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Low-Temperature Thermal Treatment of Contaminated Soils: Simple Mathematical Models

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ABSTRACT

Mathematical models for low-temperature thermal treatment of contaminated soils for the removal of semivolatile organic compounds (SVOCs) by batch and continuous flow units are described. In one set of models the SVOC is assumed to obey a linear adsorption isotherm on the soil; in the second set the SVOC is assumed to be present as nonaqueous phase liquid (NAPL) blobs dispersed within the porous soil. The soil is represented by porous spheres of specified radius through which the escaping SVOC must diffuse. Results of calculations with both models for continuous flow units are presented, and the dependence of the results on the model parameters is discussed.

INTRODUCTION

It is becoming evident that the remediation of hazardous waste sites in the United States is going to require a major commitment of resources and effort. Russell, Colglazier, and their associates at the University of Tennessee have estimated the costs as roughly $750 billion over the next 30 years, with these possibly running as high as $1.7 trillion (1). There are 1148 sites on the National Priority List (Superfund), some 4700 RCRA facilities with 60,000 waste management units, and roughly 1.8 million underground storage tanks (2). Evidently, anything which can improve the effectiveness of remediation and/or reduce costs will be of major benefit to the entire country.

One of the innovative technologies which has been developed in response to the challenge of remediation is low-temperature thermal treatment of soil, or thermal desorption. Ayen, Swanstrom, and Palmer (3) recently reviewed the technique. Thermal desorption includes a number of variants. In one common approach, the soil is heated in the absence of oxygen to a temperature of less than 500°C. The organics present (sorbed or as liquids or solids) are removed by volatilization and are carried out of the heating unit by a stream of nitrogen. The contaminants are then either removed by condensation or destroyed by incineration or some other process. In such units the flow rate of purge gas is generally much less than the flow rate of combustion gases in incineration of a similar amount of soil, and condensed organics may be recycled or given further treatment. In other variations, higher temperatures may be used (perhaps substantially above 500°C), and the purge gas may contain oxygen. If the unit is direct-fired, purge gas flow rates may be relatively large. In some units the organics exiting the system are not condensed but are removed or destroyed by other techniques. EPA has listed thermal desorption as the treatment of choice in a number of recent Records of Decision, noting that the technology is effective against a wide spectrum of organics, mobile commercial units are available, and the public is much more accepting of the technique than it is of incineration, for example (3).

Lighty and her coworkers at the University of Utah (4–6) have carried out a number of experimental studies directed toward the basic transport phenomena involved in the thermal desorption of organics from soils. Szabo, Fox, and Thurnau (7) have carried out desorption studies in the temperature range 66 to 288°C; the soil was spread on trays and a nitrogen purge was used. Other studies have been carried out by Helsel and Groen (8), Helsel, Alperin, and Groen (9), DeLeer and his associates (10), and others (11, 12).

As one would expect, rate of desorption decreases with increasing molecular weight/boiling point, and it increases with increasing temperature. Typically, temperatures substantially above the boiling points of the organics are required in order to obtain reasonable rates of desorption. In porous media, diffusion mass transfer kinetics are generally limiting. Interestingly, the presence of moisture in the soil facilitates desorption of organics, probably both by displacing the organics from sorption sites and by steam distillation (6).

Common configurations for full-scale facilities include rotary dryers or kilns, heated screw conveyers, and fluidized bed dryers. For further practical details concerning the process, see the article by Ayen, Swanstrom, and Palmer (3).

The ease of evaluation of a technology and the ease of design of facilities implementing the technology in any particular application depend on the availability of mathematical models which permit one to utilize the data obtained from bench and then pilot-scale experiments to produce a full-scale design which is as nearly optimal as possible. This involves extracting from the bench- and pilot-scale work the parameters needed in designing the full-scale facility. In the following we develop some models for small-scale batch units and for large-scale continuous-flow kiln units which make a few preliminary steps toward the objective of complete, validated mathematical modeling capability, including interpretation of lab unit results, design of full-scale facilities, and estimation of costs.

ANALYSIS

Vapor Pressures

As mentioned above, it is well established that the vapor pressures of organics have a great deal to do with the rates of their removals. Vapor pressures are very strongly temperature-dependent, typically more than doubling for every 20°C temperature rise. Representative data for some polynuclear aromatic hydrocarbons are given in Table 1. The CRC *Handbook of Chemistry and Physics* (13) contains a very large collection of vapor pressure data which can be used with Eq. (1) to calculate vapor pressures at virtually any desired temperatures.

$$\log_e P(T) = A - B/T \qquad (1)$$

where $P(T)$ = vapor pressure (torr) at temperature T

T = temperature, K

A, B = constants characteristic of the compound

Diffusion, Linear Isotherm

We next address the batch low-temperature thermal treatment of soils contaminated with an organic for which the adsorption isotherm is linear. The system is assumed to be isothermal. We represent the soil as spherical porous lumps of radius b (m), through which the organic is initially uniformly dispersed. See Fig. 1. We shall first solve a diffusion problem in order to obtain a time constant for the diffusion of semivolatile organic compound (SVOC) from a lump of soil, and shall then use this time con-

TABLE 1

Vapor Pressures of Some Polynuclear Aromatic Hydrocarbons[a] [experimental data were fitted to the equation $\log_e P(\text{torr}) = A - B/T$, where T = temperature, kelvins]

Naphthalene: $A = 18.329$, $B = 5749$, mp = 80.5, bp = 218°C, MW = 128.17

T, °C	100	110	120	130	140	150
P, torr	18.57	27.76	40.66	58.44	82.54	114.67

Biphenyl: $A = 18.960$, $B = 6510$, mp = 71, bp = 255.9°C, MW = 154.21

T, °C	100	110	120	130	140	150	160	170	180	190	200	225	250
P, torr	4.55	7.17	11.05	16.66	24.63	35.74	50.99	71.57	98.97	134.97	181.65	362.33	676.57

Acenaphthylene: $A = 17.202$, $B = 5846$, mp = 92.5, bp = 280°C, MW = 152.20. Parameters and vapor pressures calculated by Trouton's rule and, in parentheses, from vapor pressures at 20 and 280°C

T, °C	100	110	120	130	140	150	160	170	180	190	200	225	250
P, torr	4.64	6.99	10.30	14.90	21.16	29.56	46.67	55.15	73.79	97.49	127.30	236.65	414.63
	(3.00)	(4.68)	(7.14)	(10.65)	(15.59)	(22.41)	(31.67)	(44.08)	(60.46)	(81.80)	(109.28)	(214.19)	(383.68)

Acenaphthene: $A = 18.563$, $B = 6571$, mp = 96.2, bp = 279°C, MW = 154.21

T, °C	120	130	140	150	160	170	180	190	200	225	250
P, torr	6.36	9.62	14.27	20.79	29.75	41.90	58.11	79.48	107.27	215.37	404.53

Phenanthrene: $A = 18.313$, $B = 7157$, mp = 99.5, bp = 340.2°C, MW = 178.24

T, °C	120	130	140	150	175	200	225	250	275	300
P, torr	1.12	1.75	2.69	4.05	10.41	24.21	51.73	102.78	191.81	339.01

Anthracene, solid: $A = 24.984$, $B = 10445$, mp = 217.5, bp = 342°C, MW = 178.24

T, °C	150	160	170	180	190	200	210	217.5
P, torr	1.35	2.38	4.11	6.91	11.37	18.31	28.91	40.23

Anthracene, liquid: $A = 18.142$, $B = 7083$

T, °C	217.5	220	230	240	250
P, torr	40.68	43.77	58.23	76.61	99.74

[a] Data taken from Lide (13) and Montgomery and Welkom (14).

stant in developing equations to describe low-temperature treatment in a batch apparatus.

Let

$c^g(r, t)$ = SVOC vapor concentration at time t and a distance r from the center of the porous lump, kg/m^3

$c^s(r, t)$ = adsorbed SVOC concentration, kg/kg of soil

ρ_s = soil density, kg/m^3

ν = soil porosity

$c(r, t) = \nu c^g + \rho_s c^s$ = total SVOC concentration, kg/m^3

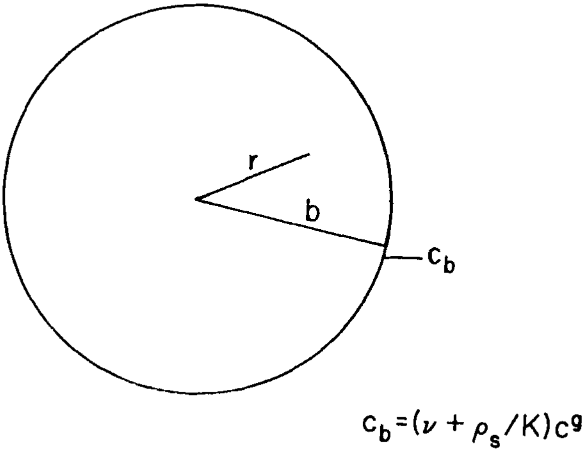

FIG. 1 Diffusion of adsorbed SVOC from a porous sphere.

K = c^g/c^s at equilibrium, the isotherm constant, kg/m^3. Note that K typically increases quite strongly with increasing temperature

D = diffusivity of the SVOC in the porous medium, m^2/s. Diffusivity increases weakly with increasing temperature

We assume local equilibrium between $c(r, t)$ and $c^g(r, t)$ within the porous lump, which yields

$$c(r, t) = (\nu + K^{-1}\rho_s)c^g(r, t) \tag{2}$$

and the equation governing diffusion

$$\frac{\partial c}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c^g}{\partial r} \tag{3}$$

becomes

$$\frac{\partial c}{\partial t} = D'\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c}{\partial r} \tag{4}$$

where

$$D' = \frac{D}{\nu + \rho_s K^{-1}} \tag{5}$$

Equation (4) is then solved by the method of separation of variables and the substitution $u(r) = rR(r)$; the general solution, which is well-behaved at $r = 0$ (the center of the porous lump), is

$$c(r, t) = c_b + \sum_{n=1}^{\infty} \frac{A_n}{r} \sin \frac{n\pi r}{b} \exp\left[-\left(\frac{n\pi}{b}\right)^2 D't\right] \tag{6}$$

where b = radius of porous lump, m
c_b = total SVOC concentration at the surface of the lump, assumed in equilibrium with a constant SVOC concentration in the gas phase surrounding the lump

If we assume that the initial total SVOC concentration in the soil is c_0, then one can readily construct the Fourier series solution to this diffusion problem. It is

$$c(r, t) = c_b + \frac{2(c_0 - c_b)b}{r} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sin \frac{n\pi r}{b} \exp\left[-\left(\frac{n\pi}{b}\right)^2 2D't\right] \tag{7}$$

We see from Eq. (7) that a good time constant estimate for a time constant treatment of isothermal batch low-temperature thermal treatment of a soil contaminated with a SVOC obeying a linear adsorption isotherm is

$$t^{-1} = k = \pi^2 D'/b^2 \tag{8}$$

Batch Apparatus, Linear Isotherm

We now turn to the isothermal batch apparatus. See Fig. 2. Define

V_{soil} = volume of soil being treated, m^3
V_g = volume of the gas phase in the unit, m^3
$m_s(t)$ = mass of SVOC in apparatus at time t

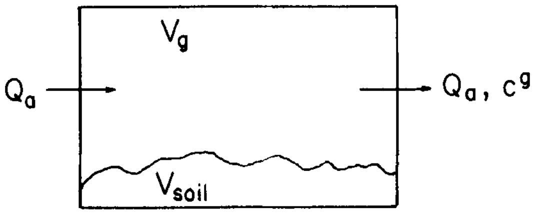

FIG. 2 Diagram of model for batch low-temperature thermal apparatus.

Q_a = volumetric air flow rate at the temperature of the unit, m^3/s
K_H = K/ρ_s, dimensionless isotherm parameter (vapor concentration/concentration adsorbed in soil, both kg/m^3)
c^g = SVOC concentration in the purge gas, kg/m^3
c^s = mean SVOC concentration in the soil being treated, kg/m^3
= m_s/V_{soil}

On the basis of the above results, we take

$$\frac{1}{V_{\text{soil}}}\left(\frac{\partial m_s}{\partial t}\right)_{\text{mass transport}} = \left(\frac{\partial c^s}{\partial t}\right)_{\text{mass tr}} = -k(c^s - c^g/K_H) \tag{9}$$

Making the steady-state approximation for the gas-phase SVOC concentration yields

$$V_g\frac{dc^g}{dt} = -Q_a c^g - \left(\frac{\partial m_s}{\partial t}\right)_{\text{mass tr}} = 0 \tag{10}$$

This result is combined with Eq. (9) to yield an expression for c^g,

$$c^g = \frac{kV_{\text{soil}}c^s}{Q_a + kV_{\text{soil}}/K_H} \tag{11}$$

Our steady-state assumption implies that

$$dm_s/dt = -Q_a c^g \tag{12}$$

which in turn gives

$$\frac{dm_s}{dt} = -\frac{Q_a k}{Q_a + kV_{\text{soil}}/K_H}m_s \tag{13}$$

The solution to Eq. (13) is

$$m_s(t) = m_s(0)\exp[-kt/(1 + kV_{\text{soil}}/Q_aK_H)] \tag{14}$$

Continuous-Flow Apparatus, Linear Isotherm

We next turn to isothermal low-temperature thermal treatment in a continuous-flow kiln of soil containing an SVOC obeying a linear isotherm. The kiln is shown schematically in Fig. 3. For mathematical analysis let the kiln be partitioned into n compartments as indicated, each containing a volume ΔV_s of soil and a volume ΔV_g of vapor phase. We note that if an axial temperature profile is available for the kiln, one could accommodate spatially variable temperatures simply by making the temperature, iso-

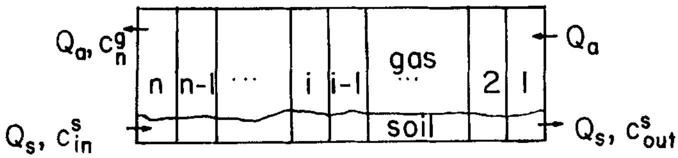

FIG. 3 Diagram of model for a continuous-flow kiln-type low-temperature thermal treatment unit.

therm constant, diffusion rate constant, and purge gas volumetric gas flow rate vary from compartment to compartment of the kiln. Let

c_i^g = vapor-phase SVOC concentration in ith compartment, kg/m^3
c_i^s = soil SVOC concentration in ith compartment, kg/m^3
m_i^s = mass of SVOC in ith compartment, kg
Q_s = soil feed rate, m^3/s
T = residence time of soil in kiln, s
Q_a = purge gas flow rate at kiln temperature, m^3/s

From our work above we have the following expression for diffusional mass transport between the stationary phase and the vapor phase in the ith compartment:

$$\frac{1}{\Delta V_{\text{soil}}}\left(\frac{\partial m_i^s}{\partial t}\right)_{\text{mass tr}} = \left(\frac{\partial c_i^s}{\partial t}\right)_{\text{mass tr}} = -k(c_i^s + c_i^g/K_{\text{H}}) \qquad (15)$$

Making the steady-state approximation for SVOC in the vapor phase in the ith compartment gives

$$Q_a(c_{i-1}^g - c_i^g) - \left(\frac{\partial m_i^s}{\partial t}\right)_{\text{mass tr}} = 0 \qquad (16)$$

Substitution of Eq. (15) into Eq. (16) and solution for c_i^g then yields

$$c_i^g = \frac{Q_a c_{i-1}^g + k m_i^s}{Q_a + \Delta V_{\text{soil}} k/K_{\text{H}}} \qquad (17)$$

A mass balance on adsorbed SVOC in the ith compartment yields, on use of Eq. (16),

$$\frac{dm_i^s}{dt} = Q_s(c_{i+1}^s - c_i^s) + Q_a(c_{i-1}^g - c_i^g) \qquad (18)$$

Now $\Delta V_{\text{soil}} = Q_s T/n$, where T is the residence time of the soil in the kiln and n is the number of compartments into which it is partitioned. Also, $c_i^s = m_i^s/\Delta V_{\text{soil}}$ for all i. Use of these relationships in Eq. (18) results in

$$\frac{dm_i^s}{dt} = \frac{n}{T}(m_{i+1}^s - m_i^s) + Q_a(c_{i-1}^g - c_i^g) \tag{19}$$

The model consists of Eqs. (17) and (19), together with boundary conditions

$$c_0^g = 0 \tag{20}$$

and

$$m_{n+1}^s = c_{\text{initial}}^s \, \Delta V_{\text{soil}} \tag{21}$$

Use of the steady-state approximation for the vapor-phase SVOC concentrations permits one to use much larger values of Δt in the numerical integration of the equations, thereby greatly reducing the time required to run the system until steady-state operation is achieved.

Diffusion, Distributed NAPL SVOC

We next examine models in which the SVOC is present as nonaqueous phase liquid (NAPL) distributed as droplets/blobs/ganglia within the pores of the lumps of contaminated soil. Decontamination requires the evaporation of this liquid and its diffusion from the interiors of the lumps out into the moving gas stream. In this section we examine the diffusion problem. In the following two sections we apply the results of this analysis to low-temperature thermal treatment in batch apparatus and in a continuous-flow kiln.

The model for diffusion-limited evaporation of NAPL blobs distributed in porous lumps of medium is illustrated in Fig. 4. Let

c_{sat} = SVOC concentration of saturated vapor, kg/m^3
= $0.01603 P_{\text{vap}}(T)(\text{MW})/T$, P_{vap} in torr, T in degrees K
$P_{\text{vap}}(T)$ = equilibrium vapor pressure of the SVOC at temperature T
(MW) = molecular weight of SVOC, g/mol
c_g = SVOC concentration in the bulk vapor phase surrounding the soil lump, kg/m^3
b = radius of soil lump, m
$a(t)$ = radius of domain within the lump from which the SVOC has not yet evaporated at time t, m
$\mu(t)$ = contaminant mass in the lump at time t, kg
μ_0 = initial contaminant mass in the lump, kg

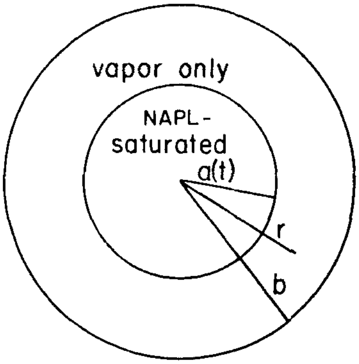

FIG. 4 Evaporation and diffusion of SVOC present as NAPL blobs in porous spheres.

The steady-state solution for the diffusion equation for a spherically symmetric system is

$$c(r) = A + B/r \tag{22}$$

where r is the distance from the center of the sphere. Our boundary conditions are

$$c(a) = c_{\text{sat}} \tag{23}$$

and

$$c(b) = c_g \tag{24}$$

from which one obtains

$$A = \frac{bc_g - ac_{\text{sat}}}{b - a} \tag{25}$$

$$B = \frac{ab(c_{\text{sat}} - c_g)}{b - a} \tag{26}$$

The rate of SVOC mass loss from the lump by evaporation and diffusion is then given by

$$\frac{d\mu}{dt} = D \int_0^{2\pi} \int_0^{\pi} \frac{\partial c}{\partial r} r^2 \sin \theta d\theta d\phi \tag{27}$$

where

$$\frac{\partial c}{\partial r} = - \frac{ab(c_{\text{sat}} - c_g)}{(b - a)r^2} \tag{28}$$

and D is the diffusivity of the SVOC vapor in the porous medium, m^2/s. This yields

$$\frac{d\mu}{dt} = -4\pi \frac{Dab}{b - a} (c_{\text{sat}} - c_g) \tag{29}$$

Since

$$a(t)/b = [\mu(t)/\mu_0]^{1/3} \tag{30}$$

we may rewrite Eq. (29) as

$$\frac{d\mu}{dt} = -\frac{4\pi Db(\mu/\mu_0)^{1/3}}{1 - (\mu/\mu_0)^{1/3}} (c_{\text{sat}} - c_g) \tag{31}$$

We will use Eq. (31) in the following two sections to handle evaporative mass transport.

Batch Apparatus, Evaporation of Distributed NAPL SVOC

The apparatus being modeled is shown schematically in Fig. 2. Let

$m(t)$ = mass of NAPL SVOC in the soil being treated at time t, kg
M = mass of soil being treated, kg
N = number of spherical lumps of radius b used to represent M kg of soil
ρ_s = density of soil, kg/m^3

Then

$$N = 3M/\rho_s 4\pi b^3 \tag{32}$$

and

$$\frac{dm}{dt} = N\frac{d\mu}{dt} = -\frac{4\pi NDb(m/m_0)^{1/3}}{1 - (m/m_0)^{1/3}} (c_{\text{sat}} - c_g) \tag{33}$$

Making the steady-state approximation for the bulk vapor phase also gives

$$dm/dt = -Q_a c_g \tag{34}$$

Substituting Eq. (32) in Eq. (33), equating Eqs. (33) and (34), and solving for c_g then yields

$$c_g = \frac{c_{\text{sat}}(m/m_0)^{1/3}}{(m/m_0)^{1/3} + Q_a\rho_s b^2[1 - (m/m_0)^{1/3}]/3DM} \tag{35}$$

Substitution of Eq. (35) into Eq. (34) then yields our final result,

$$\frac{dm}{dt} = -\frac{Q_a c_{\text{sat}}(m/m_0)^{1/3}}{(m/m)^{1/3} + Q_a \rho_s b^2[1 - (m/m_0)^{1/3}/3DM} \tag{36}$$

Integration of this equation forward in time then gives the residual mass of contaminant as a function of time during the course of the treatment.

Continuous-Flow Apparatus, Evaporation of Distributed NAPL SVOC

We next turn to the modeling of low-temperature thermal treatment in kilns of soil in which the porous lumps contain the SVOC as blobs of NAPL. See Fig. 3 for the layout. Again, for mathematical analysis let the kiln be partitioned into n compartments as indicated, each containing a volume ΔV_s of soil and a volume ΔV_g of vapor phase. Let

c_i^g = vapor-phase SVOC concentration in ith compartment, kg/m^3
c_i^s = soil SVOC concentration in ith compartment, kg/m^3
m_i^s = mass of SVOC in ith compartment, kg
Q_s = soil feed rate, m^3/s
τ = residence time of soil in kiln, s
Q_a = purge gas flow rate at kiln temperature, m^3/s
$m_i^g(t)$ = mass of SVOC in the vapor phase in the ith compartment, kg
$m_i^s(t)$ = mass of NAPL SVOC in the ith compartment, kg
b = effective radius of porous soil lumps, m
$a_i(t)$ = radius of SVOC-saturated region in soil lumps in the ith compartment at time t, m

Making the steady-state approximation for the mass of SVOC in the vapor phase in the ith compartment yields

$$\frac{dm_i^g}{dt} = Q_a(c_{i-1}^g - c_i^g) - \left(\frac{\partial m_i^s}{\partial t}\right)_{\text{mass tr}} = 0 \tag{37}$$

From our work above on the simple batch unit with NAPL SVOC, we have

$$\left(\frac{\partial m_i^s}{\partial t}\right)_{\text{mass tr}} = -\frac{4\partial NDa_i b}{b - a_i}(c_{\text{sat}} - c_i^g) \tag{38}$$

where N, the number of porous lumps of soil in compartment i, is given by

$$N = 3Q_s\tau/4n\pi b^3 \tag{39}$$

and

$$a_i(t) = b[m_i^s(t)/m_0]^{1/3} \tag{40}$$

Substitution of Eq. (38) into Eq. (37) and solution for c_i^g yields

$$c_i^g = \frac{Q_a c_{i-1}^g + 4\pi NDba_i c_{\text{sat}}/(b - a_i)}{Q_a + 4\pi NDba_i/(b - a_i)} \tag{41}$$

Substitution of Eqs. (39) and (40) into Eq. (41) then gives

$$c_i^g = \frac{c_{i-1}^g(1 - x_i) + (3Q_sD\tau c_{\text{sat}}/nQ_ab^2)x_i}{(1 - x_i) + (3Q_sD\tau/nQ_ab^2)x_i} \tag{42}$$

where

$$x_i = [m_i^s(t)/m_0]^{1/3} \tag{43}$$

and the boundary condition at $i = 1$ is

$$c_0^g = 0 \tag{44}$$

A total mass balance on SVOC in the ith compartment gives

$$dm_i/dt = Q_s(c_{i+1}^s - c_i^s) + Q_a(c_{i-1}^g - c_i^g) \tag{45}$$

where $m_i(t)$ = mass of SVOC in the ith compartment, equal to $m_i^s(t)$ to a quite good approximation. Then

$$c_i^s = nm_i/\tau Q_s \tag{46}$$

Use of this relationship in Eq. (45) then gives

$$\frac{dm_i}{dt} = \frac{n}{\tau}(m_{i+1} - m_i) + Q_a(c_{i-1}^g - c_i^g) \tag{47}$$

The boundary condition at $i = n$ is

$$m_{n+1} = c_{\text{init}}Q_s\tau/n \tag{48}$$

where c_{init} is the SVOC concentration (kg/m^3) in the soil being fed to the kiln.

Equations (42) and (47), together with the boundary condition Eqs. (44) and (48), then constitute the model. One initializes by inputting all the model parameters and setting the initial values of the m_i equal to m_{n+1} as calculated from Eq. (48). The c_i^g are calculated recursively from Eq. (42), after which the masses of SVOC in the compartments at time $t + \Delta t$ [$m_i(t + \Delta t)$] are calculated from the masses at time t by integration of Eq. (47) forward in time one step. This two-stage process is then continued until the $m_i(t)$ become independent of time, at which point the operation of the kiln has itself reached a steady state. At this point, incidentally, the steady-state approximation for the c_i^g becomes exact, since then the quantities dc_i^g/dt are in fact zero.

An alternative approach to the modeling of isothermal low-temperature thermal desorption is to not make the steady-state approximation for the gaseous SVOC concentrations, but to integrate the differential equations for both the soil SVOC concentrations and the vapor-phase SVOC concentrations. This approach was explored in detail as a check on the steady-state approximation. Sets of runs were made which determined the behavior of the system with varying soil feed rate, soil transit time, air flow rate, soil lump diameter, and initial contaminant concentration. It was found that one requires much smaller values of Δt than can be used in the steady-state model (0.1 to 1 second as compared to a typical value of 2.5 to 10 seconds for the steady-state model) if unstable mathematical behavior is to be avoided. The steady-state approximation appears to be roughly 5 to 10 times as fast as the method involving integration of both sets of differential equations. Solutions were virtually identical on the scale of the graphs presented in the next section, so only results obtained with the steady-state algorithm are shown.

RESULTS

We first examine results obtained with the model of a continuous flow kiln in which a soil containing a contaminant obeying a linear adsorption isotherm is being treated. The default parameters for the model are listed in Table 2; variations from this parameter set are indicated in the captions to the figures.

Figure 5 shows the effects of the residence time of the soil in the treatment unit; SVOC concentration (mg/kg) in the soil discharged from the kiln is plotted versus the residence time. The expected strong negative dependence of residual SVOC concentration on residence time over the range 250–5000 seconds is observed.

The effects of soil lump diameter on residual SVOC concentration are shown in Fig. 6. As the porous lumps increase in size, resistance to diffusion increases, resulting in less efficient mass transport of SVOC to the

TABLE 2

Default Parameters for the Modeling of Continuous-Flow Kiln Treatment of a Soil Containing a Contaminant Obeying a Linear Adsorption Isotherm

Throughput rate of soil	0.1 kg/s
Residence time of soil in treatment unit	1500 s
Soil density	1.7 g/cm^3
Mean diameter of soil lumps	1 cm
Gas flow rate	0.015 m^3/s
Initial soil contaminant concentration	1000 mg/kg of soil
Air-filled porosity of soil	0.4
Diffusivity of contaminant in porous medium	2×10^{-6} m^2/s
Isotherm parameter (C_{vap}/C_{soil})	0.01
Number of compartments representing unit	10
Operating temperature of unit	150°C
Δt	10 to 100 s

surface of a lump, with drastically increased residual SVOC concentrations in the treated soil.

Gas flow rates must be sufficiently high to carry away the SVOC as it diffuses from the lumps or the residual SVOC concentration will be excessively high, as seen in Fig. 7. We note that the break here at approximately 0.1 m^3/s is fairly sharp.

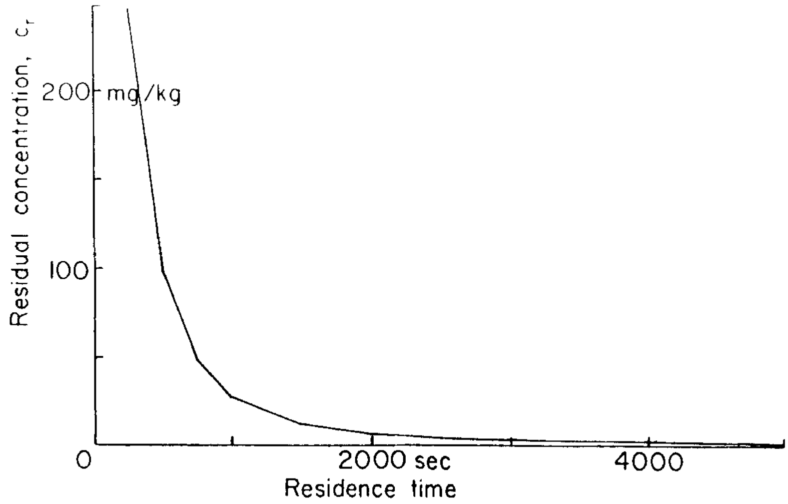

FIG. 5 Plot of effect of soil residence time on residual SVOC concentration. The SVOC is assumed to obey a linear adsorption isotherm. Default parameters for Figs. 5 through 10 are given in Table 2.

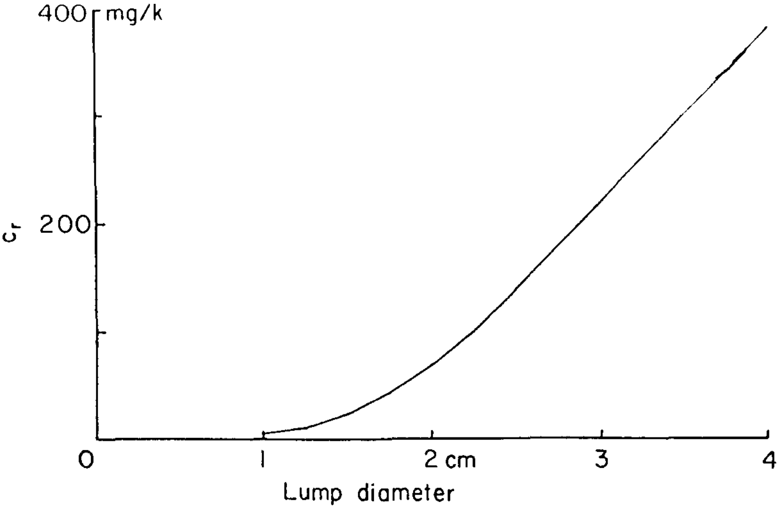

FIG. 6 Plot of effect of soil porous lump diameter on residual SVOC concentration, linear adsorption model.

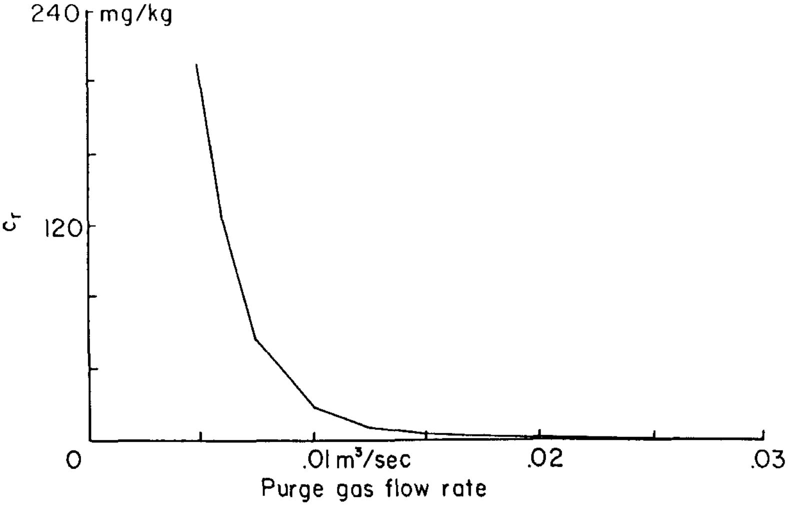

FIG. 7 Effect of purge gas flow rate on residual SVOC concentration, linear adsorption model.

This model is linear in the concentrations, so one expects that residual soil SVOC concentrations will be directly proportional to initial soil SVOC concentrations. It is seen in Fig. 8 that this is in fact the case, which provides a test of the analysis and the code.

The magnitude of the linear isotherm parameter (effective Henry's constant) has a very strong effect on the residual SVOC concentration, as shown in Fig. 9. The magnitude of this parameter is controlled by the temperature, increasing rapidly with increasing temperature.

The rate at which soil is fed to the kiln is also an important parameter, with excessively high loading rates resulting in very marked deterioration in cleanup efficiency. In Fig. 10 we see that the curve of residual SVOC concentration versus soil loading rate shows a relatively sharp break when overload conditions occur.

We next turn to the model of soil treatment in a continuous-flow kiln in which the SVOC is present as liquid NAPL dispersed throughout the porous lumps of soil, from which it is removed by evaporation and diffusion. Default parameters for this model are given in Table 3. Note that the default soil lump diameter has been increased from 1 to 5 cm. Diffusion of VOC from the dispersed DNAPL assumed in this model is substantially more rapid than is desorption/diffusion of VOC from the distributed adsorbed VOC in the first model. Therefore, in order to exhibit the effects

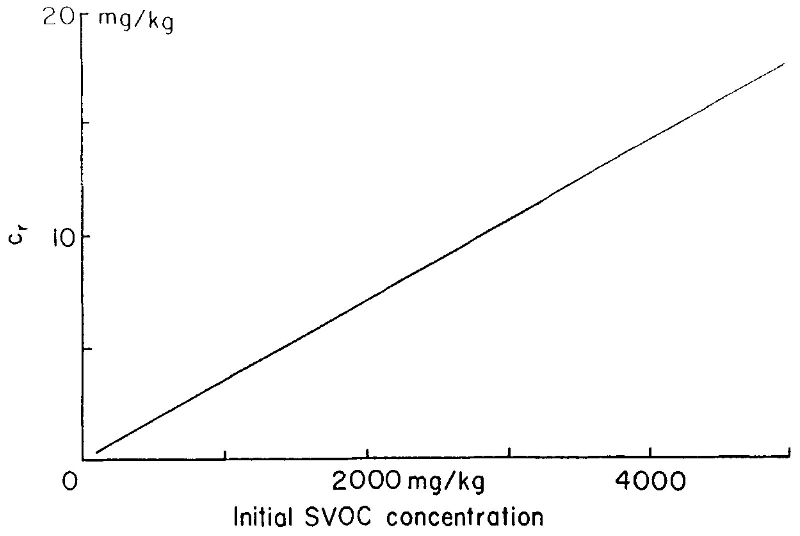

FIG. 8 Effect of initial soil SVOC concentration on residual SVOC concentration, linear adsorption model.

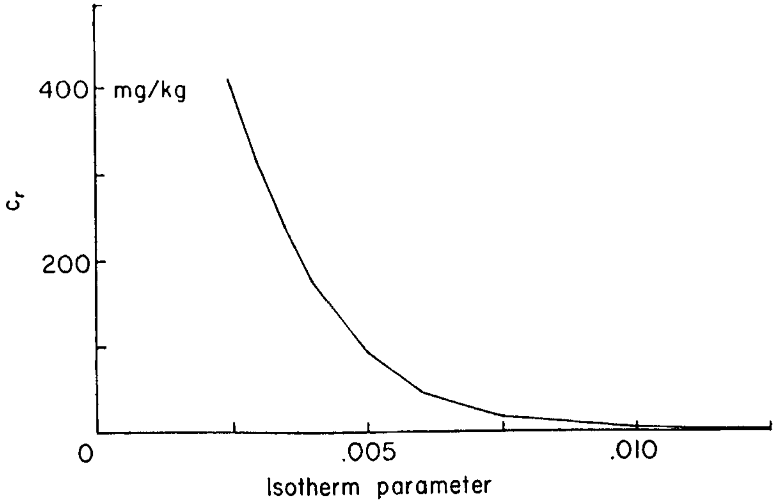

FIG. 9 Effect of linear isotherm parameter value on residual SVOC concentration.

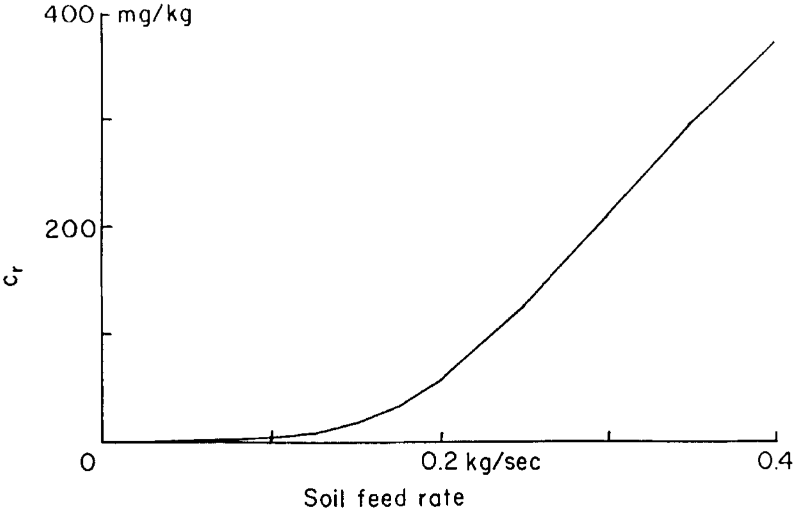

FIG. 10 Effect of soil feed rate on residual SVOC concentration, linear isotherm model.

TABLE 3
Default Parameters for the Modeling of Continuous-Flow Kiln Treatment of a Soil Containing Contaminant Present as NAPL Blobs and Removed by Evaporation and Diffusion

Throughput rate of soil	0.1 kg/s
Residence time of soil in the treatment unit	1000 s
Soil density	1.7 g/cm^3
Mean diameter of soil lumps	5 cm
Air-filled porosity of soil	0.4
Gas flow rate	0.015 m^3/s
Initial contaminant concentration	2000 mg/kg of soil
Vapor pressure of contaminant (biphenyl)	35.74 torr
Molecular weight of contaminant (biphenyl)	154.2 g/mol
Operating temperature of unit	150°C
Number of compartments representing the unit	10
Δt	2.5–10 s

of diffusion kinetics, it was necessary to assume larger soil lumps in the second model than were used in the first. Actually, it is possible to select parameters for the second model which yield results virtually identical to those obtained from the first model. This makes it very difficult to determine which of the two models is better; however, this also makes it quite unimportant to do so. If headspace analysis of SVOCs above a soil sample indicated SVOC vapor concentrations approaching saturation, one should, in principle, use the second model. If, on the other hand, headspace analysis indicates SVOC vapor concentrations substantially below those at saturation, one should use the first model in which the SVOCs are held by adsorption.

Figure 11 illustrates the rather strong effect of soil residence time on the residual soil SVOC concentration. Evidently it is essential that units be sized and operated so as to provide an adequate residence time for SVOC removal.

The effect of soil lump diameter on SVOC removal is shown in Fig. 12. As in the linear isotherm model, excessively large lumps result in poor diffusion transport, with very damaging results to removal efficiency. In this model the onset of the deterioration in cleanup efficiency is quite sharp.

The effect of purging gas flow rate through the kiln is seen in Fig. 13. As the gas flow rate is decreased, we observe a rather flat plateau for which the limiting factor is diffusion transport of SVOC from the soil lumps. At low gas flow rates, however, the capacity of the purge gas to

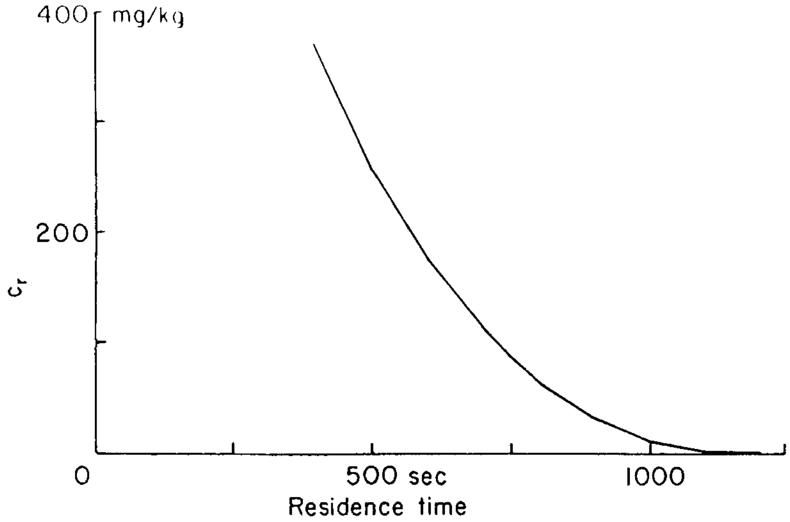

FIG. 11 Effect of soil residence time on residual SVOC concentration, NAPL evaporation model. See Table 3 for default parameter values.

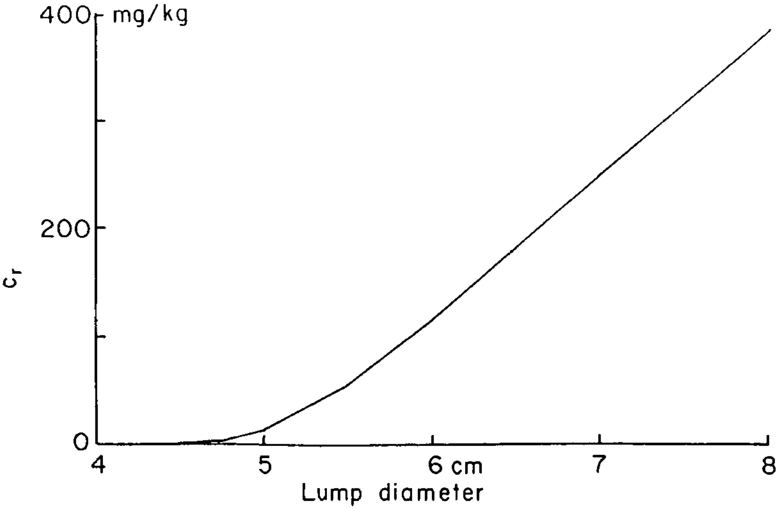

FIG. 12 Effect of soil porous lump diameter on residual SVOC concentration, NAPL evaporation model.

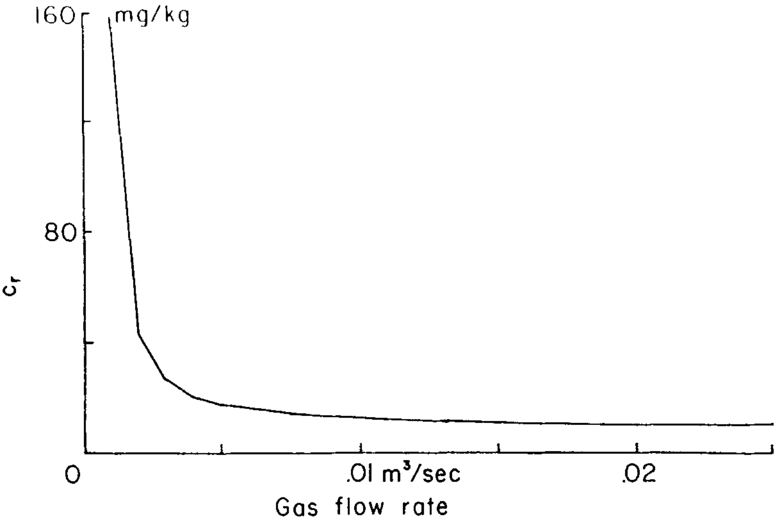

FIG. 13 Effect of purge gas flow rate on residual SVOC concentration, NAPL evaporation model.

carry away the released SVOC becomes limiting, and we see a very strong rise in residual soil SVOC concentration.

The effect of initial soil SVOC concentration on residual SVOC concentration is shown in Fig. 14. The equations for this model are not linear in the concentrations, and as a result we see that the dependence of residual SVOC on initial SVOC concentration is not linear, unlike the earlier model.

The effect of soil feed rate on residual SVOC is seen in Fig. 15. At the air flow rate being used, overload conditions are just starting to arise at soil feed rates in the range of 0.4 to 0.6 kg/s, as one would expect from the plot shown in Fig. 13.

The effect of *n*, the number of compartments into which the kiln is partitioned (the number of theoretical transfer units), is shown in Fig. 16. It is evident that the reduction of axial mixing in these kilns can be expected to pay relatively large dividends in terms of improved SVOC removal. This may require considerable mechanical ingenuity, but looks as though it might well be worth the effort.

The effect of temperature on the removal of a SVOC (biphenyl) is illustrated in Fig. 17. It is well known to practitioners of low-temperature thermal treatment that increased temperatures can greatly increase removal efficiencies; our model results are certainly in agreement with this.

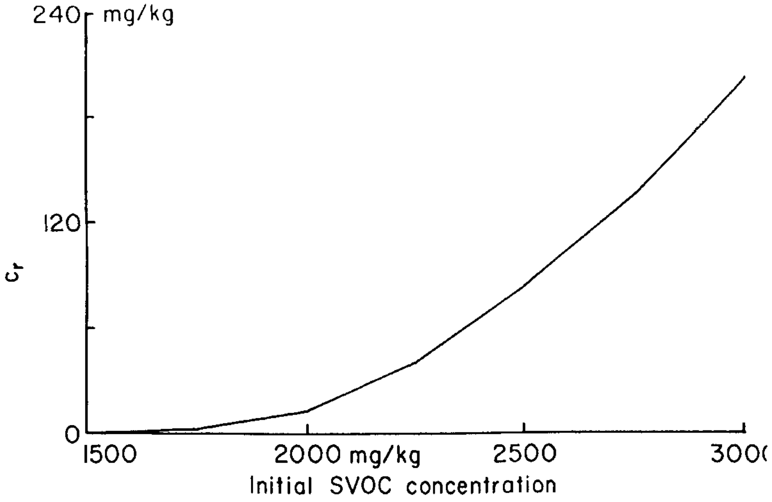

FIG. 14 Effect of initial SVOC soil concentration on residual SVOC concentration, NAPL evaporation model.

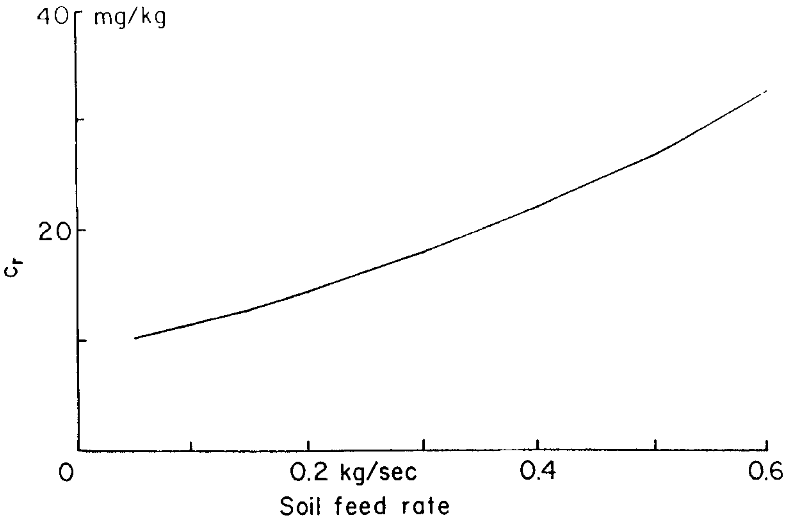

FIG. 15 Effect of soil feed rate on residual SVOC concentration, NAPL evaporation model.

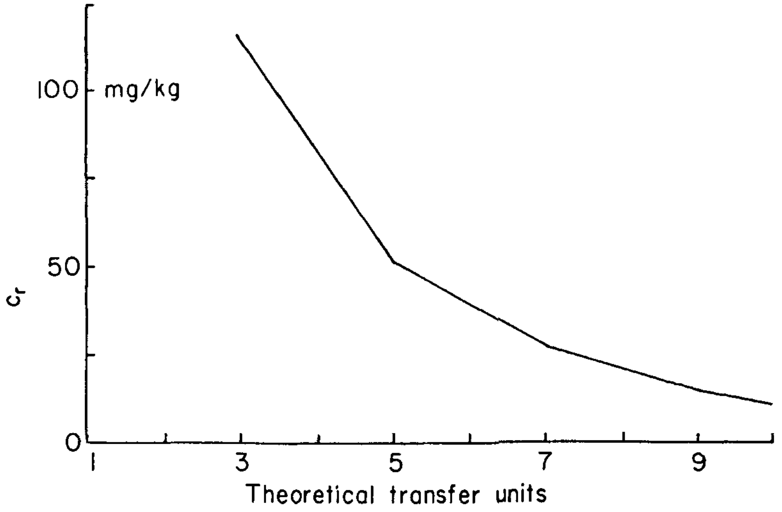

FIG. 16 Dependence of residual SVOC concentration on number of compartments used to represent the treatment unit (number of theoretical transfer units), NAPL evaporation model.

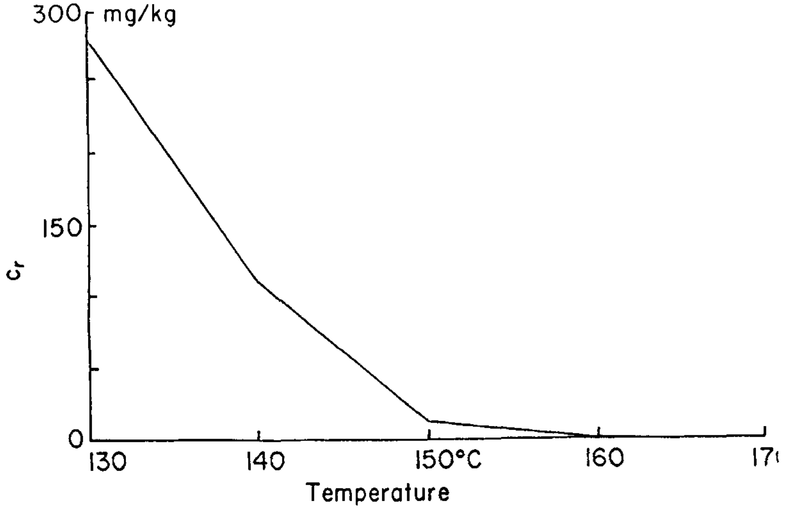

FIG. 17 Dependence of residual SVOC concentration on treatment temperature, NAPL evaporation model. The SVOC represented is biphenyl, for which calculated vapor pressures at 130, 140, 150, 160, and 170°C are 16.66, 24.63, 35.74, 50.99, and 71.57 torr, respectively.

A 30° temperature increase converts a treatment which removes only 86% of the SVOC into one which removes virtually 100% of the contaminant.

CONCLUSIONS

The behavior of the two models for isothermal, continuous-flow low-temperature thermal treatment of SVOC-contaminated soils appears to be consistent with expectations. The parameters needed should not be difficult to obtain, although lab-scale batch experiments may be necessary to get estimates of diffusivities and adsorption parameters. The models should provide helpful insight in the design of such facilities and in the selection of optimal operating parameters for their use. The models can be easily run on readily available microcomputers. Extension of the models to systems with temperatures varying along the axis of the system should be quite straightforward.

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