Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Semivolatiles from Soils by Steam Stripping. III. Steam Dynamics and the Stripping of Contaminants in a Column

J. M. Rodríguez-Maroto[a]; C. Gómez-Lahoz[a]; D. J. Wilson[ab]; Ann N. Clarke[c]
[a] DEPARTAMENTO DE INGENIERÍA QUÍMICA FACULTAD DE CIENCIAS CAMPUS UNIVERSITARIO DE TEATINOS, UNIVERSIDAD DE MÁLAGA, MÁLAGA, SPAIN [b] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE, USA [c] ECKENFELDER, INC, NASHVILLE, TENNESSEE, USA

To cite this Article Rodríguez-Maroto, J. M. , Gómez-Lahoz, C. , Wilson, D. J. and Clarke, Ann N.(1995) 'Removal of Semivolatiles from Soils by Steam Stripping. III. Steam Dynamics and the Stripping of Contaminants in a Column', Separation Science and Technology, 30: 3, 317 — 336

To link to this Article: DOI: 10.1080/01496399508013874

URL: http://dx.doi.org/10.1080/01496399508013874

SEPARATION SCIENCE AND TECHNOLOGY, **30**(3), pp. 317–336, 1995

Removal of Semivolatiles from Soils by Steam Stripping. III. Steam Dynamics and the Stripping of Contaminants in a Column

J. M. RODRÍGUEZ-MAROTO, C. GÓMEZ-LAHOZ,
and D. J. WILSON*
DEPARTAMENTO DE INGENIERÍA QUÍMICA
FACULTAD DE CIENCIAS
CAMPUS UNIVERSITARIO DE TEATINOS
UNIVERSIDAD DE MÁLAGA
29071 MÁLAGA, SPAIN

ANN N. CLARKE
ECKENFELDER, INC.
227 FRENCH LANDING DRIVE, NASHVILLE, TENNESSEE 37228, USA

ABSTRACT

The initial transients during the heating phase of steam stripping of soil in a column are examined and found to be typically of very short duration compared to the time required for the steam flow to dry the soil. Two one-dimensional models for steam stripping are developed which include these transients. The first permits semivolatile organic compounds to be present as nonaqueous phase liquid or dissolved, and postulates the validity of Henry's law and of the local equilibrium assumption. The second includes the effects of diffusion kinetics. The dependence of soil remediation rates on the parameters of the models is explored. The use of steam stripping for the remediation of soils contaminated with Lindane and its congeners is discussed.

---

* Permanent address: Department of Chemistry, Box 1822 Sta. B, Vanderbilt University, Nashville, Tennessee 37235, USA.

INTRODUCTION

Steam stripping for the removal of semivolatile compounds from contaminated soils permits the remediation of soils contaminated with organics the volatilities and biodegradabilities of which are sufficiently low that they cannot be effectively removed by ambient temperature techniques. We recently presented an introduction to the technique and a review of the literature (1). Earlier models (2, for example) utilize a steady-state treatment for the movement of the steam in the soil, and also generally make the local equilibrium assumption, although we recently examined the effect of diffusion kinetics on steam stripping (3). That paper includes an updated review of the steam stripping literature; we therefore include here only references of particular bearing on this work or obtained since that review.

Hornsby and Jensen (4, 5) described the application of a variant of steam stripping, Dow Chemical's AquaDetox system, to the remediation of a site in Burbank, California, which was contaminated with tetrachloroethylene, trichloroethylene, and hydrocarbons. The technology used was an integrated system consisting of a low-pressure steam-stripping technique (AquaDetox) and soil vapor extraction (SVE). The three-bed granular activated carbon unit is regenerated on-site with steam. The authors provide cost information about the operation.

Falta et al. (6, 7) carried out quite detailed modeling of the use of steam injection for the removal of nonaqueous phase liquids from the subsurface. They note that the behavior of volatile compounds is quite different from that of semivolatiles, and concluded that light nonaqueous phase liquids (LNAPLs) having boiling points lower than about 175°C may be efficiently removed as a separate phase by steam stripping. Although the displacement of LNAPLs with higher boiling points is not as efficient, their rates of removal are still much larger than those of other remediation techniques such as air injection and soil vapor extraction.

DePercin (8) has reported on the September–October 1989 field demonstration of the Nova Terra Inc. "Detoxifier" performed under EPA's SITE program. Contaminants included solvents, plasticizers, coatings, adhesives, paint additives, and other chemicals.

In an earlier paper (3) we explored the initial transient effects which can be expected in steam stripping operations as the soil is heated up by the injection of the steam. It was concluded that the soil is heated up to 100°C relatively rapidly by condensation of the injected steam (which results in the release of a great deal of heat), but that the rate of evaporation of the moisture from the soil at 100°C would be a quite slow and very energy-intensive process. This implies that the steam stripping of volatile and semivolatile organic compounds (VOCs and SVOCs) from contaminated soils is most likely to be carried out with the soil wet and both the soil and the steam at a temperature of essentially 100°C. This indicated that steady-state steam stripping models employing these conditions should provide a fairly realistic picture of what is going on during steam stripping operations, at least for contaminants of relatively low volatility.

The model used, however, was a quite simple one-compartment model which could reasonably be criticized as somewhat unrealistic. We have therefore developed a one-dimensional column model for steam dynamics in moist soil to see if the conclusions based on the earlier, very simple picture, could be confirmed. In the following sections we first present the analysis leading to the modeling equations, followed by some results showing the dependence of steam dynamics in soil columns on the model parameters, and conclusions. We then use this picture as the basis for two models for the operation of a steam-stripping column in which the SVOC is assumed to obey Henry's law up to the solubility limit of the compound at 100°C. In the first, the assumption of local equilibrium between SVOC in the moving vapor phase and the stationary aqueous (and possibly NAPL) phase(s) is assumed to be valid. In the second, mass transport of SVOC by diffusion between the stationary phase(s) and the advecting vapor phase is included by means of a distributed diffusion approach. The dependence of results obtained with these two models on the parameters is explored, use of the models is illustrated by an assessment of the feasibility of steam stripping for remediating soils contaminated with benzene hexachloride (BHC) congeners, and conclusions based on these results and the illustration are reported.

STEAM DYNAMICS

Analysis, Steam Dynamics

Consider a soil column as illustrated in Fig. 1. Let

t = time, s
L = column length, m
r = column radius, m
ρ_{soil} = dry soil density, kg/m^3
ω_I = initial water-filled porosity of soil, dimensionless
ρ_{water} = density of water, kg/m^3
T_b = boiling point of water at 1 atm (approximately), °C
λ = latent heat of vaporization of water, J/kg
C_{water} = specific heat of water, J/kg·deg
C_{steam} = specific heat of steam, J/kg·deg

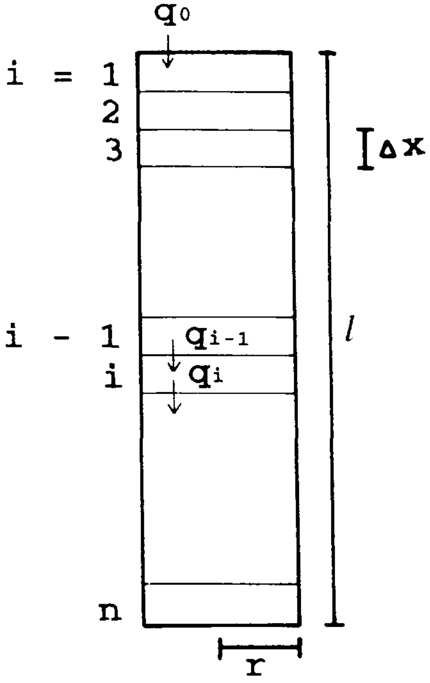

FIG. 1 Geometry and notation of the steam-stripping column.

C_{soil} = specific heat of soil, J/kg·deg
T_{init} = initial column temperature, °C
T_0 = influent steam temperature, °C
Q_0 = influent steam flow, kg/s
n = number of compartments into which the column is partitioned for analysis
M^s = mass of soil in the ith compartment of the column, kg
$M_i(t)$ = mass of water in the ith compartment, kg
$T_i(t)$ = temperature of the ith compartment, °C
$Q_i(t)$ = flux of steam from the ith compartment into the $(i + 1)$th compartment, kg/s
Δx = length of one compartment, L/n, m
$\Delta V = \pi r^2 \Delta x$ = volume of one compartment, m^3

The mass of dry soil in one compartment is given by

$$M^s = \rho_{\text{soil}} \Delta V \tag{1}$$

The initial mass of water in one compartment is given by

$$M_i(0) = \rho_{\text{water}}\omega_I \Delta V, \qquad i = 1, 2, \ldots, n \tag{2}$$

We then carry out water mass and heat balances on the *i*th compartment, as follows. (These are done in order of increasing *i*—that is, in the direction of the steam flow.)

1. If $T_{i-1} < T_b$:

$$Q_i = 0 \tag{3}$$

$$dT_i/dt = 0 \tag{4}$$

$$dM_i/dt = 0 \tag{5}$$

2. If $T_{i-1} \geq T_b$ and $T_i < T_b$ and $M_i > 0$:

$$Q_i = 0 \tag{6}$$

$$\frac{dT_i}{dt} = Q_{i-1}\frac{\lambda + C_{\text{water}}(T_b - T_i) + C_{\text{steam}}(T_{i-1} - T_b)}{C_{\text{soil}}M^s + C_{\text{water}}M_i} \tag{7}$$

$$dM_i/dt = Q_{i-1} \tag{8}$$

3. If $T_{i-1} \geq T_b$ and $T_i \geq T_b$ and $M_i > 0$:

$$Q_i = Q_{i-1} - \frac{dM_i}{dt} \tag{9}$$

$$T_i = T_b \tag{10}$$

$$\frac{dM_i}{dt} = -\frac{Q_{i-1}C_{\text{steam}}}{\lambda}(T_{i-1} - T_b) \tag{11}$$

4. If $T_{i-1} > T_b$ and $T_i > T_b$ (and $M_i = 0$):

$$Q_i = Q_{i-1} \tag{12}$$

$$M_i = 0 \tag{13}$$

$$\frac{dT_i}{dt} = \frac{Q_{i-1}C_{\text{steam}}(T_{i-1} - T_i)}{C_{\text{soil}}M^s} \tag{14}$$

Results, Steam Dynamics

One assigns values for the various parameters and initial conditions, and then integrates the system of differential equations forward in time. Default values of the parameters and initial conditions are given in Table 1. Computations were done in TurboBASIC on an AlphaSystem microcomputer running at 50 MHz and equipped with an 80486 microprocessor.

TABLE 1

Default Values for Parameters and Initial Conditions for the Modeling of Steam Dynamics in a Moist Soil Column

Column length	5 m
Column diameter	1 m
Volume of soil in column	3.93 m^3
Initial column temperature	15°C
Initial water-filled porosity of soil, ω_i	0.2
Influent steam temperature	110°C
Steam flow	5 kg/h
Dry soil density	1700 kg/m^3
Specific heat of dry soil	800 J/kg·deg
Water density	1000 kg/m^3
Specific heat of liquid water	4183 J/kg·deg
Specific heat of steam	1860 J/kg·deg
Latent heat of vaporization of water	2.259×10^6 J/kg
Number of compartments representing column	20
Δt	50 seconds

Time required for a run ranged from a few minutes for runs having high steam temperatures to slightly over 2 hours for a run made with a steam temperature of 105°C.

The effect of influent steam temperature is shown in Table 2. We examine the effect of influent steam temperature on the times required to heat the entire column to 100°C (t100°C), and the additional times beyond these to dry the first 1/20th of the column (t5%) and to dry the entire column (t100%). Times are given in days. We also include the value of ω_f, the water-filled porosity of the soil after the initial heating period t100°C.

The effect of the value of the initial water-filled porosity ω_i (volumetric soil moisture content) is shown in Table 3. As expected, the time required to heat the soil in the column to 100°C increases with the amount of water initially in the soil, but even with an initial water-filled porosity of 0.30,

TABLE 2

Effect of Influent Steam Temperature on t100°C, t5%, t100%, and ω_f

Influent steam temperature (°C)	t100°C (days)	t5% (days)	t100%, (days)	ω_f (dimensionless)
105	2.69	112.55	2251	0.2827
110	2.67	56.46	1129	0.2827
120	2.65	28.32	566.4	0.2827
140	2.63	14.22	284.4	0.2827
180	2.55	7.189	143.8	0.2827

TABLE 3
Effect of Initial Water-Filled Porosity, ω_i, on t100°C and ω_f

Initial water-filled porosity ω_i (dimensionless)	t100°C (days)	Final water-filled porosity ω_f (dimensionless)
0.10	2.18	0.1670
0.15	2.44	0.2249
0.20	2.67	0.2827
0.25	2.95	0.3406
0.30	3.20	0.3984

only 3.20 days is required to heat the column up to 100°C. All values were obtained on the basis of the graphical display of temperature and water content of the compartments of the column as the runs progressed. For these runs the value of the final water-filled porosity when the column is heated to 100°C, ω_f, is given by

$$\omega_f = 1.157\omega_i + 0.0513, \qquad r^2 = 0.9999 \tag{15}$$

from the graphical results. The constant term corresponds to the steam required to heat the dry soil to 100°C; the linear term, to the water initially present plus the steam required to heat it to 100°C. The expression resulting from our earlier one-compartment model (2) for this system is

$$\omega_f = 1.154\omega_i + 0.0502 \tag{16}$$

A linear least squares of plot of the values of t100°C obtained graphically and given in Table 3 versus ω_i gives

$$t100^\circ\text{C (days)} = 1.668 + 5.100\,\omega_i, \qquad r^2 = 0.9993 \tag{17}$$

The calculated expression from the one-compartment model for this system is

$$t100^\circ\text{C (days)} = 1.661 + 5.109\omega_i \tag{18}$$

Evidently the simple one-compartment model discussed earlier (2) is satisfactory for estimating the time required to heat the soil up to 100°C.

Conclusions, Steam Dynamics

We conclude on the basis of these results that 1) the initial time period required to heat the soil up to 100°C is relatively short, 2) the amount of water condensed in the soil during this heating process is relatively modest, and 3) the time required to dry the soil with superheated steam is quite long. Evidently, steam stripping operations are likely to be economical only if the semivolatiles can be removed from the wet soil by steam at temperatures of about 100°C. Such operations are readily approximated by steady-state steam-stripping models, provided that 1) the compounds being removed are sufficiently nonvolatile that the time required for their removal is long in comparison with t100°C, yet 2) not of such low volatility that the water is removed from the column before the SVOC. For this last case (extremely low volatility), steam stripping is probably a less viable option than other treatments, such as low-temperature thermal desorption.

STEAM-STRIPPING COLUMN MODELS

In this section we first develop the equations for 1) a model for steam stripping in a column which uses the local equilibrium assumption, and 2) a model for steam-stripping column operation which includes the effects of mass transport kinetics of SVOC between the stationary and the mobile phases by means of a distributed diffusion picture. The analysis is then followed by results showing the dependence of steam-stripping cleanup rates on the various parameters of the two models. Use of the models is illustrated by their application to assessing the feasibility of removing so-called benzene hexachloride (BHC) from contaminated soils. A discussion of conclusions closes the section.

Analysis, Steam-Stripping, Local Equilibrium Model

The physical setup is as in Fig. 1. Notation is as in the previous section, with the following additions.

M_i^c = mass of contaminant in compartment i, kg
C_i^w = aqueous contaminant concentration in compartment i, kg/m^3 of water
C_i^g = vapor concentration of contaminant in compartment i, kg/m^3
P_0^c = vapor pressure of pure contaminant at 100°C, torr
C_0^w = aqueous solubility of contaminant in water at 100°C, kg/m^3
C_0^g = concentration of contaminant in saturated vapor at 100°C, kg/m^3
MW_c = molecular weight of contaminant, kg/mol
MW_{H_2O} = molecular weight of water, 0.018 kg/mol
Q_i^v = volumetric flux of steam from the ith compartment, m^3/s
R = gas constant, 8.206×10^{-5} m^3·atm/mol·deg

The aqueous contaminant concentration is related to M_i^c as follows.

$$C_i^w = \frac{M_i^c \rho_{\text{water}}}{M_i}, \qquad \text{if } C_i^w \leq C_0^w \tag{19}$$

$$C_i^w = C_0^w, \qquad \text{if } C_i^w \text{ calculated from Eq. (19)} > C_0^w \tag{20}$$

Here we have made the assumption that $C_i^g \ll C_i^w$. Then Henry's law gives

$$C_i^g = (C_0^g/C_0^w)C_i^w \tag{21}$$

We assume that the pressure drop in the column is sufficiently small that we may regard the pressure as constant throughout, equal to 1 atm (P_a). The volumetric steam flux is then given in terms of the mass steam flux by

$$Q_i^v = \frac{Q_i R T_b}{P_a \text{MW}_{\text{H}_2\text{O}}} \tag{22}$$

Also, C_0^g (the contaminant saturation vapor concentration) is given in terms of P_0^c by

$$C_0^g = \frac{P_0^c \text{MW}_c}{760 \text{ torr/atm} \cdot R T_b} \tag{23}$$

A mass balance for contaminant in the ith compartment then gives

$$\frac{dM_i^c}{dt} = Q_{i-1}^v C_{i-1}^g - Q_i^v C_i^g \tag{24}$$

Finally, substitution of Eqs. (21) and (22) in Eq. (24) yields

$$\frac{dM_i^c}{dt} = \frac{R T_b C_0^g}{P_a(\text{MW}_{\text{H}_2\text{O}})C_0^w}(Q_{i-1}C_{i-1}^w - Q_i C_i^w) \tag{25}$$

The model then consists of Eqs. (3)–(14) for describing the behavior of the steam, and Eq. (25) which describes the movement of the contaminant. We shall be interested in following the total masses of both water and contaminant during the course of the steam-stripping operation. These are given by

$$M_{\text{water}} = \sum_{i=1}^{n} M_i \tag{26}$$

and

$$M_{\text{contam}} = \sum_{i=1}^{n} M_i^c \tag{27}$$

Analysis, Steam-Stripping, Distributed Diffusion Model

The effects of diffusion-controlled mass transport are included by means of a distributed diffusion model used previously for representing diffusion effects in soil vapor extraction and in-situ air sparging (9, 10). Diffusion of SVOC is assumed to take place from lamellar porous structures (lenses) of low permeability (perhaps clay, till, or silt) out to the permeable porosity—what would be called the fracture porosity in porous rock—through which the steam is assumed to move. We use the same notation as in the previous sections, with additional symbols as follows.

D = diffusivity of SVOC in the low-permeability structures, m^2/s
$2l$ = thickness of a low-permeability structure, m
A = cross-sectional area of low-permeability structures in one volume element of the column, V, m^2; $A = V/2l$
$2n_u$ = number of slabs into which a low-permeability lens is partitioned for mathematical analysis
Δu = l/n_u, the thickness of one of the slabs, m
M_{ij}^c = mass of contaminant in the jth slab of the lenses in the ith volume element [represented by (i, j)], kg
C_{ij} = aqueous concentration of contaminant in (i, j), kg/m^3 of water
C_i = concentration of contaminant in the mobile porosity vapor phase in the ith volume element, kg/m^3
M_{ij}^w = mass of liquid water in (i, j), kg, $= M_i/n_u$
M_i = mass of liquid water in the ith volume element, kg
ν^I = immobile porosity
ν^m = mobile porosity

Within a single volume element, the area through which diffusion occurs within and from the low-permeability lenses is given by

$$2A = \Delta V/l \tag{28}$$

The picture of diffusion transport used is shown schematically in Fig. 2. Within a slab we assume local equilibrium between M_{ij}^c and C_{ij}, so that

$$C_{ij} = \frac{M_{ij}^c \rho_{\text{water}}}{M_{ij}^w} \tag{29}$$

If this calculation gives $C_{ij} > C_0^w$, the solubility of the SVOC in water at 100°C, then

$$C_{ij} = C_0^w \tag{30}$$

Then the mass of SVOC in the jth slab of the ith volume element is controlled by diffusion processes as described by Eqs. (31)–(33):

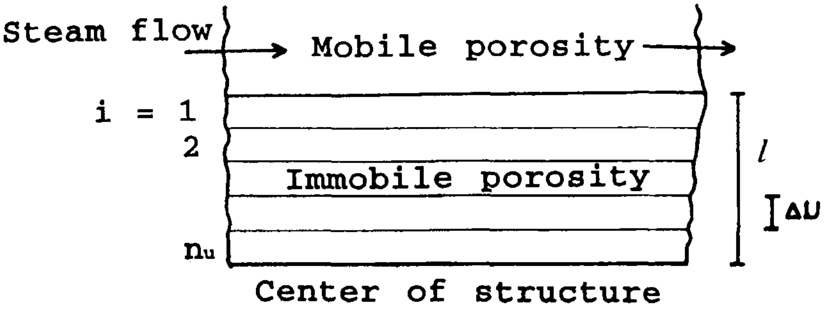

FIG. 2 Schematic of the upper half of a low-permeability porous structure from which SVOC diffuses into the mobile porosity.

$$\frac{dM^c_{ij}}{dt} = 2A\frac{D}{\Delta u}(C_{i,j+1} - 2C_{ij} + C_{i,j-1}), \qquad j = 2, 3, \ldots, n_u - 1 \tag{31}$$

$$\frac{dM^c_{i,nu}}{dt} = 2A\frac{D}{\Delta u}(C_{i,nu-1} - C_{i,nu}) \tag{32}$$

$$\frac{dM^c_{i1}}{dt} = 2AD\left[\frac{(C_i/K_H - C_{i1})}{\Delta u/2} + \frac{C_{i2} - C_{i1}}{\Delta u}\right] \tag{33}$$

We next turn to the mass balance for SVOC in the vapor phase in the ith volume element. Diffusion of SVOC from the outermost slab of the lenses gives

$$v^m\Delta V\left[\frac{\partial C_i}{\partial t}\right]_{\text{diff}} = -\frac{2AD}{\Delta u/2}(C_i/K_H - C_{i1}) \tag{34}$$

Advective transport by the steam gives

$$v^m\Delta V\left[\frac{\partial C_i}{\partial t}\right]_{\text{adv}} = Q^v_{i-1}C^g_{i-1} - Q^v_iC^g_i \tag{35}$$

so that finally

$$\frac{dC_i}{dt} = \frac{1}{v^m\Delta V}\left[Q^v_{i-1}C^g_{i-1} - Q^v_iC^g_i - \frac{2AD}{\Delta u/2}(C_i/K_H - C_{i1})\right], \quad i = 1, 2, \ldots, n \tag{36}$$

Equations (31)–(33) and (36) then constitute the model.

The total mass of contaminant in the column at time t is given by

$$M_{\text{contam}} = \sum_{i=1}^{n} \left[\nu'^{m} \Delta V C_i + \sum_{j=1}^{n_u} M_{ij}^{c} \right] \tag{37}$$

This completes the analysis of the diffusion-limited steam-stripping column.

Results, Steam-Stripping, Local Equilibrium Model

The model was implemented in TurboBASIC and run on the personal computer described above. A typical run required roughly 15 minutes. Default parameters for the first sets of runs modeling steam stripping are given in Table 4; when other parameter values are used, they are given in the captions to the figures.

The effect of the water solubility of the SVOC on the rate of remediation of soil in the column is shown in Figs. 3 and 4. The vapor pressure of the SVOC at 100°C is held constant at 10 torr, and SVOC solubilities of 2000, 4000, 6000, and 8000 mg/L are used in Fig. 3. Note that these are solubili-

TABLE 4
Default Parameters for the Steam-Stripping Column Runs

Column length	5 m
Column diameter	1 m
Initial column temperature	15°C
Initial water-filled porosity	0.2
Influent steam temperature	110°C
Steam flow rate	5 kg/h
Dry soil density	1.7 g/cm^3
Thickness of diffusion structures in soil (Fig. 7)	2.0 cm
SVOC solubility in water at 100°C:	
Fig. 5	6000 mg/L
Figs. 7 and 8	100 mg/L
SVOC vapor pressure at 100°C	10 torr
SVOC molecular weight	200 g/mol
Effective diffusion constant of SVOC in soil (Fig. 8)	10^{-9} m^2/s
Initial contaminant concentration in dry soil	1000 mg/kg
Number of compartments representing column	20
Number of slabs into which the low-permeability structures are partitioned (Figs. 7 and 8)	6
Δt:	
Figs. 3–6	50 seconds
Figs. 7 and 8	5 seconds
Initial mass of water in column	785.4 kg
Initial mass of SVOC in column	6.676 kg

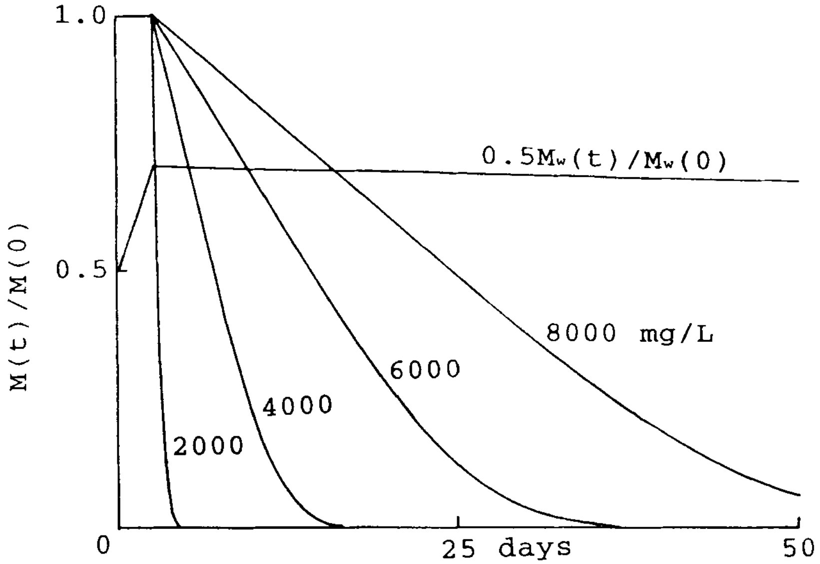

FIG. 3 Plots of $M_{SVOC}(t)/M_{SVOC}(0)$ versus t, and plots of $0.5M_{water}(t)/M_{water}(0)$ for these runs (superimposed). Effect of water solubility of SVOC in the high range; solubility = 2000, 4000, 6000, and 8000 mg/L, bottom to top; other parameters as in Table 4.

ties of the SVOC in water at 100°C. Plots of $M_{svoc}(t)/M_{svoc}(0)$ versus time indicate that increased solubilities result in decreased remediation rates. This is as expected, since the Henry's constant of the SVOC is proportional to its vapor pressure (held constant in these runs) divided by its solubility. If the solubility is sufficiently low, however, that the bulk of the SVOC is present as NAPL, there is very little effect of solubility on remediation rate, since the vapor pressure of the NAPL is the controlling factor when NAPL is present. This is seen in Fig. 4, where the vapor pressure is held constant at 1 torr and values of the solubility of 0.1, 1, 10, 100 (all superimposed), 200, 300, 400, 500, and 1000 mg/L are used.

Figure 5 shows the effect of the vapor pressure of the NAPL SVOC on the rate of soil remediation. The aqueous solubility of the SVOC at 100°C is held constant at 6000 mg/L, and vapor pressures at 100°C are 5, 10, 15, and 20 torr. We see the expected large increase in remediation rate with increasing SVOC vapor pressure. If vapor pressure and solubility are used to characterize the SVOC, the vapor pressure is always significant—either in its own right when NAPL is present, or as a factor in the Henry's constant when only dissolved SVOC is present.

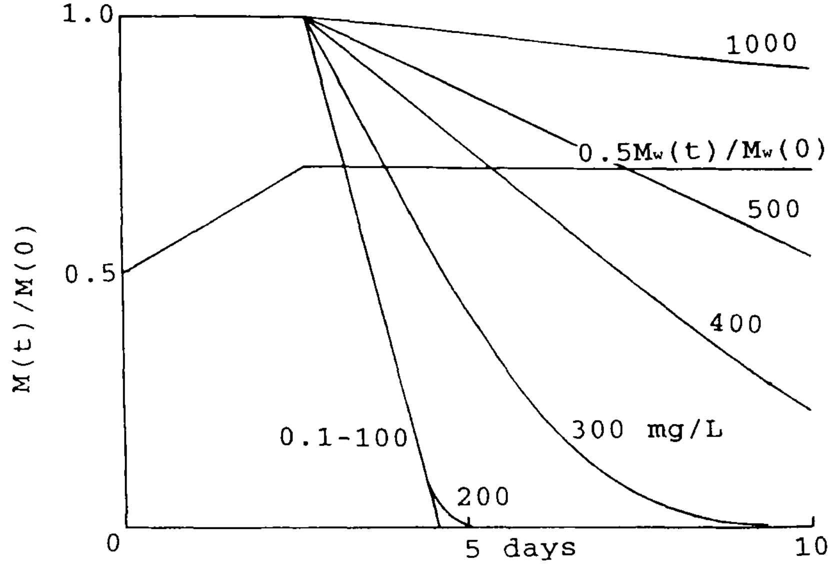

FIG. 4 Plots of $M_{SVOC}(t)/M_{SVOC}(0)$ versus t, and plots of $0.5M_{water}(t)/M_{water}(0)$ for these runs (superimposed). Effect of water solubility of SVOC in the low range; solubility = 0.1, 1.0, 10, and 100 (all superimposed); 200, 300, 400, 500, and 1000 mg/L, bottom to top; vapor pressure = 1 torr; other parameters as in Table 4.

The results shown in Figs. 3 and 5 pertain to SVOCs of relatively high vapor pressures and solubilities in water; the vapor pressures and solubilities of such compounds of environmental interest as PCBs and other chlorinated organics such as the pesticide Lindane and its less biologically active isomers are a good deal lower. There seem to be little data available on aqueous solubilities and vapor pressures of these compounds at 100°C, so rough estimates of these quantities were made for the beta isomer of benzene hexachloride (β-BHC) from data at lower temperatures from Montgomery and Welkom's compilation (11) and Trouton's rule. These authors report a vapor pressure of 0.5 torr at 60°C for β-BHC. Use of this figure with Trouton's rule gives an estimate for the vapor pressure at 100°C of 3.37 torr; use of this figure with a value for the boiling point of Lindane at 760 torr of 323.4°C in the integrated form of the Clausius–Clapeyron equation yields a second estimate of 2.96 torr. They report a solubility of 0.3 mg/L at 20°C; we assume that the solubility at 100°C is 1.0 mg/L. The parameters for the first run (starred) simulating β-BHC removal by steam stripping are given in Table 5.

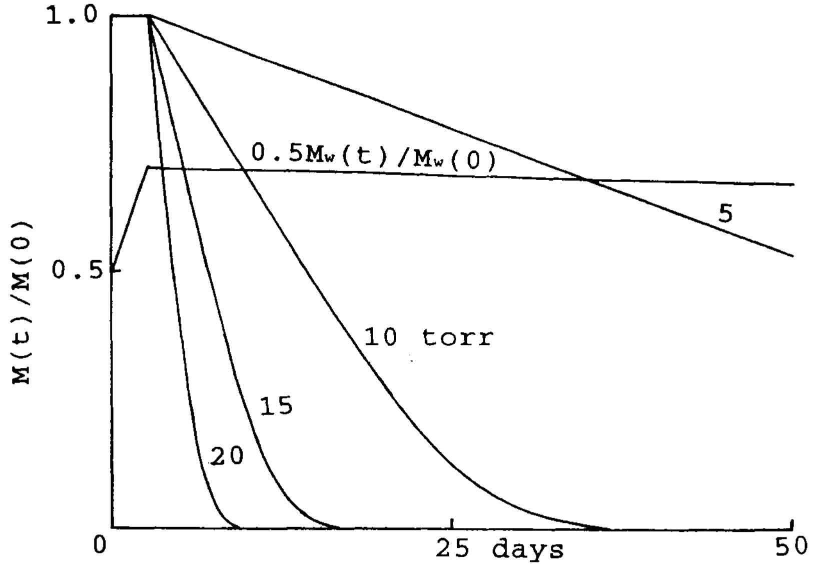

FIG. 5 Plots of $M_{SVOC}(t)/M_{SVOC}(0)$ versus t, and plots of $0.5M_{water}(t)/M_{water}(0)$ for these runs (superimposed). Effect of vapor pressure of SVOC; vapor pressure = 5, 10, 15, and 20 torr, top to bottom; water solubility of SVOC = 6000 mg/L; other parameters as in Table 4.

TABLE 5
Default Parameters for the Steam-Stripping Column Runs Simulating β-BHC Removal

Column length	5 m
Column diameter	1 m
Initial column temperature	15°C
Initial water-filled porosity	0.2
Influent steam temperature	110°C
Steam flow rate	5 kg/h
Dry soil density	1.7 g/cm^3
Solubility of β-BHC in water at 100°C	1 mg/L
Vapor pressure of β-BHC at 100°C	3.37 torr
Molecular weight of β-BHC	290.83 g/mol
Initial contaminant concentration in dry soil	500 mg/kg
Number of compartments representing column	20
Δt	10 seconds
Duration of run	10 days
Initial mass of water in column	785.4 kg
Initial mass of β-BHC in column	3.338 kg

As is readily seen, the estimation of the vapor pressure and the aqueous solubility of β-BHC is fraught with considerable uncertainty. We therefore made several other runs in which the β-BHC solubility was increased (from 1 to 3 mg/L) and/or its vapor pressure was decreased (from 3.37 to 1, 0.3, and 0.2 torr). Plots of $M_{svoc}(t)/M_{svoc}(0)$ versus time are given for these runs in Fig. 6. For the most unfavorable case (solubility = 3 mg/L, vapor pressure = 0.2 torr), remediation is complete in 9.1 days. For the most favorable case (solubility = 1 mg/L, vapor pressure = 3.37 torr), remediation is complete in 2.8 days. Vapor pressure is the controlling parameter; at such low solubilities the bulk of the SVOC is present as nonaqueous phase material until the cleanup is almost complete. Other runs (not shown) which explored further variation in the aqueous solubility showed that this has very little effect.

Results, Steam Stripping, Distributed Diffusion Model

This model was coded in TurboBASIC and run on the computer described above. It was necessary to use time increments Δt of only 5 sec-

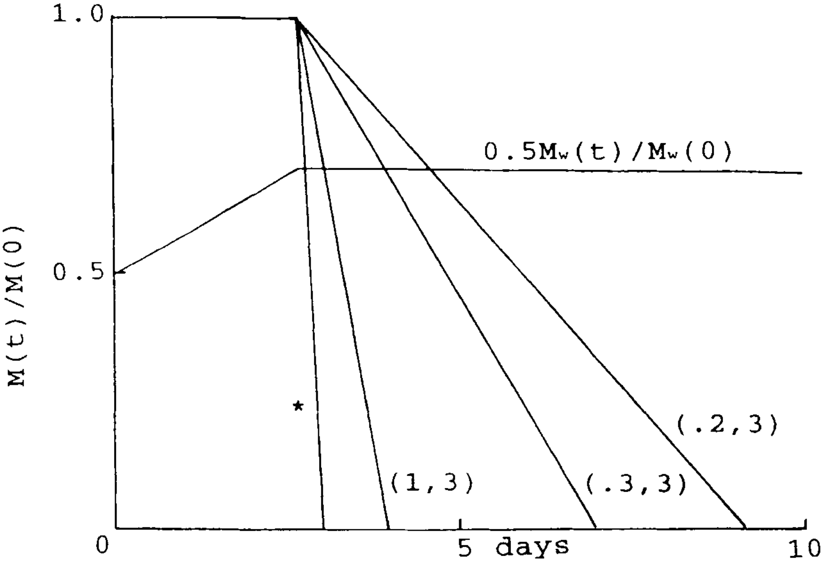

FIG. 6 β-BHC simulations. Plots of $M_{SVOC}(t)/M_{SVOC}(0)$ versus t, and plots of $0.5M_{water}(t)/M_{water}(0)$ for these runs (superimposed). Effect of β-BHC vapor pressure and solubility values on cleanup rate. From bottom to top, the values of (vapor pressure, solubility) are given by (3.67, 1.0) (*), (3.67, 3.0) (superimposed), (1.0, 3.0), (0.3, 3) and (0.2 torr, 3 mg/L). The time scale in this plot is from 0 to 10 days.

onds in most of these runs, and they typically required about 4 hours of computer time. Default parameters for the runs made using the distributed diffusion model for steam stripping are given in Table 4.

Figure 7 exhibits the effect of the diffusion constant of the SVOC in the low-permeability porous medium. Values of D used are ∞, 20, 10, 5, 2, and 1×10^{-8} m^2/s, and the structure thickness $2l$ is 2.0 cm. The rate of cleanup decreases drastically as the diffusion constant is decreased, as expected. If the soil is initially rather wet, so that it is approaching saturation by the time it has been heated up to temperature, one can expect gas diffusivities to be greatly reduced, with quite damaging results for the effectiveness of steam stripping. Evidently one would be well-advised to work with soils which are initially as dry as possible to avoid reducing the SVOC diffusivity by the presence of excessive amounts of moisture in the soil when stripping is taking place.

The effect of the thickness of the low-permeability porous structures is shown in Fig. 8. Thicknesses are 0 (local equilibrium model), 0.5, 1.0, 1.5, and 2.0 cm. As expected, we see a large decrease in cleanup rate as the length through which the SVOC must diffuse is increased. We conclude that soils which are highly layered, which contain low-permeability

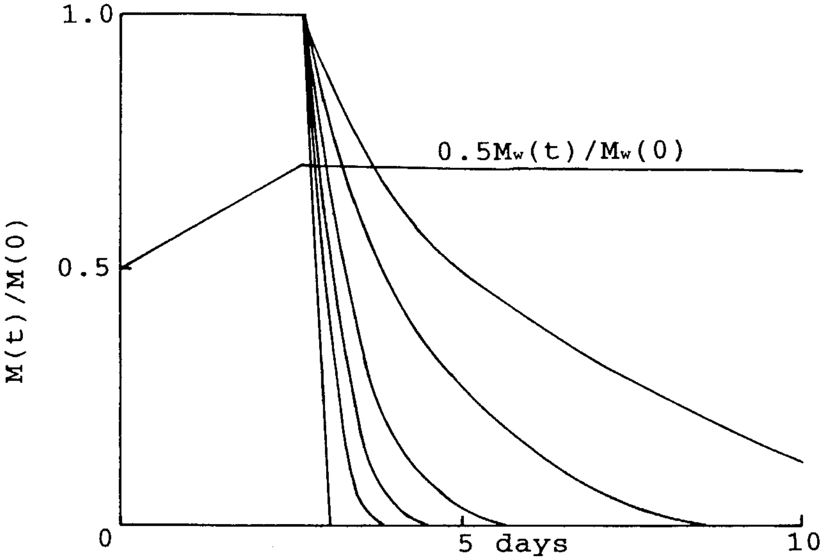

FIG. 7 Effect of diffusion constant on rate of steam stripping soil cleanup. $D = \infty$, 20, 10, 5, 2, and 1×10^{-8} m^2/s; $2l = 2$ cm; immobile porosity = 0.2; mobile porosity = 0.05; solubility of SVOC = 100 mg/L; other parameters as in Table 4.

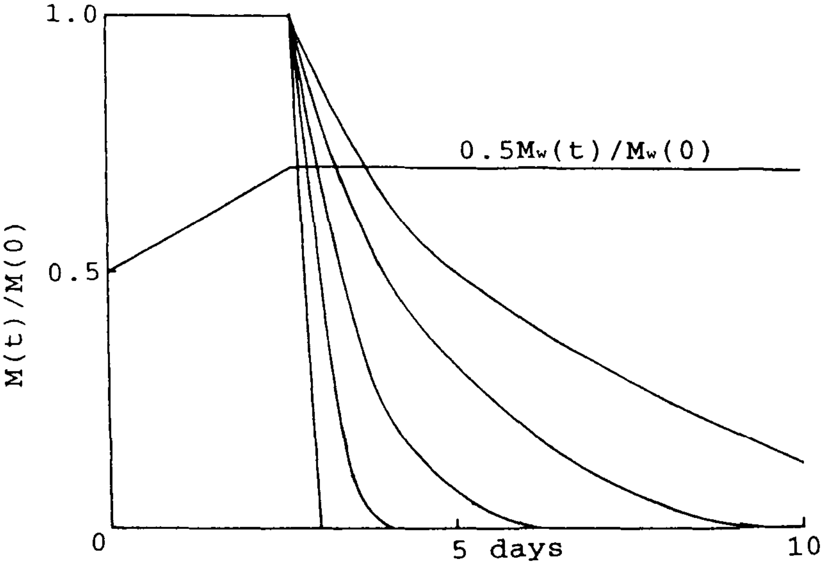

FIG. 8 Effect of the thickness of the low-permeability structures on the rate of steam stripping soil cleanup. Diffusion constant = 1×10^{-8} m²/s; structure thickness $2l$ = 0 (local equilibrium model), 0.5, 1.0, 1.5, and 2.0 cm, from left to right. Other parameters as in Fig. 7.

lenses, or which contain high-permeability channels can be expected to be cleaned up slowly by steam stripping due to diffusion-limited mass transport effects.

Conclusions, Steam Stripping

Within the framework of the first model (Henry's law, local equilibrium), the controlling variables are the vapor pressure and the aqueous solubility of the SVOC, both at 100°C. If the solubility is sufficiently high that a substantial fraction of the SVOC is present in the aqueous phase, an increase in solubility results in a decrease in remediation rate. If the solubility is low, so that very little of the SVOC present is dissolved, aqueous solubility has little effect on cleanup rate.

SVOC vapor pressure and solubility are important in the second model (Henry's law, distributed diffusion), too, but to these variables we must add the diffusion constant of the SVOC and the thickness of the low-permeability structures through which diffusion must transport the SVOC before it can be removed by the advecting steam. Slow diffusion mass transport rates can greatly reduce the rate of remediation by steam stripping.

The temperature of the influent steam is essentially irrelevant as long as its pressure is sufficient to produce the necessary advective flow through the column.

Model calculations with the local equilibrium model on the removal of β-BHC from soil by steam stripping indicate quite rapid removal rates of this compound. These must be interpreted with some caution, however, since the model neglects a number of factors which may reduce cleanup rates below those estimated by this approach. These include mass transport limitations due to 1) diffusion processes from within porous lumps of soil, and 2) the kinetics and equilibria of adsorption/desorption processes in the soil. Another unknown factor is the extent to which steam may channel—i.e., follow preferred paths through the column, thereby leaving some portions of the soil unstripped. These questions can only be answered by laboratory, pilot, and ultimately field-scale studies.

If initially the soil is not quite wet, the relatively small amount of water which condenses in it during the heating phase of the steam stripping is probably insufficient to interfere seriously with the steam flow through the column. With wet (fairly nearly saturated) soils this might be a problem, however. The drier the soil initially, the lower the energy requirements for bringing it up to a temperature of 100°C.

In the runs simulating β-BHC removal, the removal rate is sufficiently rapid that a simple steady-state approach, which neglects the time period required for the initial heating of the soil to 100°C, is not adequate, since this heating period is an appreciable fraction of the total time required. On the other hand, the times required for cleanup are sufficiently short for these runs that one is not likely to be particularly concerned about the discrepancy.

These very preliminary calculations suggest that steam stripping be given serious consideration for the remediation of soils contaminated with benzene hexachloride congeners and similar compounds. The existence of a number of sites which are heavily contaminated with Lindane and its congeners (12, for example) makes this a matter of some practical interest.

We have in steam stripping potential for the same types of diffusion kinetics limitations as are observed in soil vapor extraction, in-situ air sparging, and pump-and-treat. Test protocols are needed to determine on a site-specific basis the extent to which such limitations are operative, and work is needed on practical methods for reducing their impact on remediation times.

ACKNOWLEDGMENTS

D.J.W. is greatly indebted to the University of Málaga for its hospitality and the use of its facilities, to Dr. J. J. Rodríguez-Jiménez for making his visit to Málaga possible, to Vanderbilt University for financial support during his leave, and to the Spanish Government (DGICYT) for a fellowship in support of this work.

REFERENCES

1. A. N. Clarke, D. J. Wilson and P. R. dePercin, "Thermally Enhanced Vapor Stripping," in *Hazardous Waste Site Soil Remediation: Theory and Application of Innovative Technologies* (D. J. Wilson and A. N. Clarke, Eds.), Dekker, New York, p. 243.
2. D. J. Wilson and A. N. Clarke, "Removal of Semivolatiles from Soils by Steam Stripping. I. A Local Equilibrium Model," *Sep. Sci. Technol.*, *27*, 1337 (1992).
3. J. M. Rodríguez-Maroto, C. Gómez-Lahoz, D. J. Wilson, and A. N. Clarke, "Removal of Semivolatiles from Soils by Steam Stripping. II.' Effects of Diffusion Kinetics," *Ibid.*, *30*, 159 (1995).
4. R. G. Hornsby and D. J. Jensen, "Zero Air Emissions Groundwater and Soil Remediation Using an Integrated System," *Hazard. Mater. Consult.*, p. 46 (July/August 1992).
5. R. G. Hornsby and D. J. Jensen, "Operating Results from an Integrated Soil and Groundwater Remediation System," in *Proceedings, Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, Houston, Texas, November 1992*, p. 205.
6. R. W. Falta, K. Pruess, I. Jawardel, and P. A. Witherspoon, "Numerical Modeling of Steam Injection for Removal of Nonaqueous Phase Liquids from the Subsurface. I. Numerical Formulation," *Water Resour. Res.*, *28*, 433 (1992).
7. R. W. Falta, K. Pruess, I. Jawardel, and P. A. Witherspoon, "Numerical Modeling of Steam Injection for Removal of Nonaqueous Phase Liquids from the Subsurface. II. Code Validation and Application," *Ibid.*, *28*, 451 (1992).
8. P. R. dePercin, "Demonstration of In Situ Steam and Hot Air Stripping Technology," *J. Air Waste Manage. Assoc.*, *41*, 873 (1991). See also *U.S. EPA Report 540/A5-90/008*.
9. J. M. Rodríguez-Maroto, C. Gómez-Lahoz, and D. J. Wilson, "Soil Cleanup by In-Situ Aeration. XVIII. Field Scale Models with Diffusion from Clay Structures," *Sep. Sci. Technol.*, *29*, 1367 (1994).
10. C. Gómez-Lahoz, J. M. Rodríguez-Maroto, and D. J. Wilson, "Groundwater Cleanup by In-Situ Sparging. VII. VOC Concentration Rebound Caused by Diffusion after Shutdown," *Ibid.*, *29*, 1509 (1994).
11. J. H. Montgomery and L. M. Welkom, *Groundwater Chemicals Desk Reference*, Vol. 1, Lewis Publishers, Chelsea, Michigan, 1990.
12. I. Quintana, "Suelos Contaminados por Residuos de Lindano," *Ing. Quim.*, p. 119 (January 1994).

Received by editor June 14, 1994