta r)^2}{V_{ij}} v^{\mathrm{T}}_{ij}[S(-v^{\mathrm{T}})c_{i,j+1} + S(v^{\mathrm{T}})c_{ij}] + \left[\frac{\partial c_{ij}}{\partial t}\right]_{\text{from DNAPL}} \end{aligned} \tag{11}$$

Now solution of DNAPL is a conservative process within the *ij*th volume element, which gives

$$V_{ij}\nu\left[\frac{\partial c_{ij}}{\partial t}\right]_{\text{from DNAPL}} + V_{ij}\frac{dC_{ij}}{dt} = 0 \qquad (12)$$

For $dC_{ij}/dt$ we use an expression developed in our model for the flushing of VOC from an aquifer contaminated by spherical DNAPL droplets which dissolve by diffusion of VOC through a thick stagnant aqueous boundary layer into the mobile water moving to a recovery well (*9*). See Fig. 2. The result is

$$\frac{dC_{ij}}{dt} = -\frac{3C_0^{2/3}D(c_s - c_{ij})}{\rho a_0^2}C_{ij}^{1/3} \qquad (13)$$

Here $\rho$ = DNAPL density, kg/m$^3$
$C_0$ = initial DNAPL concentration, kg/m$^3$ of aquifer
$D$ = VOC diffusivity in water-saturated porous medium, m$^2$/s
$c_s$ = VOC solubility in water, kg/m$^3$
$a_0$ = initial DNAPL droplet radius, m

From Eqs. (12) and (13) we obtain

$$\left[\frac{\partial c_{ij}}{\partial t}\right]_{\text{from DNAPL}} = \frac{3C_0^{2/3}D(c_s - c_{ij})}{\rho a_0^2\nu}C_{ij}^{1/3} \qquad (14)$$

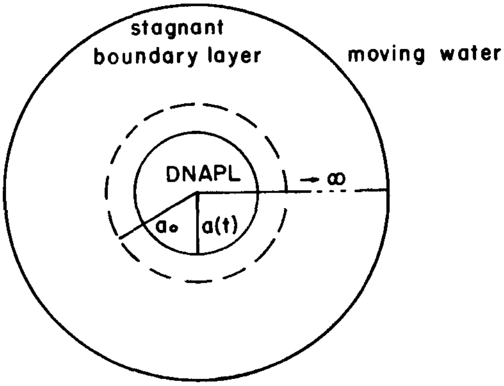

FIG. 2. Model for diffusion from a DNAPL droplet.

Substitution of Eq. (14) into Eq. (11) plus Eq. (13) then provides the modeling equations governing the $C_{ij}$ and $c_{ij}$ for most of the volume elements.

We next examine the effect of the central aeration pipe. It will be represented as a single, well-stirred tank aerator, with the dissolved VOC obeying Henry's law and with local equilibrium between the aqueous and the vapor phases. We let

$K_H$ = Henry's constant for the VOC, dimensionless
$c_l$ = dissolved VOC concentration in the aerator, kg/m$^3$
$Q_a$ = air flow rate through the central aeration pipe, m$^3$/s

In steady state the flux of VOC into the aerator at the bottom must equal the sum of the two fluxes out of the aerator at the top, which gives

$$Q_w c_{11} = (Q_w + Q_a K_H) c_l \tag{15}$$

so

$$c_l = \frac{c_{11}}{1 + Q_a K_H / Q_w} \tag{16}$$

Then in the 1,1th volume element (at the bottom of the pipe), we must modify Eq. (11) by subtracting a term on the right-hand side as indicated:

$$\frac{dc_{11}}{dt} = -\frac{Q_w c_{11}}{V_{11}} + \text{advective and dissolution terms} \tag{17}$$

to take into account the movement of VOC from the 1,1th volume element into the aeration region. In similar fashion, in the 1,*J*th element (at the top of the pipe) we must modify Eq. (11) by adding a term on the right-hand side:

$$\frac{dc_{1J}}{dt} = \frac{Q_w c_{11}}{V_{1J}(1 + Q_a K_H / Q_w)} + \text{advective and dissolution terms} \tag{18}$$

which accounts for the movement of VOC from the aeration region into the 1,*J*th volume element.

In addition to the parameters given above, it is necessary to assign the radius of the domain which is contaminated. Then one simply integrates Eqs. (11), (14), (17), and (18) forward in time.

## Sparging with a Horizontal Slotted Pipe

We next develop a model for sparging by means of a horizontal slotted pipe buried in an aeration curtain configuration as indicated in Fig. 3. This approach might be useful when the contamination is rather shallow but extends over a fairly wide area. Again we assume an isotropic, constant permeability for the aquifer. A velocity potential function which satisfies boundary conditions of no normal flow at the top and bottom of the aquifer ($y = h$ and $y = 0$, respectively) and has a source at $(0, h)$ and a sink at $(0, 0)$ is easily constructed by the method of images; this is

$$W = \frac{Q_w}{2\pi l v} \sum_{n=-\infty}^{\infty} \{-\log [x^2 + (y - 2nh)^2] + \log [x^2 + (y - (2n + 1)h)^2]\} + v_0 x \quad (19)$$

This represents flow in the aquifer from a source $Q_w$ at $(0, h)$ to a sink $-Q_w$ at $(0, 0)$ superimposed on a uniform natural flow in the $x$ direction having a velocity $v_0$ m/s.

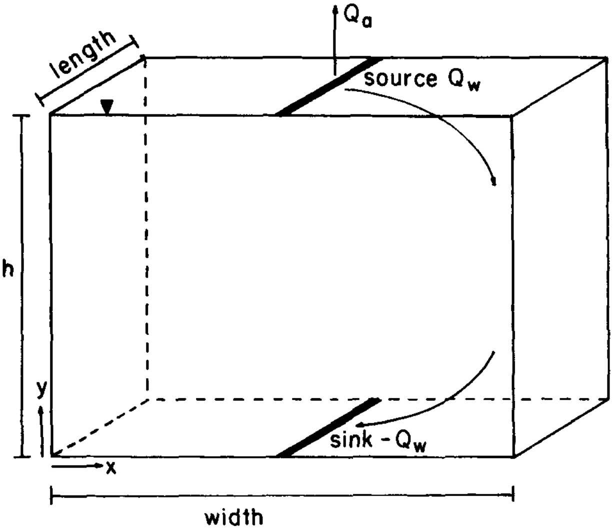

FIG. 3. Sparging curtain geometry and notation.

The potential function $W$ yields the following expressions for the $x$- and $y$-components of the fluid velocity:

$$v_x = v_0 + \frac{Q_w}{\pi l v} \sum_{n=-\infty}^{\infty} \left[ \frac{x}{x^2 + [y - (2n + 1)h]^2} - \frac{x}{x^2 + [y - 2nh]^2} \right] \tag{20}$$

and

$$v_y = \frac{Q_w}{\pi l v} \sum_{n=-\infty}^{\infty} \left[ \frac{y - (2n + 1)h}{x^2 + [y - (2n + 1)h]^2} - \frac{y - 2nh}{x^2 + [y - 2nh]^2} \right] \tag{21}$$

The domain of interest is partitioned into rectangular prism volume elements such that the size of the $ij$th volume is given by

$$\Delta V_{ij} = \Delta V = \Delta x \Delta y l \tag{22}$$

Also

$$x_i = (i - i_{\text{well}} - \tfrac{1}{2})\Delta x \tag{23}$$

$$y_j = (j - \tfrac{1}{2})\Delta y \tag{24}$$

Here $i_{\text{well}}$ is the $x$-index of the volume elements containing the source and sink.

We use Eq.(13) to model the rate of solution of the DNAPL droplets, as before. The equation describing advection of the dissolved VOC is

$$\begin{aligned} \frac{dc_{ij}}{dt} = {} & \frac{v_{ij}^{\mathrm{L}}}{\Delta x}[S(v^{\mathrm{L}})c_{i-1,j} + S(-v_{\mathrm{L}})c_{ij}] - \frac{v_{ij}^{\mathrm{R}}}{\Delta x}[S(-v^{\mathrm{R}})c_{i+1,j} + S(v_{\mathrm{R}})c_{ij}] \\ & + \frac{v_{ij}^{\mathrm{B}}}{\Delta y}[S(v^{\mathrm{B}})c_{i,j-1} + S(-v_{\mathrm{B}})c_{ij}] - \frac{v_{ij}^{\mathrm{T}}}{\Delta y}[S(-v^{\mathrm{T}})c_{i,j+1} + S(v_{\mathrm{T}})c_{ij}] \\ & + \text{a solution term and a source (sink) term if needed} \end{aligned} \tag{25}$$

Here

$$v_{ij}^{\mathrm{L}} = v_x[(i - 1)\Delta x, (j - \tfrac{1}{2})\Delta y] \tag{26}$$

$$v_{ij}^{\mathrm{R}} = v_x[i\Delta x, (j - \tfrac{1}{2})\Delta y] \tag{27}$$

$$v_{ij}^{\mathrm{B}} = v_y[(i - \tfrac{1}{2})\Delta x, (j - 1)\Delta y] \tag{28}$$

$$v_{ij}^{\mathrm{T}} = v_y[(i - \tfrac{1}{2})\Delta x, j\Delta y] \tag{29}$$

The solution term is given by Eq. (14). The sink term at the bottom of the sparging unit is given by

$$\left[\frac{dc_{i\mathrm{well},1}}{dt}\right]_{\mathrm{sink}} = -\frac{Q_w c_{i\mathrm{well},1}}{\Delta V} \tag{30}$$

The source term at the top of the aquifer is given by

$$\left[\frac{do_{i\mathrm{well},J}}{dt}\right]_{\mathrm{source}} = \frac{Q_w c_{i\mathrm{well},J}}{\Delta V(1 + Q_a K_{\mathrm{H}}/Q_w)} \tag{31}$$

As in the earlier model, we have represented the sparging unit itself as a single-stage aerator with equilibrium between the vapor and liquid phases.

## Diffusion-Controlled Sparging

We can obtain a formula useful in the limit as diffusion becomes the controlling factor in the solution of DNAPL droplets by setting $c_{ij} = 0$ in Eq. (13), corresponding to the assumption that advective transport is sufficiently rapid to remove dissolved VOC as fast as it is formed. The resulting equation is readily integrated, yielding

$$C(t) = C_0\left[1 - \frac{2Dc_a}{a_0^2}t\right]^{3/2} \tag{32}$$

for $0 < t < a_0^2/2Dc_a = t_c$, the time required for complete dissolution of the DNAPL.

## RESULTS

Computer programs were written in TurboBASIC implementing the models on microcomputers using 80286 or 80386 microprocessors. The results described below were obtained with machines having math coprocessors, using MS-DOS, and running at 12, 16, and 33 MHz. Running times for the runs presented below ranged from 45 minutes to 4 hours on an 80386 SX machine.

We first examine the results obtained for a single sparging well. Default values of the model parameters are given in Table 1; departures from these values are indicated in the captions. Figure 4 shows the effect on VOC removal of the initial effective diameter $a_0$ of the DNAPL droplets being dissolved. If we are in the diffusion-limited regime, the occurrence of $a_0^2$ in the denominator of Eq. (13) leads us to expect rather drastic increases in remediation times with increasing values of $a_0$, as is, in fact, observed in Fig. 4. Evidently the effective radius of the DNAPL blobs dispersed in the aquifer medium is an important parameter in the modeling.

TABLE 1
Default Parameters for Sparging Well Computations

| | |
|---|---|
| Thickness of aquifer | 5 m |
| Radius of domain of interest | 15 m |
| Porosity of aquifer medium | 0.3 |
| Air flow rate through sparging well | 0.01 $m^3/s$ |
| Induced water flow rate | 0.0025 $m^3/s$ |
| Aquifer medium density | 1.7 $g/cm^3$ |
| Aqueous solubility of DNAPL | 1100 mg/L |
| Henry's constant of DNAPL | 0.2 |
| Density of DNAPL | 1.46 $g/cm^3$ |
| Diffusivity of DNAPL in porous medium | $2 \times 10^{-10}$ $m^2/s$ |
| Initial DNAPL concentration in aquifer | 2000 mg/kg |
| Radius of DNAPL-contaminated zone | 5 m |
| Initial DNAPL droplet diameter $2a_0$ | 2 mm |

One expects that the air flow rate in the sparging well ($Q_a$) and the associated induced water flow rate ($Q_w$) are linked, with increasing values of $Q_a$ resulting in increased values of $Q_w$. The functional nature of this dependence is not known, and surely depends on the nature of the aquifer medium. In Fig. 5 it is assumed that $Q_w$ is proportional to $Q_a$, and the dependence of VOC removal on the linked flow rates is shown. As the system parameters are such that diffusion limitations are important, cleanup times are not inversely proportional to the flow rates. For this system, little would be gained by increasing the air flow rate above 0.01 $m^3/s$.

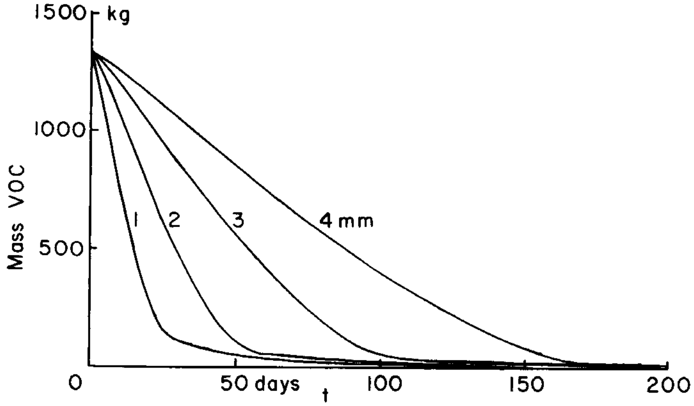

FIG. 4. Plots of total residual VOC versus time for a single sparging well; effect of droplet size. Droplet diameters are (from left to right) 1, 2, 3, and 4 mm. Other parameters are given in Table 1.

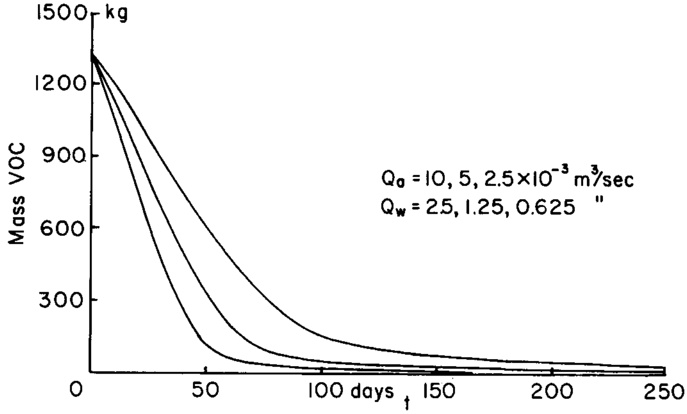

FIG. 5. Plots of total residual VOC versus time for a single sparging well; effect of linked $Q_a$ and $Q_w$. From left to right, values of ($Q_a$, $Q_w$) are (0.01, 0.0025), (0.005, 0.00125), and (0.0025, 0.000625) m$^3$/s. Other parameters as in Table 1.

Another feature we observe in Fig. 5, as well as in Fig. 4, is marked tailing. This occurs after all of the DNAPL has been dissolved, and is due to the very slow movement of dissolved VOC out around the periphery of the domain of interest. Operation of a single sparging well results in the slow movement of dissolved VOC *away* from the well in the upper half of the aquifer; the streamlines turn around at the median plane, and the VOC returns to the well in the lower half of the aquifer. The removal of dissolved VOC which moves along streamlines which extend far out from the axis of the well is quite slow, leading to quite long cleanup times if very high levels of removal (99+%) are sought. These results suggest the use of arrays of sparging wells in which the wells around the periphery of the domain of contamination are sited in uncontaminated aquifer for the purpose of establishing no-flow boundary conditions for the wells operating in the domain of contamination. An alternative might be the placement of impermeable barriers to restrict the outward flow of water around a sparging well.

The effect of the radius of the contaminated zone is shown in Fig. 6. Since diffusion kinetics are important, cleanup times are not strongly dependent upon the size of the DNAPL-contaminated domain, with an increase in contaminated zone radius from 3 to 5 m resulting in a very minor increase in the time required to remove the DNAPL. Again we see tailing toward the end of the run, associated with the movement of dissolved VOC out away from the well in the upper half of the aquifer.

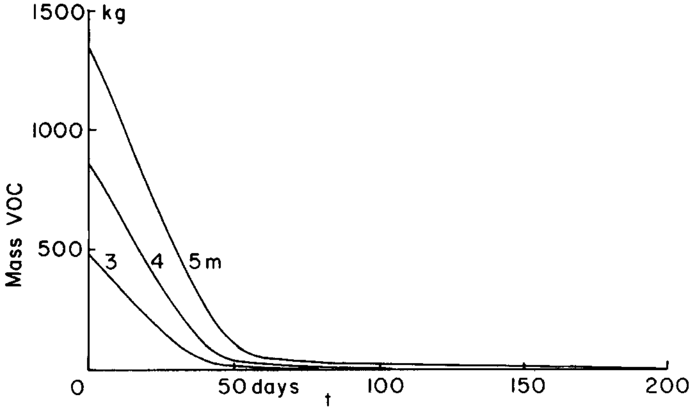

FIG. 6. Plots of total residual VOC versus time for a single sparging well; effect of radius of contaminated zone. Contaminated zone radii are 5, 4, and 3 m, from top to bottom. Other parameters as in Table 1.

The results shown in Figs. 7–11 pertain to the sparging curtain configuration. Default values of the parameters used in these runs are given in Table 2, with departures indicated in the captions. One matter which was of interest was the effect of the extent of the domain modeled on either side of the sparging curtain. This should be such that the results obtained

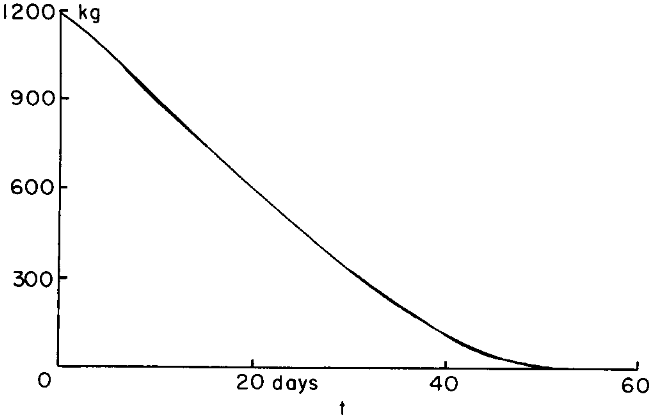

FIG. 7. Plots of total residual VOC versus time for a single sparging curtain; effect of length of domain. Domain lengths (at right angles to the curtain) are 15, 17, and 19 m; other parameters as in Table 2. At the scale of the figure, the three curves are esentially superimposed.

TABLE 2
Default Parameters for Sparging Curtain Calculations

| | |
|---|---|
| Thickness of aquifer | 5 m |
| Length of domain of interest | 15 m |
| Length of curtain | 10 m |
| Porosity of aquifer medium | 0.3 |
| Air flow rate of sparging curtain | 0.01 $m^3/s$ |
| Induced water flow rate | 0.0025 $m^3/s$ |
| Natural groundwater flow velocity normal to curtain | 0 m/d |
| Aquifer medium density | 1.7 $g/cm^3$ |
| Aqueous solubility of DNAPL | 1100 mg/L |
| Henry's constant of DNAPL | 0.2 |
| Density of DNAPL | 1.46 $g/cm^3$ |
| Diffusivity of DNAPL in the porous medium | $2 \times 10^{-10}$ $m^2/s$ |
| Initial DNAPL concentration in the aquifer | 2000 mg/kg |
| $x$-Coordinate of left boundary of contaminated zone | −3.5 m |
| $x$-Coordinate of right boundary of contaminated zone | 3.5 m |
| Initial DNAPL droplet diameter $2a_0$ | 2 mm |

are independent of the length of the domain. Figure 7 shows three runs, identical except that the domain lengths are 15, 17, and 19 m. On the scale of the figure, these runs are indistinguishable. Similar results were obtained with the sparging well model.

The effect of the initial effective DNAPL droplet radius $a_0$ on DNAPL removal is shown in Fig. 8. As was the case with the sparging well model

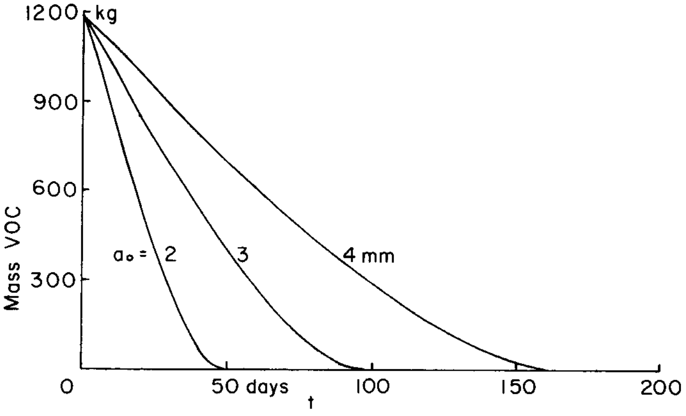

FIG. 8. Plots of total residual VOC versus time for a single sparging curtain; effect of initial DNAPL droplet size. From left to right, droplet diameters are 2, 3, and 4 mm. Other parameters as in Table 2.

(see Fig. 4), this is a crucial parameter in determining the cleanup time of a site. In the limit of purely diffusion-controlled sparging, cleanup time is proportional to $a_0^2$; see Eq. (13). The results plotted in Fig. 8 show substantially less tailing with the sparging curtain configuration than was found with a single sparging well.

The effect of the Henry's constant of the VOC on DNAPL removal is seen in Fig. 9. With the other parameters used in the runs modeled here, an increase in $K_H$ by a factor of 4 (from 0.05 to 0.2, dimensionless) results in a quite modest decrease in cleanup time. Evidently the removal of dissolved VOC from the water in the immediate vicinity of the well by aeration is not a major bottleneck under these conditions.

The transport of VOC dissolved from the stationary DNAPL droplets to the sparging curtain depends upon the water flow rate induced by the sparging curtain, $Q_w$. One therefore expects that the rate of VOC removal increases with increasing $Q_w$, as is seen to be the case in Fig. 10. Here $Q_a$ is being held constant. Since the principal bottleneck in the process is diffusion from the DNAPL droplets under the conditions modeled, cleanup rates increase only relatively slightly with increasing $Q_w$.

The effect of the extent of the contaminated zone on either side of the sparging curtain on the VOC removal rate is shown in Fig. 11. The time required for cleanup increases with increasing size of the domain of contamination, but the effect is not large under the conditions modeled here, where diffusion of VOC away from the DNAPL droplets is the major rate-limiting step. In all three runs shown here, the circulation of the water and

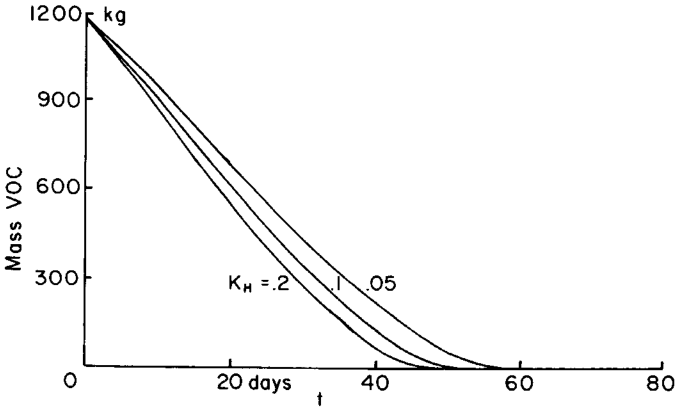

FIG. 9. Plots of total residual VOC versus time for a single sparging curtain; effect of VOC Henry's constant. From left to right, dimensionless Henry's constants are 0.2, 0.1, and 0.05. Other parameters as in Table 2.

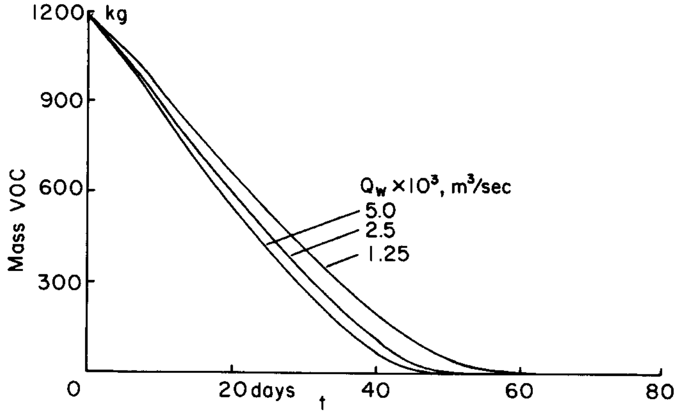

FIG. 10. Plots of total residual VOC versus time for a single sparging curtain; effect of induced water flow rate $Q_w$. From left to right, $Q_w$ values are 0.005, 0.0025, and 0.00125 m³/s. Other parameters are given in Table 2.

the aeration of the water at the curtain are sufficient to make diffusion kinetics the controlling factor.

In Fig. 12 we see the results of superimposing a uniform natural flow of water upon the flow field resulting from the sparging curtain. The upper curve shows the natural solution and migration of the VOC from the domain of interest when there is no sparging; the lower curve depicts a

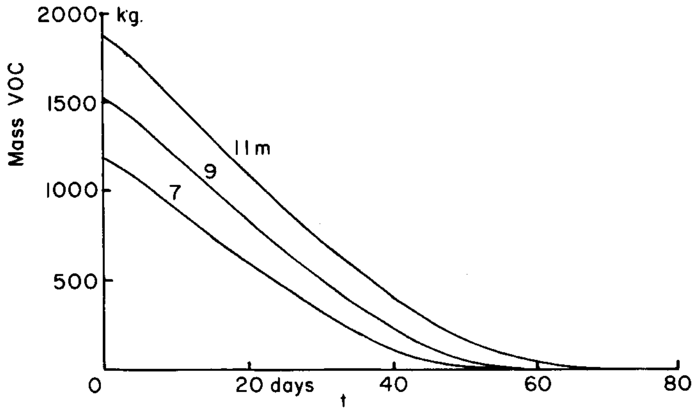

FIG. 11. Plots of total residual VOC versus time for a single sparging curtain; effect of width of DNAPL-contaminated domain. From bottom to top, the width of the contaminated domain is 7, 9, and 11 m. Other parameters as in Table 2.

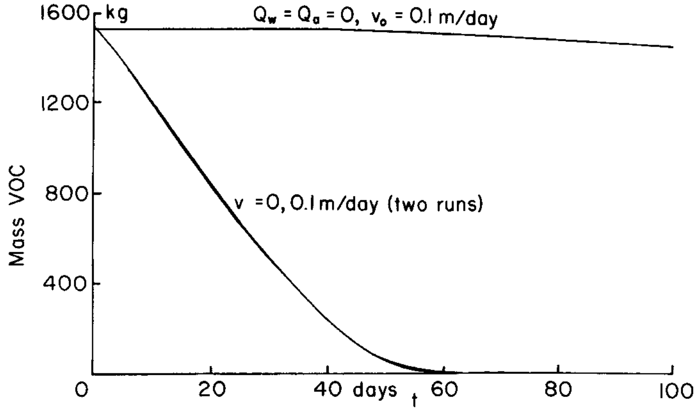

FIG. 12. Plots of total residual VOC versus time for a single sparging curtain; effect of natural groundwater movement. The top curve describes a run in which no sparging is occurring, the two runs in which sparging is taking place (one with, one without natural groundwater movement) are essentially superimposed. Groundwater velocity is 0.1 m/day, domain lengths are 19 m, and the contaminated zone is 9 m wide and centered on the sparging curtain. The other parameters are as in Table 2.

run with the sparging curtain in operation. The distribution of VOC in the domain of interest during both runs demonstrated loss of VOC by migration from the zone of interest; evidently sparging operations may require careful monitoring to avoid movement of VOC off the site during the course of the sparging.

## CONCLUSIONS

The models presented provide a simple, two-parameter method for including diffusion kinetics in the sparging of residual DNAPL droplets from a saturated aquifer. Estimation of diffusion constants in porous media by the method of Millington and Quirk (*10*) provides a means for getting this parameter from porosities and diffusion constants of the VOCs in free water. Estimation of the initial effective radius of the DNAPL droplets is more difficult, but crucial to the success of a modeling effort. This will probably require some field measurements, perhaps a small pilot-scale experiment in which clean water is injected into the aquifer and allowed to stand for an extended period, during which samples are taken at various times to determine the way in which the dissolved VOC concentration increases with time.

The models predict that increases in air and water flow rates beyond the point where diffusion kinetics become limiting is a waste of effort. They also allow one to estimate the distance to which a well may be effective in removing DNAPL at a reasonable rate. They also permit one to estimate the effect of VOC Henry's constants on removal rates.

A major item of unfinished business is the relationship between the air flow rate through the sparging well or curtain and the water circulation which this air flow induces. Lab or pilot scale studies with dissolved tracers should provide some insight into this. The dependence of $Q_w$ on $Q_a$ is probably rather site-specific.

Extension of these models to aquifers of varying or anisotropic permeability should be easily accomplished by using relaxation methods to calculate the velocity potential of the water.

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