

**A NUMERICAL SOLUTION TO THREE-DIMENSIONAL MULTIPHASE TRANSPORT  
OF VOLATILE ORGANIC COMPOUNDS IN UNSATURATED SOILS -- WITH AN  
APPLICATION TO THE REMEDIAL METHOD OF IN-SITU VOLATILIZATION\***

**PART I: THEORETICAL DEVELOPMENT†**

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**ABSTRACT**

Part I of this paper presents the development and application of a numerical model for determining the fate and transport of volatile organic compounds (VOCs) in the unsaturated zone resulting from forced volatilization and gaseous advection-dispersion of organic vapor in a multipartitioned three-dimensional environment. The model allows for single-component transport in the gas and water phases. The hydrocarbon is assumed to be in specific retention and, therefore, immobile. Partitioning of the hydrocarbon between the oil, water, gas, and soil is developed as rate-limited functions that are incorporated into sink/source terms in the transport equations. The code for the model was developed specifically to investigate in-situ volatilization (ISV) remedial strategies, predict the extent of cleanup from information obtained at a limited number of measurement locations, and to help design ISV remedial systems. Application of the model is demonstrated for a hypothetical one-dimensional ISV system. Part II of this paper will present the analysis of an existing ISV system using the full three-dimensional capability of the model.

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## INTRODUCTION

This paper presents the development of a three-dimensional numerical model for determining the fate and transport of volatile organic compounds (VOCs) in the unsaturated zone resulting from forced volatilization and gaseous advection-dispersion, two conditions created by externally imposed pressure gradients. Such pressure gradients result from a vacuum extraction process and typify in-situ volatilization (ISV) systems.

The modeling exercise includes the development of a single-component, three-dimensional numerical transport code. The code is designed to solve for transport within the air and water phases. This effort included the development of mass-transfer functions that appear as terms within the oil, water, soil, and air equations and link VOC migration between phases.

## METHOD OF ANALYSIS

The transport model developed in this study is capable of investigating the sensitivity of the ISV remedial method to the various physical processes and parameter values that determine its performance. Included among these processes and parameters are the isotherm adsorption model type, values of Henry's Law partitioning constant, soil temperature, VOC type, soil moisture content, values of intrinsic soil and environmental parameters, areal and vertical pressure-vent spacing and patterns, and pressure-vent collection and injection (air flooding) scenarios. While the transport model is self-contained, the code requires a companion simulator capable of predicting VOC velocities in the gas and/or water phases.

## MATHEMATICAL DESCRIPTION OF TRANSPORT

Development of the model began with formulation of equations pertinent to the physics of mass transport within an unsaturated flow environment. Source-sink functions that describe the kinetic/thermodynamic mass transfer between phases were then incorporated into these equations. Because the numerical model is designed for kinetic interactions, mass transport is phase-specific. This development necessitates a mass-transport equation for each phase. Once formulated, the governing equations are cast into finite-difference form and solved numerically.

For three-dimensional advective-dispersive transport of VOCs in variably saturated media, the following equation developed by Huyakorn et al. (1985) can be implemented:

$$\frac{\partial}{\partial x_i} \left( \phi S D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} V_i C - q C^* = \frac{\partial}{\partial t} \phi S C \quad (1)$$

where:

$C$  = VOC concentration ( $M/l^3$ ),

$C^*$  = VOC concentration in the source/sink ( $M/l^3$ ),

$q$  = source/sink volumetric flux per volume ( $t^{-1}$ ),

$X_i$  = direction  $x, y, z$  (l),

$\phi$  = effective porosity,

$S$  = phase saturation,

$V_i$  = phase velocity (l/t),

$t$  = time (t), and

$D_{ij}$  = dispersion tensor ( $l^2/t$ ) defined by Bear (1979) as

$$\phi S D_{ij} = \alpha_T |V| \delta_{ij} + (\alpha_L - \alpha_T) \frac{V_i V_j}{|V|} + \phi S \tau D^* \delta_{ij} \quad (2)$$

where:

$\alpha_L$  = longitudinal dispersivity (l),

$\alpha_T$  = transverse dispersivity (l),

$\delta_{ij}$  = the Kronecker delta,

$|V|$  = absolute value of the Darcy velocity (l/t), and

$\tau$  = tortuosity

In this study, contributions from diffusion ( $D^*$ ) to dispersion are considered small in comparison to contributions from dynamic dispersion and are, therefore, neglected.

Expanding Equation 1 and regrouping yields

$$\begin{aligned} \frac{\partial}{\partial x_i} \left( \phi S D_{ij} \frac{\partial C}{\partial x_j} \right) - C \left( \frac{\partial V_i}{\partial x_i} + \phi \frac{\partial S}{\partial t} + q \right) + q (C^* - C) \\ - V_i \frac{\partial C}{\partial x_i} = \phi S \frac{\partial C}{\partial t} \end{aligned} \quad (3)$$

In the application of Equation 3, the porous medium is assumed to be incompressible.

Bear (1972) described the flow-continuity equation for the fluids as:

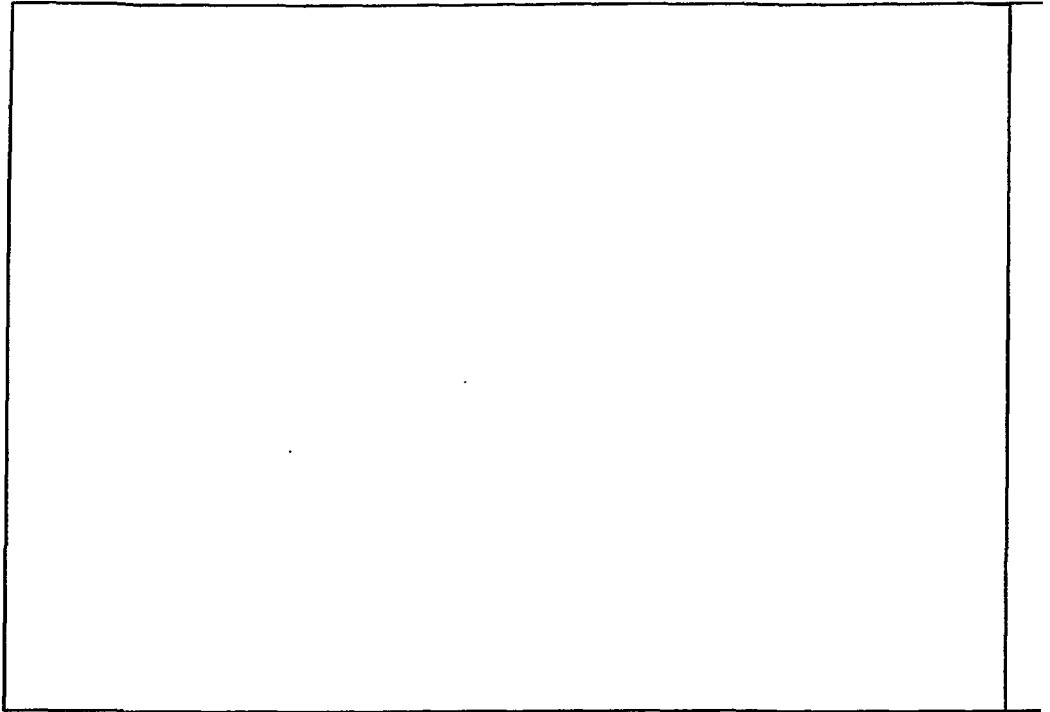
$$\frac{\partial V_i}{\partial x_i} + \phi \frac{\partial S}{\partial t} + q = 0 \quad (4)$$

Use of Equation 4 in Equation 3 yields the following transport equation:

$$\frac{\partial}{\partial x_i} \left( \phi S D_{ij} \frac{\partial C}{\partial x_j} \right) + q (C^* - C) - V_i \frac{\partial C}{\partial x_i} = \phi S \frac{\partial C}{\partial t} \quad (5)$$

### Interphase Mass-Transfer Source and Sink Terms

Volatile hydrocarbon may be present in the water, air, soil, and pure liquid phases; the hydrocarbon may also move between these phases. Figure 1 illustrates these processes.



**FIGURE 1 Four-Phase System**

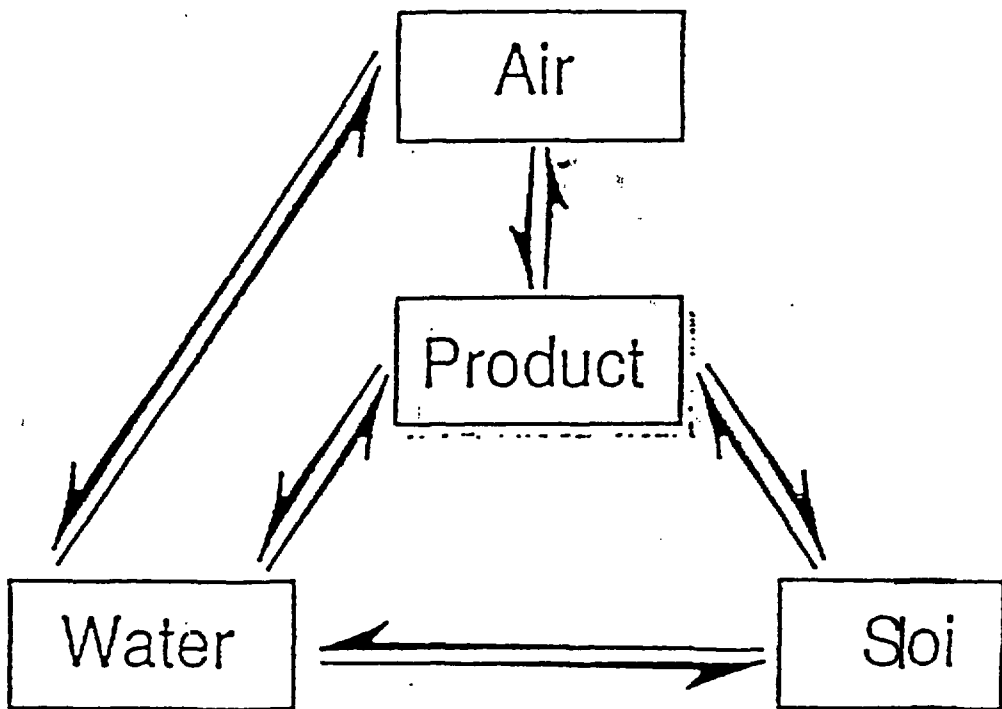


FIGURE 1: FOUR-PHASE SYSTEM

In order to account for this behavior accurately, a source/sink term,  $Q_s$ , is added to Equation 5 to incorporate interphase mass transfer.

Both the thermodynamic and kinetic aspects of interphase transfer of organic compounds are considered in describing the mass-partitioning process. Sleep and Sykes (1989) utilized kinetic partitioning functions in a mass transport model and van Genuchten et al. (1974) investigated phase partitioning and equilibrium states using nonlinear kinetic formulations. The partitioning processes used in this study assume that mass transfer is an  $n$ th order expression of the deviation from equilibrium, i.e.,

$$dC/dt = \lambda C^n \quad (6)$$

where  $C$  is the VOC phase concentration.

Equation 6 can be adapted to reflect the concentration deviation from the equilibrium condition,  $C_{eq}$ :

$$dC/dt = \lambda (C - C_{eq})^n \quad (7)$$

where  $C_{eq} = f(T)$  is only a function of temperature. Equation 7 is formulated to be sensitive to the equilibrium condition. When  $C$  is equal to  $C_{eq}$ , the right hand side of Equation 7 is equal to zero and no mass transfer occurs.

In this study, a first-order kinetic model was used ( $n = 1$ ). The equilibrium concentration ( $C_{eq}$ ) is a function of temperature and is determined from the thermodynamic definition of the phase-change process. The kinetic rate constant ( $\lambda$ ) has units of inverse time. It incorporates the effects of phase velocity, characteristic path length, and mass-transfer surface phenomena. For this analysis, the dependence of the kinetic rate constant on phase velocity is considered larger than its dependence on surface phenomena. The hydrocarbon interphase transfers include partitioning between vapor and liquid hydrocarbon,



water and vapor, soil and water, water and liquid hydrocarbon, and soil and liquid hydrocarbon. A value for  $C_{eq}$  can be determined for each of these processes.

### KINETIC RATE CONSTANT

ISV systems are characterized by relatively large vapor phase velocities. Because the vapor phase velocity is large, the rate of interphase mass transfer is assumed to be most sensitive to the contact residence time between phases, and hence, the vapor phase velocity. To determine the functional form of the kinetic rate constant ( $\lambda$ ), a Buckingham Pi analysis (Murphy 1950) was performed on Equation 5.

$$\phi S \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial X} - \phi S \lambda (C - C_{ev}) = 0 \quad (8)$$

In Equation 8, the terms take on their familiar definitions, and the dispersion term and source/sink term have been neglected to facilitate non-dimensionalization. The functional form of the dependent parameter ( $C$ ) is assumed to be

$$\Delta C = f(V_0, \lambda, L, t) \quad (9)$$

where:

$C$  = concentration ( $M/l^3$ ),

$V_0$  = characteristic velocity ( $l/t$ ),

$\lambda$  = kinetic rate constant ( $t^{-1}$ ),

$L$  = characteristic pathlength ( $l$ ) through which  $V_0$  is observed, and

$t$  = characteristic time ( $t$ ).

Performing the Pi analysis yields the following five dimensionless groups:

$\Pi_1 = C/C_{ev}$ , dimensionless concentration;

$\Pi_2 = V_0 t/L$ , dimensionless time;

$\Pi_3 = X/L$ , dimensionless distance;

$\Pi_4 = V/V_0$ , dimensionless velocity; and

$\Pi_5 = \lambda L/V_0$ , dimensionless kinetic rate constant.

Use of these Pi groups in Equation 8 yields the following non-dimensionalized transport equation:

$$\phi S \frac{\partial(\frac{C}{C_{ev}})}{\partial(\frac{V_0 t}{L})} + \frac{V}{V_0} \frac{\partial(\frac{C}{C_{ev}})}{\partial(\frac{X}{L})} - S\phi \frac{\lambda L}{V_0} (\frac{C}{C_{ev}} - 1) = 0 \quad (10)$$

The Pi variables 1, 2, 3, and 4 yield familiar groupings for dimensionless concentration, time, velocity, and distance (Bear 1979). The kinetic rate constant,  $\lambda$ , of  $\Pi_5$  is non-dimensionalized by grouping with the characteristic path length ( $L$ ) and velocity ( $V_0$ ). Field measurements (Part II of this paper) indicate that the value of the  $\Pi_5$  group is approximately 1.0. The kinetic rate constant is, therefore, a function of two parameters: the characteristic path length and characteristic velocity. This relationship is expressed as

$$\lambda = \frac{V_0}{L} \quad (11)$$

### Vapor-Liquid Hydrocarbon Partitioning

Vaporization and condensation may occur between the gas and liquid hydrocarbon phases. Thermodynamic relationships between the VOC vapor pressure and liquid hydrocarbon concentration were used to model this behavior. Assuming ideal gas behavior and using Raoult's Law, an expression relating equilibrium vapor pressure ( $P^*$ ) to an equilibrium partition coefficient ( $K_{eq}$ ) can be written (Castellan 1971) as

$$K_{eq} = \frac{MP^*}{RT} \quad (12)$$

where:

M = molecular weight of the liquid hydrocarbon,

R = universal gas constant,

T = temperature, and

P\* = VOC vapor pressure over the pure liquid.

The equilibrium-gas-phase VOC concentration,  $C_{ev}$ , can then be defined as:

$$C_{ev} = K_{eq}XY \quad (13)$$

where:

X is the mole fraction and Y is the activity coefficient. For a single-component liquid,

X and Y are equal to one and

$$C_{ev} = MP^*/RT \quad (14)$$

The vapor pressure, P\*, can be determined from the Clausius-Clapeyron equation (Castellan 1971) as:

$$\begin{aligned} \ln P^* &= -H_{vap}/RT + \ln P_{\infty} \\ P_{\infty} &= (1 \text{ atm}) \exp[H_{vap}/RT] \end{aligned} \quad (15)$$

where  $H_{vap}$  is the enthalpy of vaporization and  $P_{\infty}$  is a constant evaluated at atmospheric pressure.

Equation 7, formulated for hydrocarbon vapor-liquid partitioning, becomes:

$$-\phi S_v \frac{dC_v}{dt} = \phi S_v \lambda_{v0}(C_v - C_{ev}) = \phi \rho_0 \frac{dS_{0v}}{dt} \quad (16)$$

where:

$C_v$  = VOC gas-phase concentration ( $M/l^3$ ),

$C_{ev}$  =  $C_{eq}$  of Equation 7,

$\lambda_{v0}$  = mass-transfer coefficient for liquid-vapor partitioning ( $t^{-1}$ ),

$S_o$  = oil phase saturation, and

$\rho_o$  = oil phase density ( $M/l^3$ ).

Equation 12 also relates the rate of change in gas concentration of hydrocarbon to the rate of change in liquid hydrocarbon saturation due to volatilization from the pure liquid. This condition is required to conserve mass within the system.

### Water-Vapor Partitioning

Volatile organic compounds dissolved in the water phase can volatilize into the gas phase. To account for this phenomenon, an expression for the relationship between equilibrium gas and water-phase concentrations must be determined. Use of Henry's Law derived with the ideal gas law (Castellan 1971) yields:

$$\begin{aligned} H &= C_v/C_w \\ &= 16.04 PM/TC_{ew} \end{aligned} \quad (17)$$

where:

$H$  = dimensionless Henry's Law constant,

$P$  = vapor pressure of the VOC in the gas (mm Hg),

$M$  = molecular weight of the solute,

$T$  = temperature (K),

$C_{ew}$  = equilibrium solubility of the solute in water ( $M/l^3$ ),

$C_v$  = VOC gas-phase concentration ( $M/l^3$ ), and

$C_w$  = VOC water-phase concentration ( $M/l^3$ ).

Equation 17 states that at equilibrium and for a given temperature, a constant relationship exists between the vapor concentration  $C_v$  and the water concentration  $C_w$ . Combining Equations 17 and 7 yields:

$$\phi S_v \frac{dC_v}{dt} = \phi S_v \lambda_H (HC_w - C_v) = - \phi S_w \frac{dC_w}{dt} \quad (18)$$

where  $S_w$  and  $S_v$  are the water and vapor saturations, and  $\lambda_H$  ( $1/t$ ) is the water vapor mass transfer coefficient. Equation 18 relates the rate of change in hydrocarbon water concentration from interphase mass transfer to the rate of change in hydrocarbon vapor concentration. This condition is required to conserve mass within the system.

### Soil-Water Partitioning

The mass transfer of organic chemicals from soil surfaces to water is very sensitive to the soil matrix water content (Spencer and Cliath 1973). This finding is incorporated into the model by permitting mass transfer between the vapor and soil phases only through a water layer.

A nonlinear relationship between sorbed and water concentrations developed by Helfferich (1962) is given as:

$$K_{sw} = \frac{C_s}{C_w^n} \quad (19)$$

where:

$C_s$  = mass of solute per soil mass,

$C_w$  = solute water concentration,

$K_{sw}$  = adsorption isotherm constant, and

$n$  = a constant.

The Freundlich isotherm described by Equation 19 is an empirical relationship based on surface free energy and monolayer capacity. The Freundlich isotherm is frequently able to reproduce adsorption data at both high and low solute concentrations (Jury 1986). At low concentrations, the exponential value  $n$  is commonly taken as 1. Use of Equations 19 and 7, after assigning a value of 1 to  $n$ , yields:

$$\begin{aligned}
 -\phi S_w \frac{dC_w}{dt} &= \phi S_w \lambda_{sw} \rho_s (C_w K_{sw} - C_s) \\
 &= \rho_s S_w \phi \frac{dC_s}{dt}
 \end{aligned}
 \tag{20}$$

In Equation 20,  $\lambda_{sw}$  (1/t) is the water-soil mass transfer coefficient and  $\rho_s$  ( $M/l^3$ ) is the dry bulk soil density. Equation 20 relates the rate of change in a concentration of soil-adsorbed hydrocarbon to the rate of change in a concentration of aqueous hydrocarbon. This condition is required to conserve mass within the system.

### Water-Hydrocarbon Partitioning

A volatile organic compound can transfer between liquid hydrocarbon and water phases by dissolving or precipitation. This interphase mass transfer requires the knowledge of an equilibrium VOC water concentration. The concentration of hydrocarbon within the water phase can be related to the oil-phase saturation through

$$-\phi S_w \frac{dC_w}{dt} = \phi S_w \lambda_D (C_w - C_{ew}) = \phi \rho_o \frac{dS_o}{dt}
 \tag{21}$$

where:

$C_{ew}$  = equilibrium concentration of oil in the water phase ( $M/l^3$ ),

$\rho_o$  = density of the oil phase ( $M/l^3$ ), and

$\lambda_D$  = water-oil mass transfer coefficient ( $t^{-1}$ ).

### Soil-Hydrocarbon Partitioning

Liquid hydrocarbon in contact with soil containing organic matter can be adsorbed by the soil phase. This mass-transfer process requires the definition of a relationship between the oil phase and soil concentrations. Let  $K_{so}$  be the partition coefficient for adsorbed/liquid concentrations, then

$$K_{so} = \frac{C_s}{C_o} \quad (22)$$

where  $C_o$  is the oil component concentration ( $M/l^3$ ).

Use of Equation 22 in Equation 7 yields

$$- \phi S_o \rho_s \frac{dC_s}{dt} = \phi S_o \lambda_{so} \rho_s (C_s - C_o K_{so}) \quad (23)$$

For the one-component oil phase, Equation 23 becomes

$$- \phi S_o \rho_s \frac{dC_s}{dt} = \phi S_o \lambda_{so} \rho_s (C_s - K_{so}) = \phi \rho_o \frac{dS_o}{dt} \quad (24)$$

Equation 24 relates the rate of change of the soil-phase concentration to the rate of change of the oil-phase saturation. This condition is required to conserve mass within the system.

### Formulation of Mass-Transfer Sink and Source Terms

The term  $Q_s$ , added to Equation 5, can be formulated by summing the interphase transfer equations. For vapor-phase transport,  $Q_s$  becomes:

$$Q_s = \phi S_v \lambda_{vo} (C_{ev} - C_v) + \phi S_v \lambda_H (HC_w - C_v) \quad (25)$$

For water-phase transport,  $Q_s$  is given by:

$$Q_s = \phi S_v \lambda_H (C_v - HC_w) + \phi S_w \lambda_{sw} \rho_s (C_s - C_w K_{sw}) \\ + \phi S_w \lambda_D (C_{ew} - C_w) \quad (26)$$

Equation 5 can now be written for the vapor phase as

$$\frac{\partial}{\partial x_i} \left( \phi S_v D_{vij} \frac{\partial C_v}{\partial x_j} \right) + \phi S_v \lambda_{vo} (C_{ev} - C_v) + \phi S_v \lambda_H (HC_w - C_v) \\ + q_v (C^*_v - C_v) - V_{iv} \frac{\partial C_v}{\partial x_i} = \phi S_v \frac{\partial C_v}{\partial t} \quad (27)$$

and for the water phase as

$$\begin{aligned}
 \frac{\partial}{\partial x_i} \left( \phi S_w D_{wij} \frac{\partial C_w}{\partial x_j} \right) + \phi S_v \lambda_H (C_v - HC_w) + \phi S_w \lambda_{sw} \rho_s (C_s - C_w K_{sw}) \\
 + \phi S_w \lambda_D (C_{ew} - C_w) + q_w (C^* - C_w) - V_{iw} \frac{\partial C_w}{\partial x_i} \\
 = \phi S_w \frac{\partial C_w}{\partial t}
 \end{aligned} \tag{28}$$

### Change in VOC Concentration of the Immobile Phases

The interphase mass-transfer functions contain terms related to the VOC concentration within the soil-adsorbed ( $C_s$ ) phase and saturation of the pure hydrocarbon phase ( $S_o$ ). The change in VOC mass content of these phases can be determined by summing the interphase mass-transfer functions and solving for  $C_s$  and  $S_o$  to yield:

$$\frac{dC_s}{dt} = \lambda_{sw} [K_{sw} C_w - C_s] + \lambda_{so} [K_{so} - C_s] \tag{29}$$

$$\frac{dS_o}{dt} = \frac{\partial S_o}{\partial t} v + \frac{\partial S_o}{\partial t} S_o + \frac{\partial S_o}{\partial t} D \tag{30}$$

$$\begin{aligned}
 \frac{dS_o}{dt} = \frac{S_v \lambda_{vo}}{\rho_o} (C_v - C_{evo}) + \frac{\rho_s S_o \lambda_{so}}{\rho_o} (C_s - K_{so}) \\
 + \frac{S_w \lambda_D}{\rho_o} (C_w - C_{ew})
 \end{aligned} \tag{31}$$

### Ancillary Relationships

Initial conditions for Equations 27 and 28 consist of specification of initial values of the concentration and volume of hydrocarbon. Solution of Equations 27 and 28 also requires the specification of boundary conditions. The boundary conditions may be:



Dirichlet,

$$C(x_j, t) = C(x_i) \quad (32)$$

Neuman,

$$n \frac{\partial C}{\partial X_j} = 0 \quad (33)$$

or Cauchy

$$u(C_o - C) = V_j \frac{\partial C}{\partial X_j} n \quad (34)$$

where  $u$  is a velocity (l/t),  $C_o$  a constant concentration,  $V_j$  a fluid velocity (l<sup>2</sup>/t) across a boundary segment (l), and  $n$  is the unit vector normal to the boundary. Equations 27 through 31 describe the fate and transport of a single-component volatile hydrocarbon through an unsaturated soil.

## NUMERICAL SOLUTION OF THE TRANSPORT EQUATIONS

Mass-transport Equations 27 and 28 are solved by use of an iterative successive over-relaxation (SOR) method with an optimization accelerator. This solution algorithm utilizes concentrations in the characteristic equation at the  $n + 1$  time level as soon as they are available. In addition, incorporation of cross terms and diagonal grid blocks is easily facilitated with the SOR method. Within the simulator, the gas-transport equation is solved first, followed by the water equation. Mass balance and convergence criteria are satisfied within each phase prior to advancing the solution. After solution of the gas and water phase equations, the hydrocarbon content as an oil phase and soil hydrocarbon content are determined explicitly. The simulator is then advanced to a new time step.

Because of the presence of cross terms in the dispersion coefficients of Equations 27 and 28, values of the interblock phase velocities are required perpendicular and parallel to the grid-block faces. The perpendicular interblock velocities are computed with pressures from a flow simulator. The component of velocity parallel to the grid block face is calculated by interpolating the perpendicular interblock velocity values in adjacent grid blocks (Faust et al. 1989). For example, velocities parallel to the X face at  $i+1/2,j,k$  are determined according to

$$V_{y_{i+1/2,j,k}} = \left[ \beta_{X_{i+1/2,j,k}} \left( V_{y_{i+1,j-1/2,k}} + V_{y_{i+1,j+1/2,k}} \right) + \left( 1 - \beta_{X_{i+1/2,j,k}} \right) \left( V_{y_{i,j-1/2,k}} + V_{y_{i,j+1/2,k}} \right) \right] / 2 \quad (35)$$

where  $\beta$  is the interpolation constant

$$\beta_{X_{i+1/2,j,k}} = \frac{\Delta X_i}{\Delta X_{i+1} + \Delta X_i} \quad (36)$$

The perpendicular and parallel velocity components are used in the calculation of the dispersion coefficients

$$D_{ij} = \alpha_T V \delta_{ij} = (\alpha_L - \alpha_T) V_i V_j / V \quad (37)$$

$$V = (V_x^2 + V_y^2 + V_z^2)^{1/2} \quad (38)$$

$$\delta_{ij} = 1 \quad i=j, \quad \delta_{ij} = 0 \quad i \neq j$$

$$\alpha_T \equiv \text{transverse dispersivity} \quad (39)$$

$$\alpha_L \equiv \text{longitudinal dispersivity}$$

These values are then used in the finite-difference construction of Equations 27 and 28.

An important aspect of the numerical simulation is conservation of mass. The phase mass balance is computed within the simulator as a percent of the total mass according to the relationship:

$$(\text{SOURCE} + \text{FLOW} + \text{DEL C}) / \text{CTOT} \quad (40)$$

The numerator of Equation 40 represents the algebraic sum of interphase mass transfer (SOURCE), transport due to advection and dispersion and flow across system boundaries (FLOW), and the change in mass in the phase (DEL C). The denominator represents the total mass within the phase at the end of the current time step. Ideally, the numerator of Equation 40 will be zero. When it is not, Equation 40 is evaluated by comparison with a user-specified tolerance value for convergence. The mass balance error, as determined by Equation 40, is dependent on grid spacing, velocity, concentration, time step, and the value of the dispersion coefficient.

### MASS TRANSPORT BENCHMARK

The mass transport model was verified by analyzing relatively simple problems that have analytical solutions. Bear (1972) presents an analytical solution for Equation 1 in one-dimensional steady-state flow through a homogeneous, isotropic porous medium. For this analysis, the transport equation is subject to the initial conditions

$$\begin{aligned} t \leq 0, \quad -\infty < X < 0, \quad C = C_0 \\ 0 \leq X < +\infty, \quad C = C_1 \end{aligned} \quad (37a)$$

and boundary conditions

$$\begin{aligned} t > 0 \quad X = \pm\infty, \quad \partial C / \partial x = 0 \\ X = +\infty, \quad C = C_1 \\ X = -\infty, \quad C = C_0 \end{aligned} \quad (37b)$$

The analytical solution given by Bear (1972) is:

$$\frac{C(x,t) - C_0}{C_1 - C_0} = \frac{1}{2} \operatorname{erfc} \left\{ - \frac{x - qt/\phi}{\sqrt{4D_L t}} \right\} \quad (38)$$

where:

$\operatorname{erfc}$  = complimentary error function,

$q$  =  $\phi V$  specific discharge, L/T,

$t$  = time (t),

$\phi$  = porosity, and

$C$  = concentration.

The analytical solution at a time of ten days is plotted as the solid lines in Fig. 2 (Konikow and Bredehoft 1978). The solutions are for two values of dispersivity. On the same figure, represented by triangles and circles, are the predicted values for solution of Equation 5 from the numerical model developed in this study. As expected, some numerical dispersion exists as a result of the finite-difference discretization of the solution domain. The dispersion is more apparent at lower (circles) than higher (triangles) dispersivities

### EXAMPLE SIMULATION

The numerical model developed in this study was used to investigate the physical processes associated with ISV systems. For this analysis, a hypothetical ISV system was modeled. While the system modeled is hypothetical, the parameters chosen for the analysis are within the range of operational ISV systems.

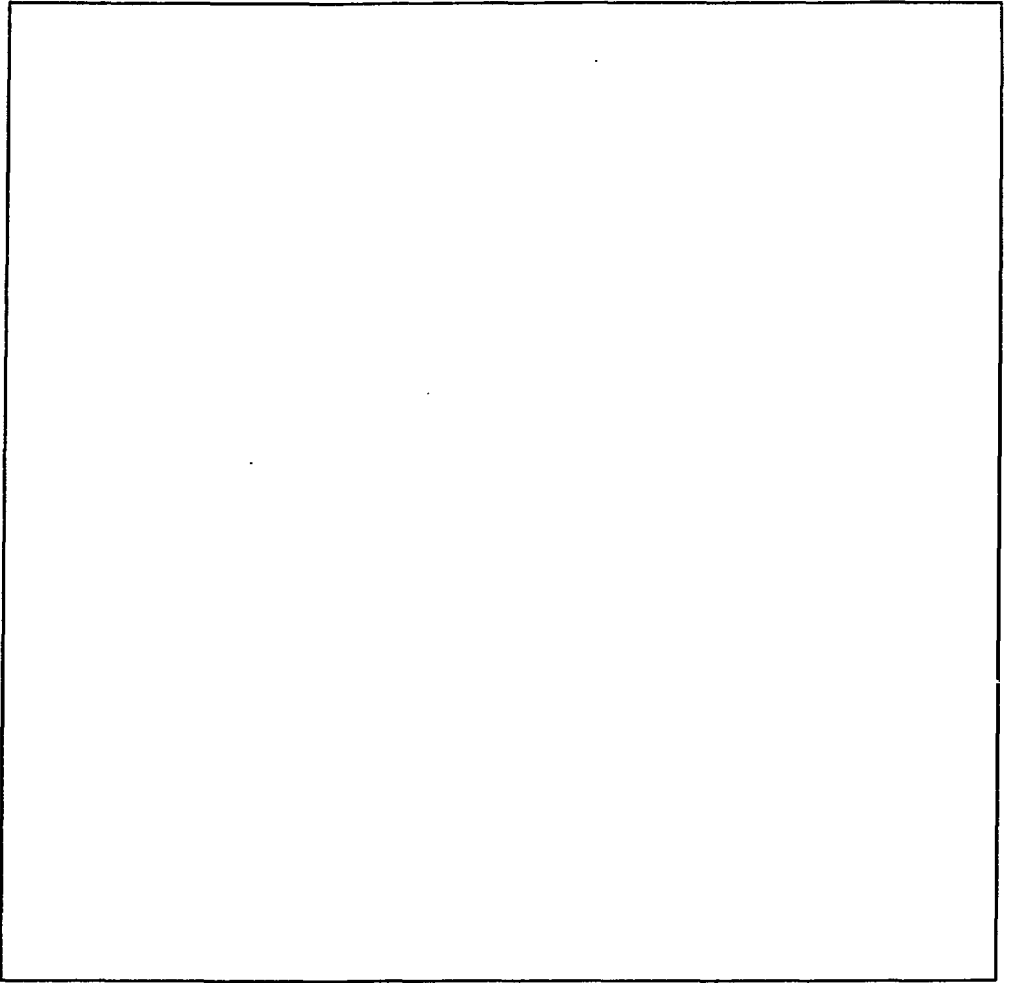
The system modeled consists of one injection and one extraction vent separated horizontally by 20 m of soil contaminated with trichloroethylene (TCE). The TCE, as an irreducible oil phase, initially saturated 0.1% of the available pore space. The soil porosity

used was 0.30. Prior to vapor extraction, the system was assumed to be in equilibrium at a temperature of 8°C. For equilibrium conditions, the initial TCE concentration is 0.25 g/L and 1.10 g/L in the vapor and water phases, respectively. An initial adsorbed soil concentration was specified as  $1.25 \times 10^{-4}$  g/g. Both the vapor phase and water phase velocities were assumed to be constant throughout the system and equal to 1.5 m/day and zero, respectively. The mass transfer coefficient was specified as  $30.15 \text{ day}^{-1}$ , and the vapor phase dispersivity was 0.01 m. The value of the Henry's Law coefficient was 0.24, and the soil-water partition coefficient was set to 0.2 mL/g.

Figures 3 through 6 show the model-predicted phase concentrations at the extraction vent for the oil, vapor, water, and soil, respectively. As indicated in these figures, TCE is removed from the soil and water phases and collected at the extraction vent. After about 20 days, the oil saturation (Figure 3) drops abruptly, to indicate a nearly complete cleanup process. This behavior is reflected both in the TCE vapor concentration (Figure 4) and in the water phase TCE concentration (Figure 5) where the TCE concentration also goes to zero. In a similar fashion, the TCE concentration in the soil (Figure 6) also goes rapidly to zero after about 20 days of extraction. Total TCE production at the extraction vent increases linearly with time and reaches nearly 100% of the initial total TCE mass after about 20 days.

If the mass transfer coefficient is increased by a factor of ten to  $301.5 \text{ day}^{-1}$ , TCE is removed from the system more rapidly, as demonstrated by the extraction vent vapor concentration curve presented in Figure 7. If the mass transfer coefficient is decreased by an order of magnitude to  $3.015 \text{ day}^{-1}$ , the cleanup process is increased to about 31 days (Figure 8).

If the advective velocity is increased by a factor of five to 7.5 m/day, cleanup can be attained in about four days, even if the mass transfer coefficient is reduced by a factor of two to  $150.3 \text{ day}^{-1}$  (Figure 9). If the mass transfer coefficient is further reduced by two orders of



**FIGURE 2 Verification of the Model Using an Analytical Solution**

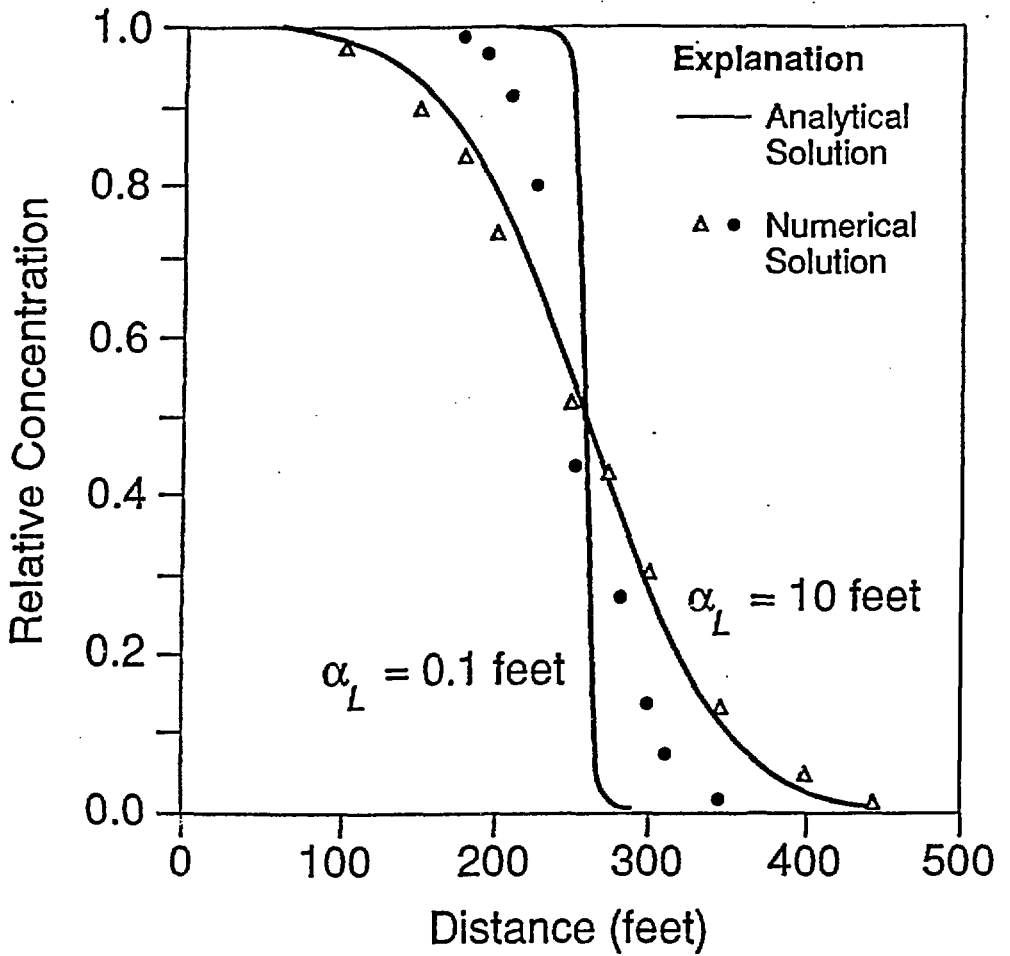
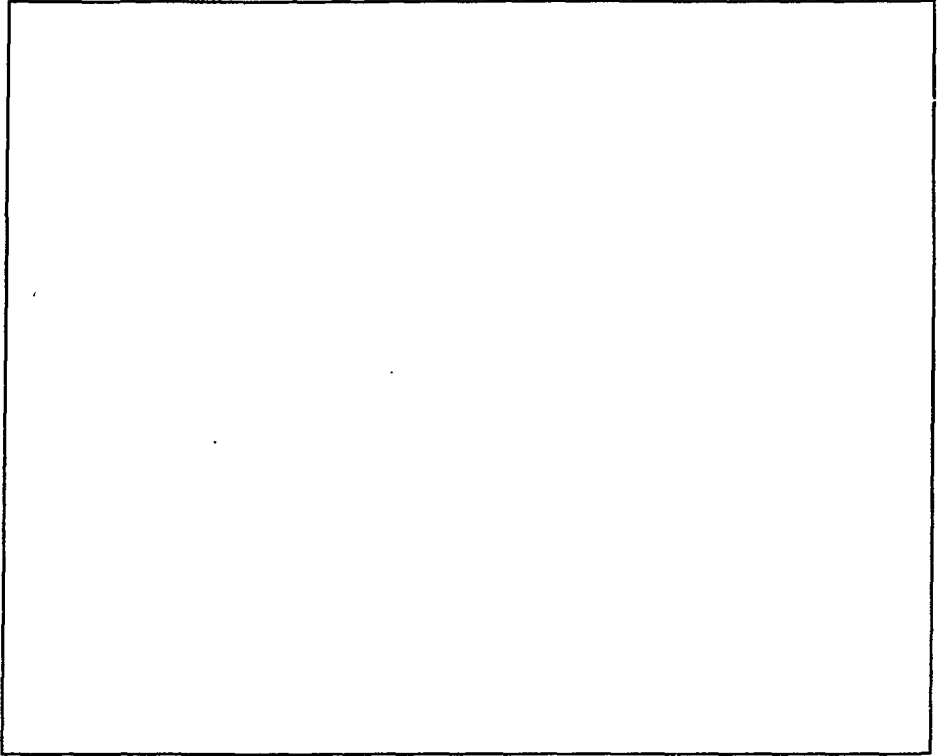


FIGURE 2: VERIFICATION OF THE MODEL USING AN ANALYTICAL SOLUTION



**FIGURE 3 Oil Saturation vs. Time for Base Case**



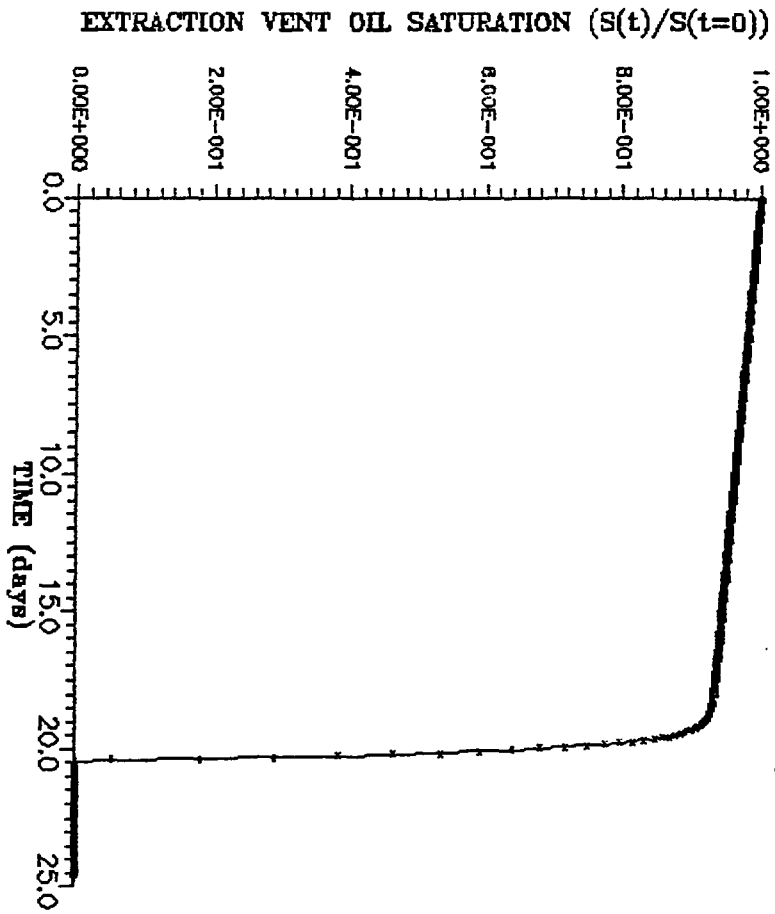
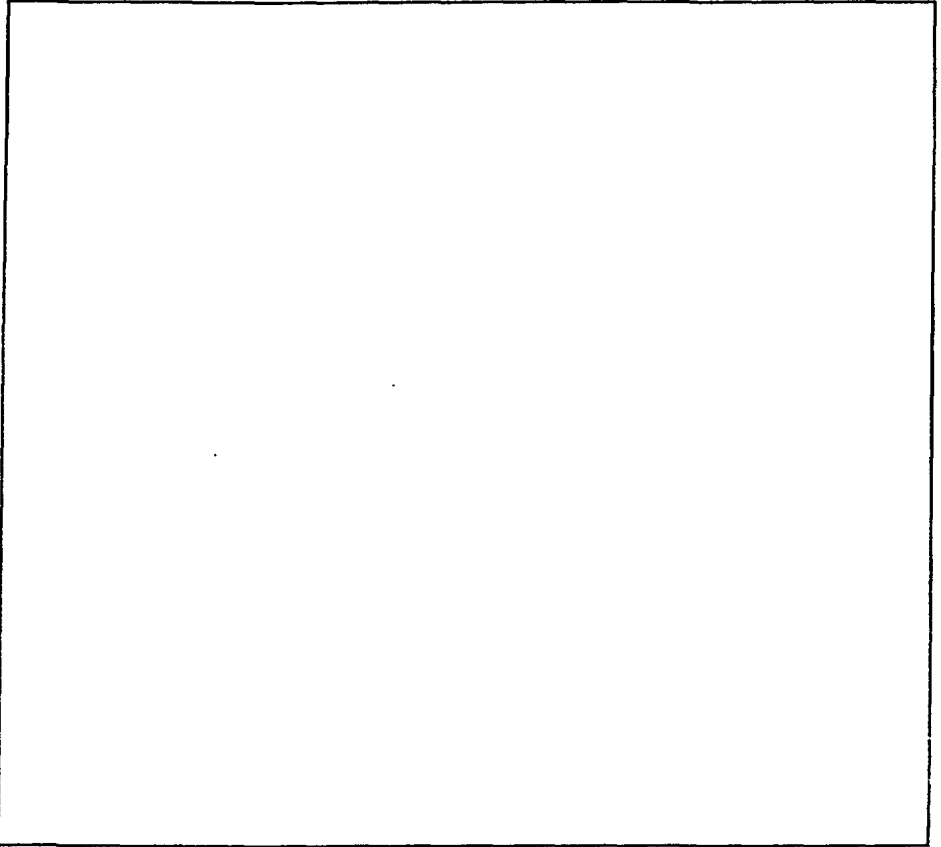


FIGURE 3 : OIL SATURATION VS TIME FOR BASE CASE



**FIGURE 4 Vapor Concentration vs. Time for Base Case**

EXTRACTION VENT VAPOR CONCENTRATION (C/C<sub>initial</sub>)

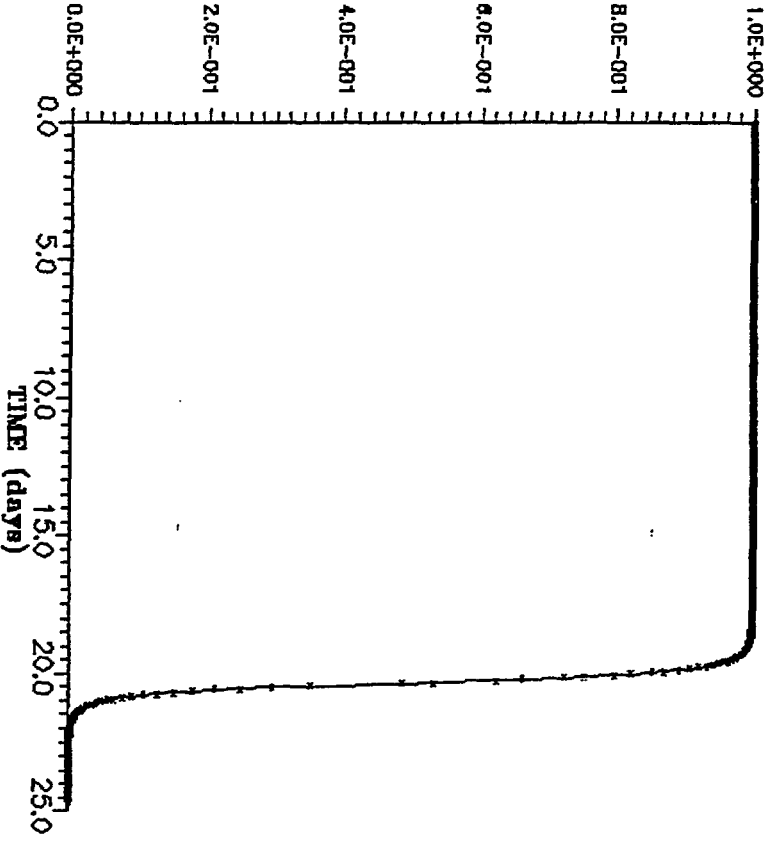
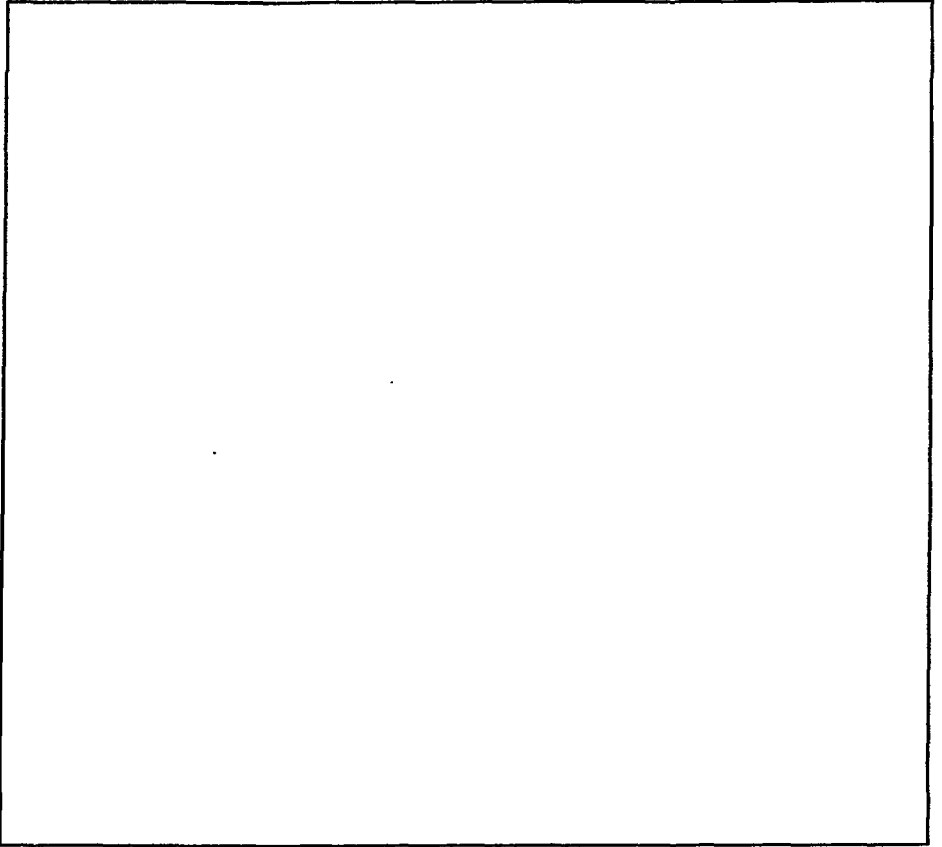


FIGURE 4 : VAPOR CONCENTRATION VS TIME FOR BASE CASE



**FIGURE 5 Water Concentration vs. Time for Base Case**

EXTRACTION VENT WATER CONCENTRATION (C/Cinitial)

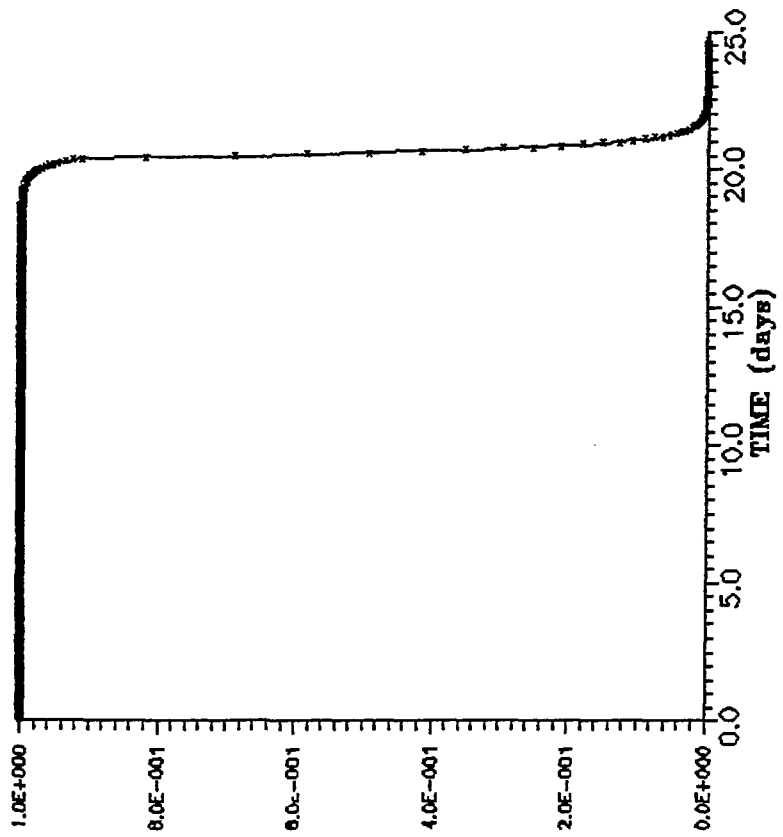
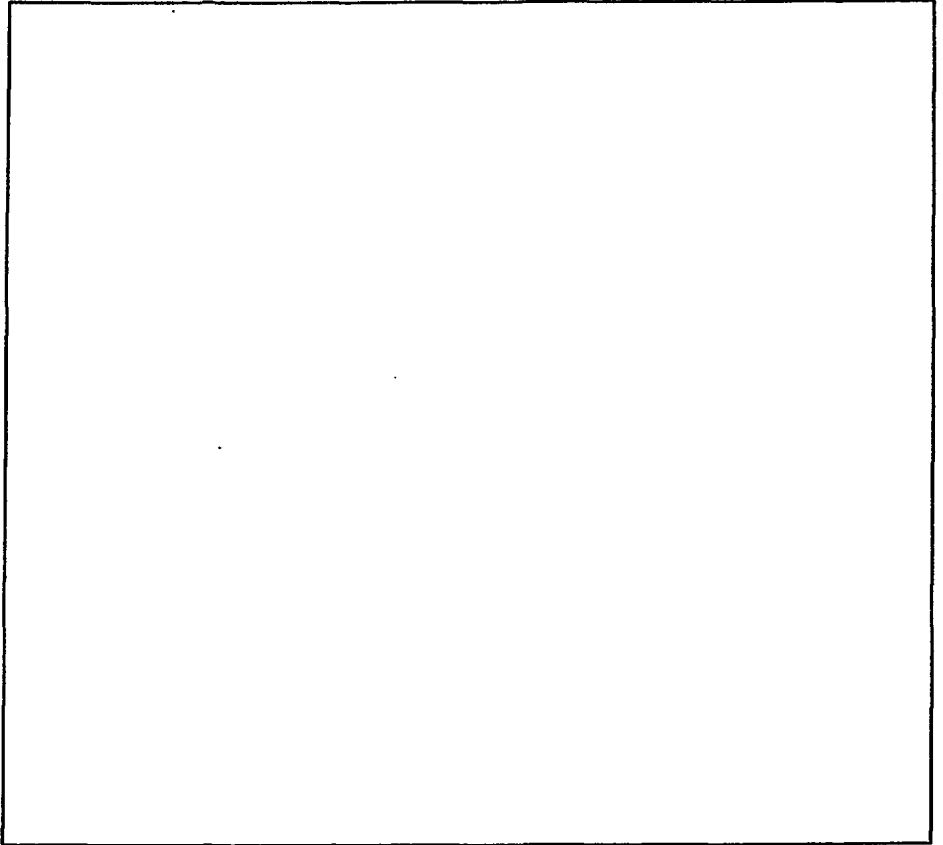


FIGURE 3: WATER CONCENTRATION VS TIME FOR BASE CASE

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**FIGURE 6 Soil Concentration vs. Time for Base Case**

EXTRACTION VENT SOIL CONCENTRATION (C/C<sub>initial</sub>)

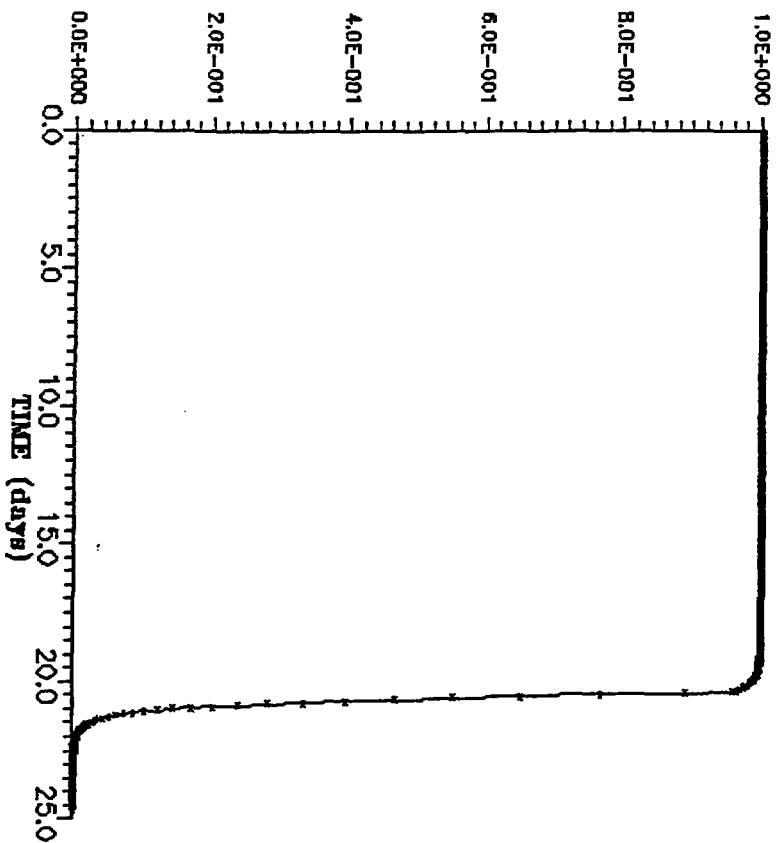
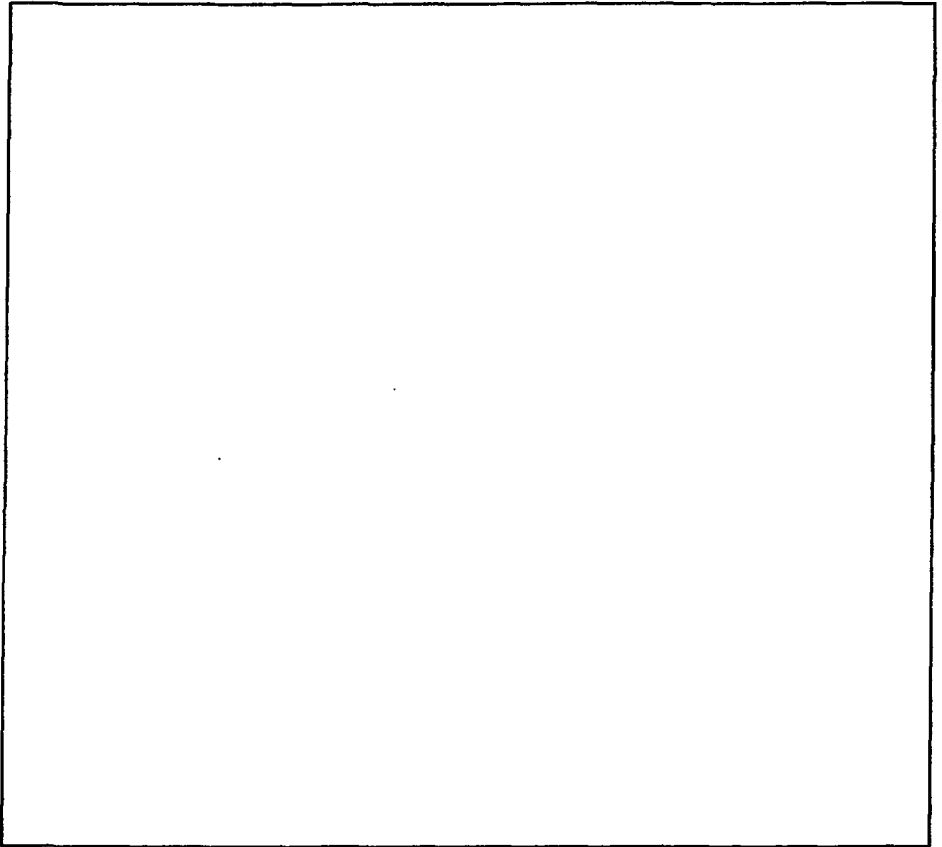


FIGURE 6: SOIL CONCENTRATION VS TIME FOR BASE CASE



**FIGURE 7 Vapor Concentration for Lambda x 10**



EXTRACTION VENT VAPOR CONCENTRATION (C/C<sub>initial</sub>)

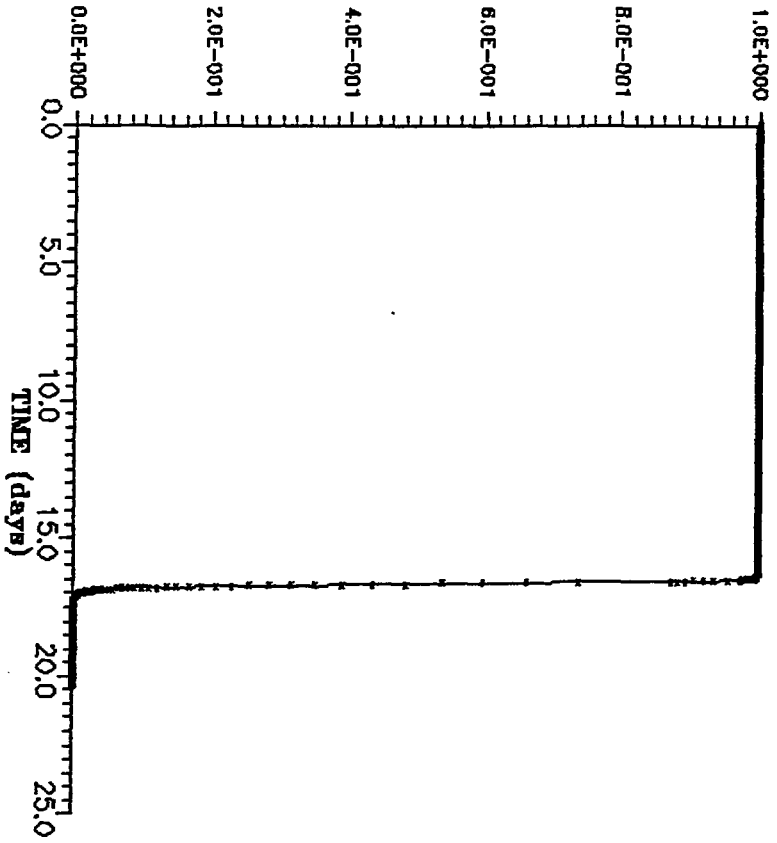
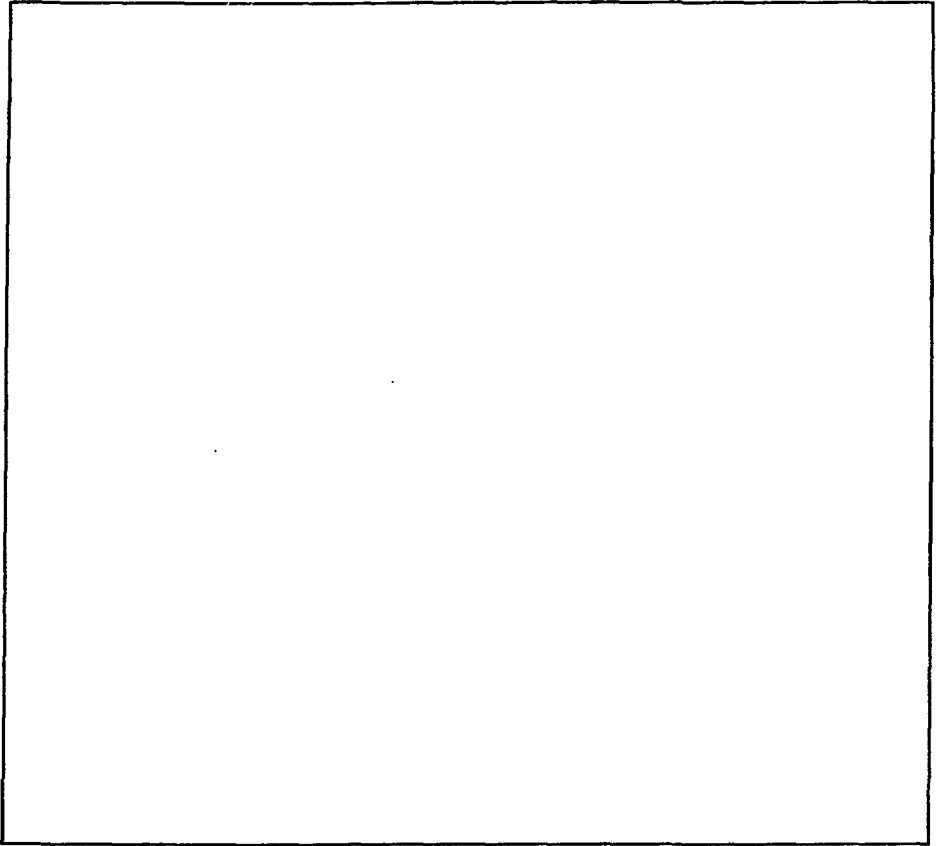


FIGURE 7 : VAPOR CONCENTRATION FOR LAMBDA TIMES 10



**FIGURE 8 Vapor Concentration for Lambda x 0.1**

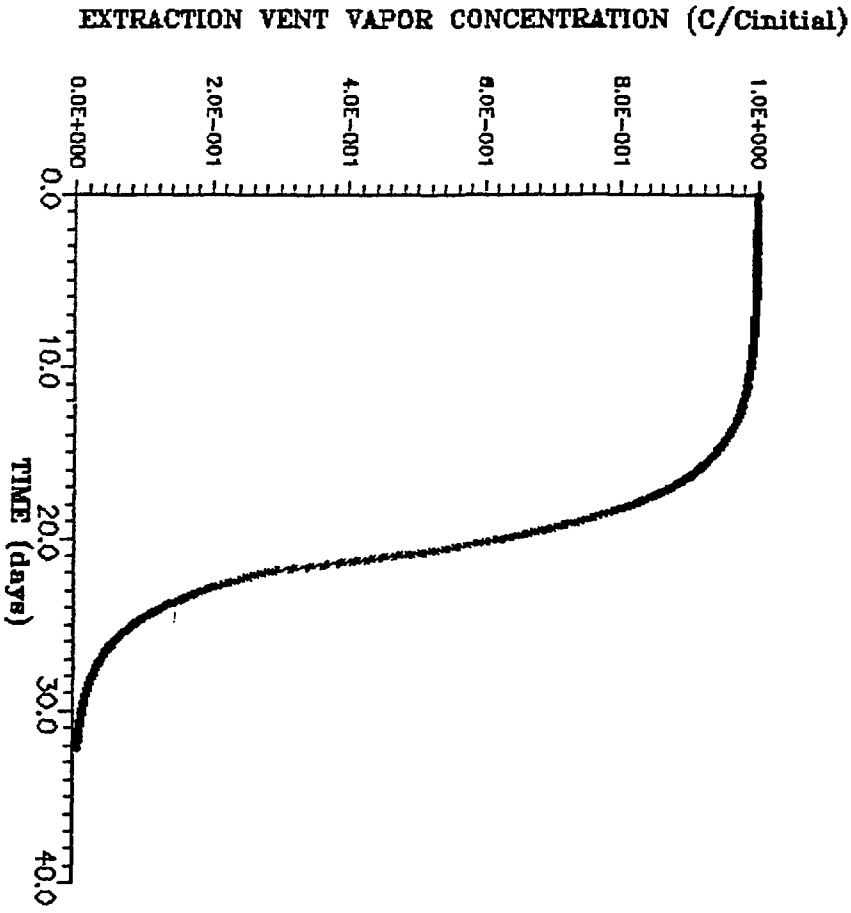
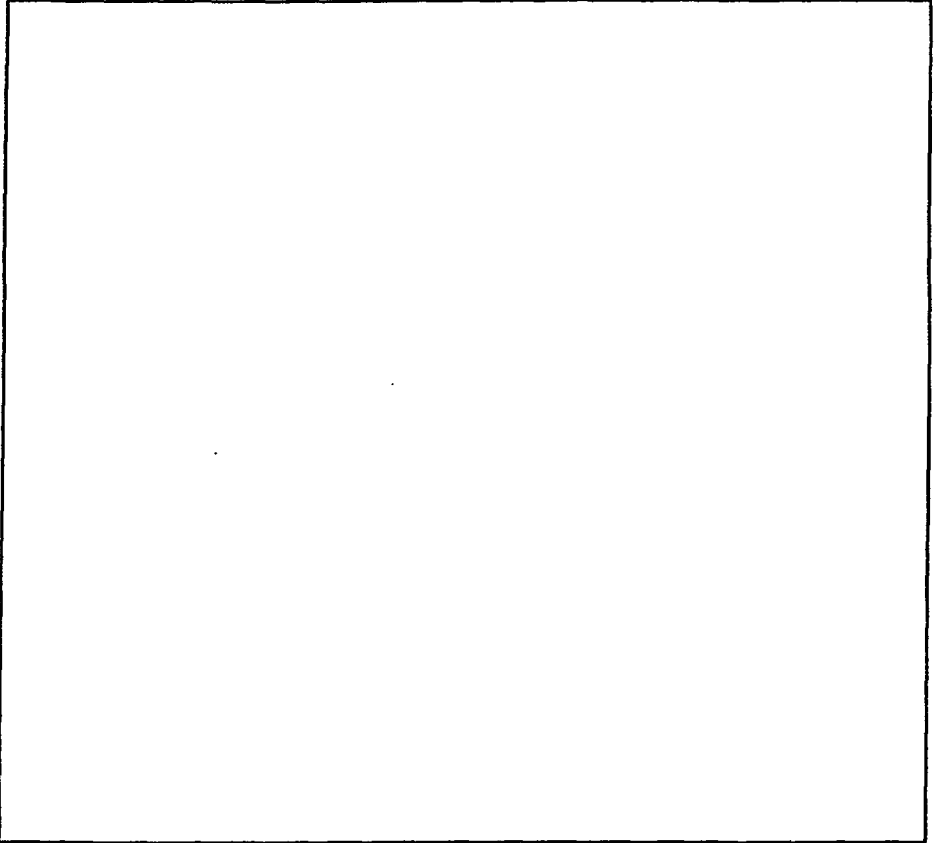


FIGURE 8 : VAPOR CONCENTRATION FOR LAMBDA TIMES 0.1



**FIGURE 9 Vapor Concentration for  $V \times 5$  and  $\text{Lambda} \times 0.5$**

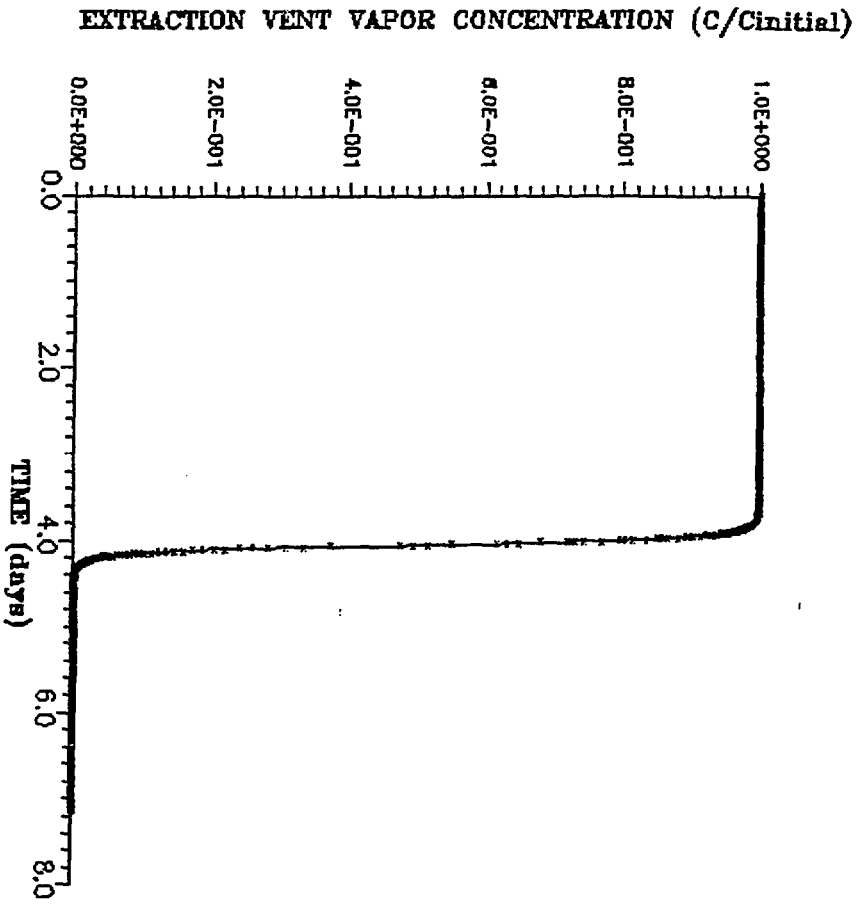
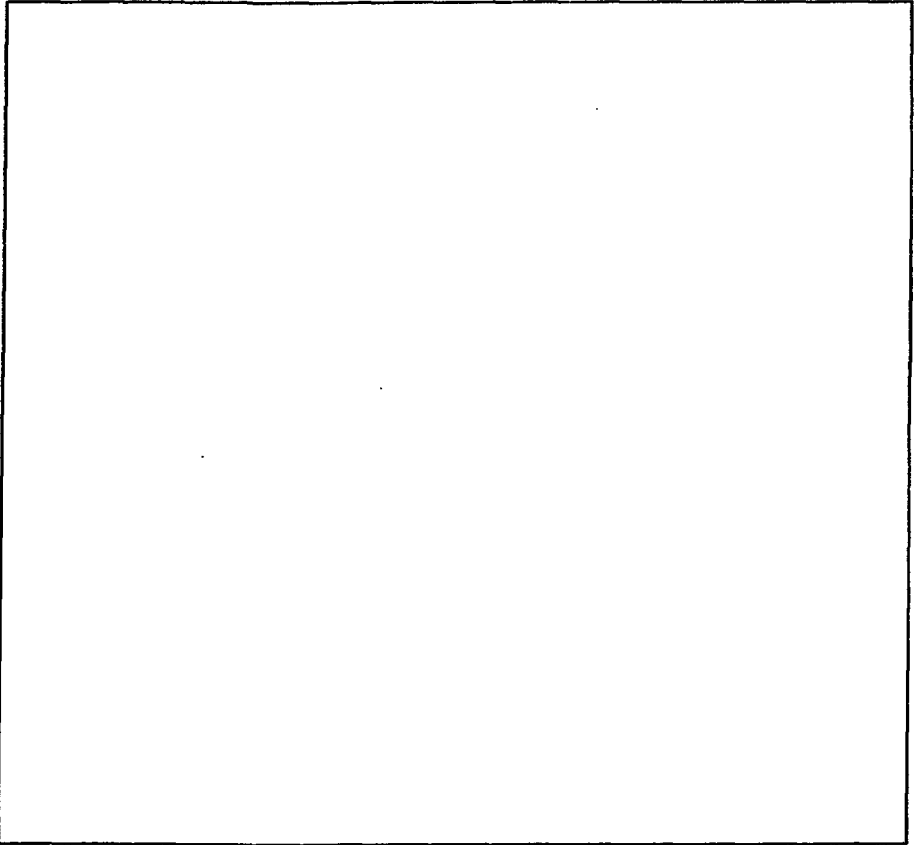


FIGURE 9 : VAPOR CONCENTRATION FOR  $\lambda$  TIMES 5 AND 0.5 LAMBDA

magnitude to  $1.5 \text{ day}^{-1}$  and the advective velocity is maintained at a high value, the concentration of TCE in the vapor phase at the extraction vent drops abruptly to 0.6 of the initial concentration and plateaus at this value (Figure 10). This plateau is created by a balance between the quantity of TCE supplied to the vapor phase by mass transfer from the oil and water phases and the quantity of TCE removed by the extraction process. This equilibrium condition persists until the oil saturation is depleted. After oil phase depletion, the vapor phase concentrations are supplied by mass transfer from the water phase only. For this case, the cleanup time is increased to more than 20 days.

The numerical model was also used to investigate the influence of venting schedules on phase concentrations for two conditions, when an oil phase is present and when it is not. Figure 11 investigates the former case and illustrates a venting schedule which incorporates 10-day increments of vapor extraction followed by 10 days of system shutdown. As shown in this figure, the vapor phase concentrations are strongly influenced by the change in extraction rate. Because TCE vaporizes from the oil phase, the vapor concentration approaches its pre-extraction concentration levels. Figure 12 illustrates a similar venting schedule for a case in which all of the oil phase has been dissipated. The concentration recovery with respect to the pre-extraction level is very slight.

The type of information shown in Figures 3 through 12 can be applied to any ISV system. Changes in ISV system performance can be predicted for site-specific studies using the numerical model. Estimates of the time required to achieve site cleanup using different configurations in vent length and spacing, and extraction rate and schedule can be made prior to system installation.



**FIGURE 10 Vapor Concentration for  $V \times 5$  and  $\Lambda \times 0.5$**

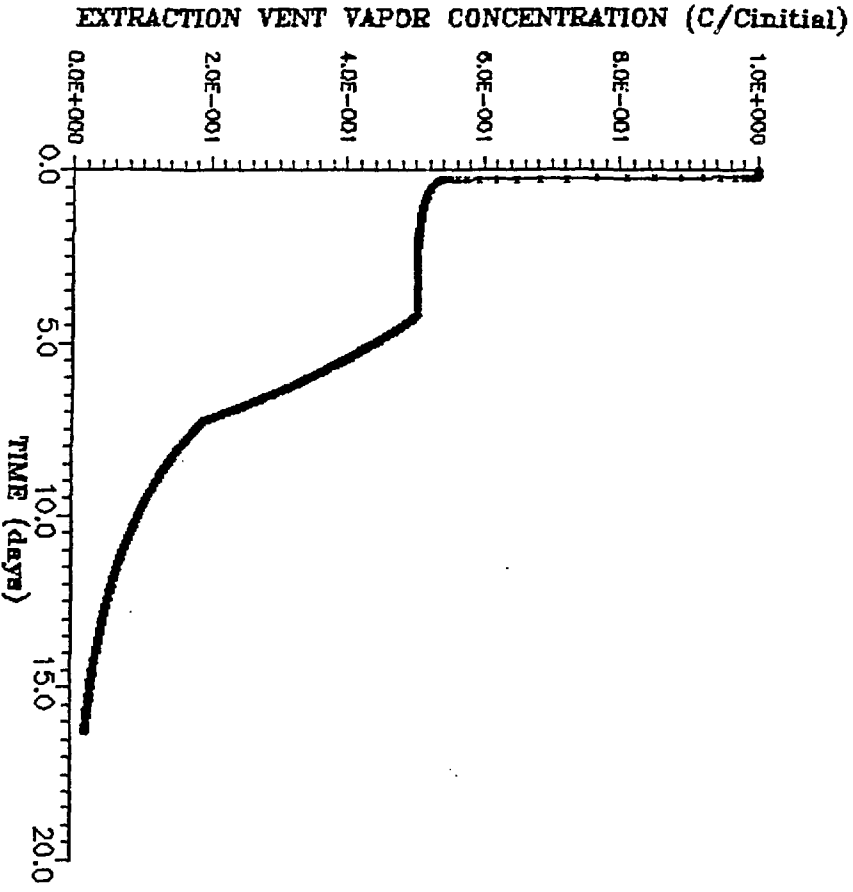
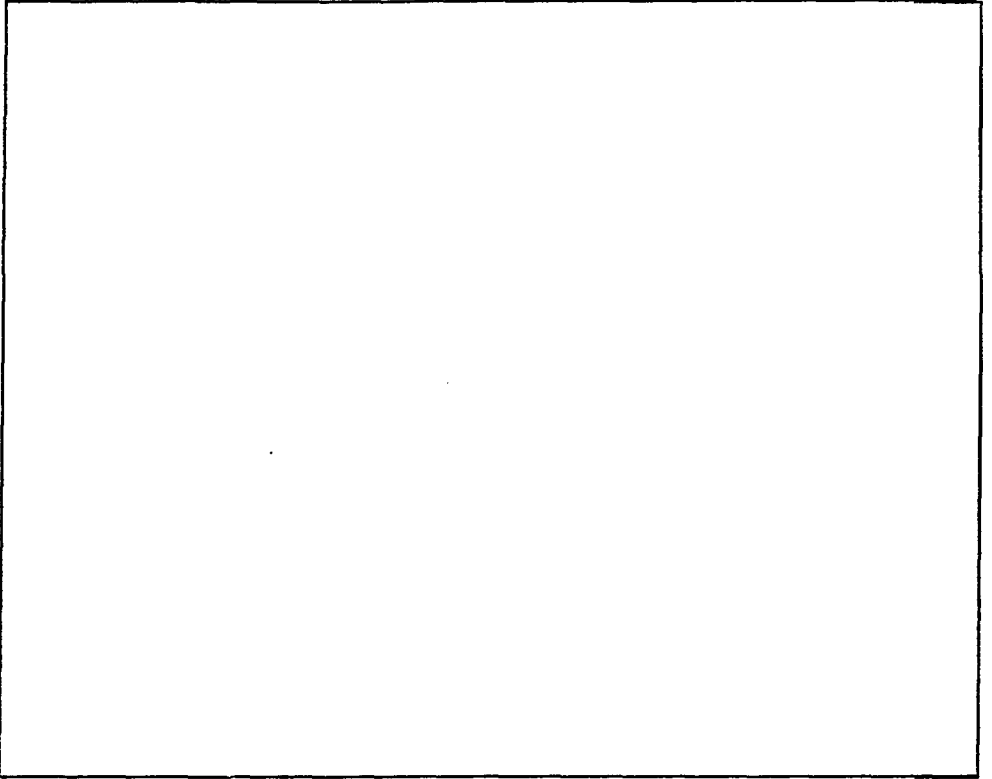


FIGURE 10: VAPOR CONCENTRATION FOR V TIMES 5 AND 0.05 LAMBDA





**FIGURE 11 Vapor Production for Cycling**

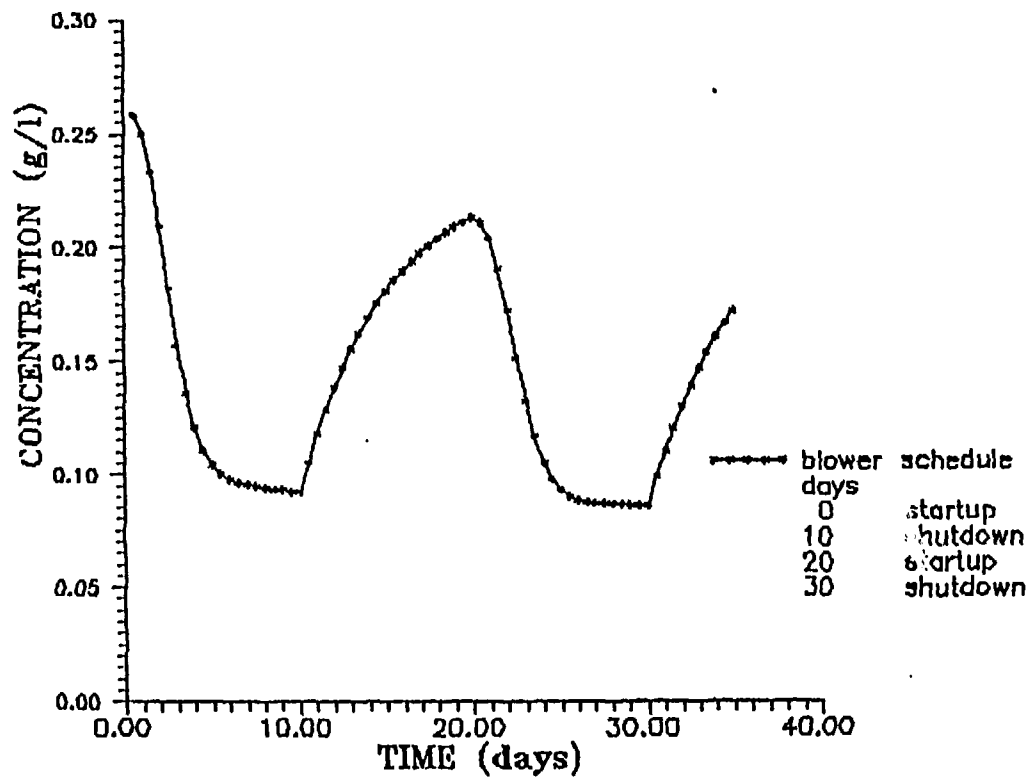
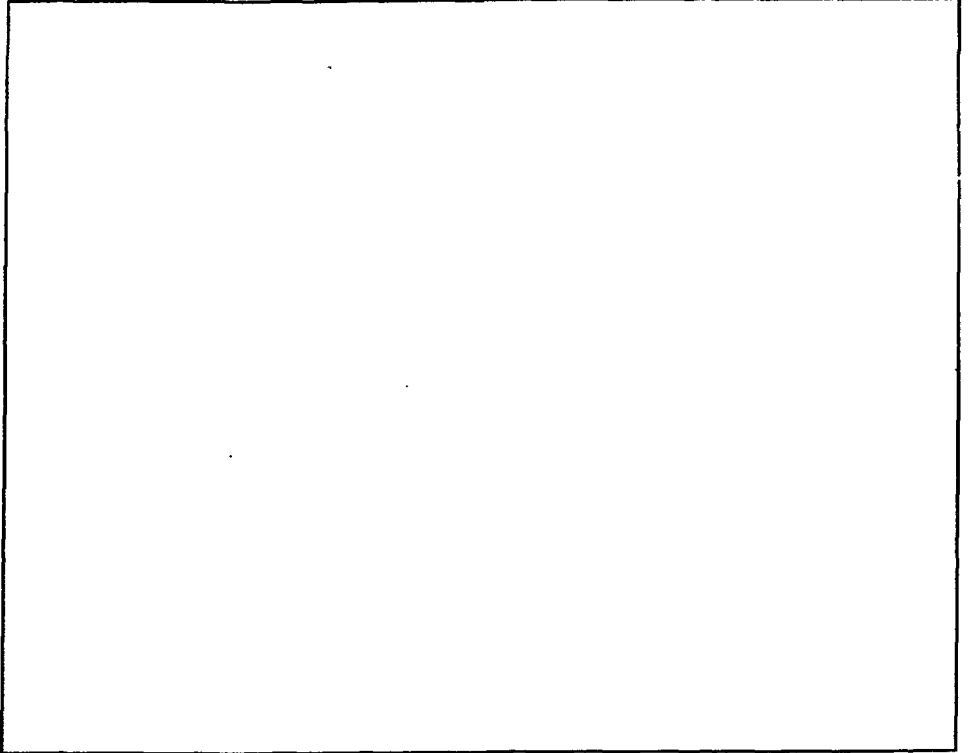


FIGURE 11: VAPOR PRODUCTION FOR CYCLING



**FIGURE 12 Vapor Production for Cycling with Depleted Oil Phase**

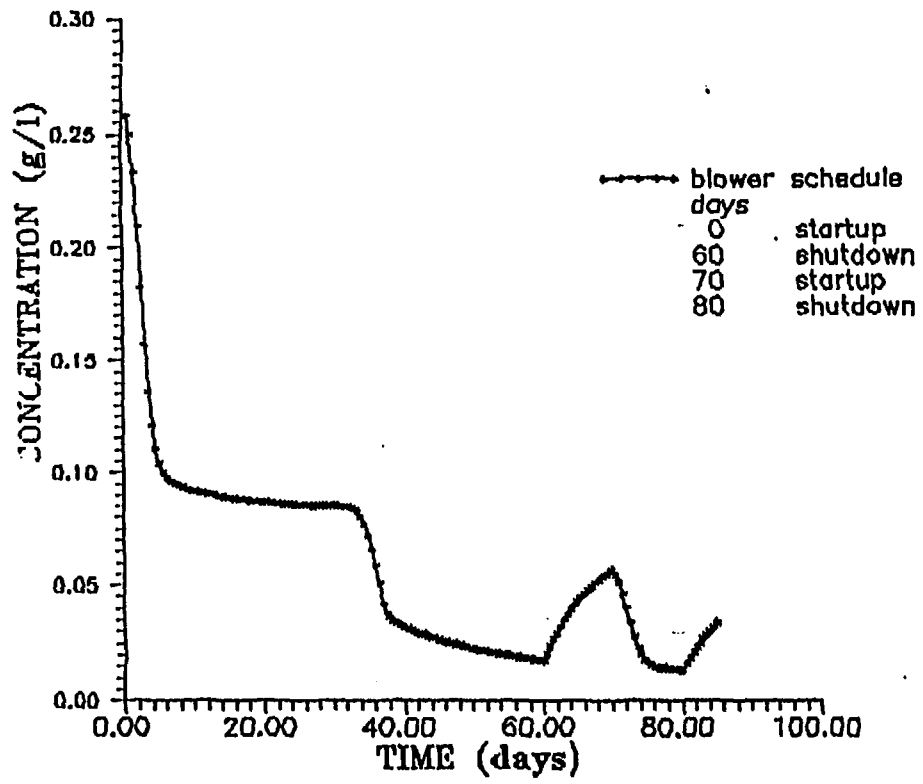


FIGURE 12: VAPOR PRODUCTION FOR CYCLING WITH DEPLETED OIL PHASE

FIGURE 13: VAPOR PRODUCTION FOR CYCLING WITH DEPLETED OIL PHASE

## SUMMARY AND CONCLUSIONS

This study developed a three-dimensional numerical model for determining the multi-phase fate and transport of volatile organic compounds in unsaturated soils. The code for the model was specifically designed to investigate ISV remediation strategies, predict the extent of cleanup from field measurements, and to help design ISV remedial systems. The model was verified against a one-dimensional analytical solution, and a hypothetical, one-dimensional extraction system was used to investigate the sensitivity of the model to various input parameters.

Part II of this paper presents a validation of the three-dimensional model using field data obtained from an operational ISV system.

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