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CHAPTER I

INTRODUCTION

It has been estimated by the United States Environmental Protection Agency that as much as 30 percent of the 3.5 million underground storage tanks containing petroleum hydrocarbons and other potentially hazardous materials are leaking (Dowd, 1984). A large portion of these leaking tanks have introduced petroleum fuels and other mixtures of volatile organic liquids into the environment. Once placed into the unsaturated zone, the fluids will move in response to gravity and soil tension, leaving behind significant quantities of immiscible, non-aqueous phase liquid (NAPL) held stably in place by capillary forces (an excellent overview is given by Hunt, et al., 1988). If a large enough quantity is released, the immiscible liquid will reach the water table, and, depending on the contaminant density, either accumulate in a floating layer or continue to travel downward through the saturated zone. Depending on the physical qualities of the contaminant mixture, a significant portion will volatilize and migrate through the unsaturated zone at much higher rates than the liquid phases.

The main threat to human health resulting from subsurface toxic compound releases has long been recognized as the movement of dissolved components in groundwater toward production wells. To address this threat, the thrust of remedial measures has been dominated by the extraction and treatment of large quantities of

groundwater. The observation of many protracted "pump-and-treat" methodologies has prompted more aggressive treatment of the contaminant sources, which may or may not be located within the saturated zone. In the case of lighter-than-water nonaqueous phase liquids (LNAPLs), product recovery methods include liquid extraction with or without attempted enhancement by water table depression (Nyer, 1985) and, more recently, vacuum-enhanced skimming (Blake, et al., 1990).

The need to address the residual contaminants that remain in the unsaturated zone, either above the original water table or an artificially depressed phreatic surface, has resulted in the profusion of vapor extraction as a remediation technique. By inducing the flow of soil vapor through volumes of soil containing the volatile compounds, levels of residual contamination can be significantly reduced. Vapor extraction is a particularly attractive remedial alternative because of the relative low cost, the virtual non-interruption of normal activities at commercial and industrial sites, and the ability to clean deeply buried soil.

Several factors are directly related to the rate at which contaminants can be removed from soil, and should be simulated in the assessment of vapor extraction feasibility or remedial system design. These factors include the distribution of soil permeability (and resultant flow fields), the distribution and composition of the contaminant mixture, soil properties which effect the vapor concentrations of the chemical compounds, and the placement of vapor extraction or injection wells. A number of vapor transport models have been formulated based on the occurrence of one compound that is present in three phases (no NAPL). This simplification allows the models to assign a constant value of retardation to the compound (Jury, et al., 1983; Mendoza and Frind, 1990; Sleep and Sykes, 1989; Falta et al. 1989).

Non-dimensional chemical equilibrium models were developed by Marley and Hoag (1984) and Johnson, et al., (1990) to describe the concentrations of compounds in vapor above a liquid chemical mixture of known composition, and to predict the changes in those concentrations with subsequent removals of quantities of vapor. These models neglect variability in the vapor-flow fields and contaminant distribution, but were certainly more representative of sites requiring remediation, because they included a fourth (NAPL) phase. Baehr and Hoag (1988) demonstrated a one-dimensional simulation of column experiments which included a four-phase chemical equilibrium formulation, but assumed zero retardation and a constant value for vapor discharge.

In this paper, a model is presented which mathematically simulates the advective and diffusive transport of virtually any number chemical compounds simultaneously in two dimensions. The model also explicitly solves the distribution of each compound among four phases (vapor, adsorbed, dissolved, and NAPL), thereby simulating the differing retarded movement of compounds with variable properties. The model tracks contaminant saturation and recalculates the flow regime to reflect the depletion of pore fluids.

CHAPTER II

THEORETICAL BACKGROUND

General Transport Equation

Consider a volume of soil contaminated with any number of chemical compounds. If the soil is within the vadose zone, then a portion of the contaminant will be present in the soil gas. Each of the compounds will be distributed within four phases: a vapor phase, a dissolved soil moisture phase, an adsorbed phase, and, if total soil concentrations are high enough, a separate non-aqueous phase (Marley and Hoag, 1984; Johnson, et al., 1990). The purpose of the model contained herein is to describe the movement of compounds in the vapor phase, and the phase distribution of each compound. The movement of the gaseous compounds may be due to molecular diffusion, the advective motion of carrier soil gas, or a combination of both.

If a volume of partially evacuated (vadose zone) soil is represented by the differential volume $dx dy dz$, then the net chemical vapor flux in each axial direction is given by:

$$\frac{\partial J_x}{\partial x} dx dy dz, \dots\dots\dots (1a)$$

$$\frac{\partial J_y}{\partial y} dx dy dz, \text{ and} \dots\dots\dots (1b)$$

$$\frac{\partial J_z}{\partial z} dx dy dz \dots\dots\dots (1c)$$

where,

$J_{x,y,z}$ = molar flux in the x, y, and z directions (mole/L²T), and
 dx, dy, and dz = differential distances in the x, y, and z directions (L).

For the purposes of this model, the molar flux is considered to be composed of the movement of compounds in the vapor phase. The flux of chemical compounds in the vapor phase is composed of the advective motion of soil gas and the dispersive flux of the compounds:

$$\mathbf{J}_n = \mathbf{q}C_n - D\nabla(C_n) \dots\dots\dots (2)$$

where,

\mathbf{J}_n = molar flux vector of compound n (mole/L²T),
 \mathbf{q} = vapor discharge vector (L/T),
 C_n = vapor molar concentration of compound n (mole/L³), and
 D = dispersion tensor (L²/T), and
 ∇ = gradient operator (1/L).

The change in molar concentration within the differential element with respect to time is the difference between the sum of the directional fluxes (equation [2]) and a chemical source/sink term. Therefore, equations (1) and (2) combine to form an expression of the vapor transport and resultant change in total soil molar concentration of the nth compound in a contaminant mixture:

$$-\nabla \cdot (\mathbf{q}C_n - D\nabla(C_n)) = \frac{\partial M_{cn}}{\partial t} + F_n \dots\dots\dots (3)$$

where,

M_{cn} = total soil molar concentration of compound n (mole/L³),

t = time, and

F_n = molar loss (or addition) rate of compound n per volume of soil
(mole/L³T).

The dispersive flux, in turn, is composed of diffusive flux, due to a molecular concentration gradient, and the velocity-dependant hydrodynamic dispersion:

$$D = (D_o + a_v \frac{q}{\epsilon}), \dots \dots \dots (4)$$

where,

D_o = molecular diffusion coefficient in the porous medium for the nth
compound (L²/T),

a_v = vapor-dispersivity of the porous medium (L), and

ϵ = vapor-occupied fraction of the porous medium (L³/L³).

Notice that equation (3) is a mixed hyperbolic and elliptic non-linear differential equation when equation (4) is used to describe dispersion. This is due to the dependance of the dispersive term on residual contamination. Solving such an equation is generally regarded as problematic due to the mixed hyperbolic and elliptic terms. A common solution technique is to use the Method of Characteristics (MOC), described by Garder et al., 1964, and Konikow and Bredehoeft, 1978. Another method is embodied in the Random Walk code (Prickett et al., 1981). These methods solve the advective (hyperbolic) portion by particle-tracking algorithms, and modify that solution with the dispersive (elliptic) portion of the transport equation.

These methods require relatively large amounts of computer memory because of the number of particles within the model domain, even for the solution of the transport of a single compound. Such methodology is necessary for dissolved solute

simulations, because total dispersion will be dominated by hydrodynamic dispersion in groundwater environments. Even at relatively low velocities, the dispersion by diffusion is often considered negligible. For this reason, simulation of dissolved-solute plume spreading under natural conditions in the saturated zone warrants velocity-dependent dispersion calculation.

In the vadose zone, however, free-air diffusion coefficients are on the order of 10,000 times greater than water diffusion coefficients for most organic chemicals (Jury, et al., 1983). Under conditions where a vapor contaminant plume is migrating away from a source, the total dispersion will be dominated by the diffusive flux. For this reason, the models presented by Jury et al., (1983, 1990) do not include hydrodynamic dispersion for the vapor phase. Recent modeling of the migration of dense soil gas plumes (Mendoza et al., 1990; Mendoza and Frind, 1990) show that natural plume velocities due to gas pressure (or density) gradients will result in hydrodynamic dispersion of less than 10 percent of the diffusive dispersion.

Under forced soil gas venting operations, an induced pressure gradient may produce vapor velocities at which the hydrodynamic dispersion will be equal to or greater than that of diffusion. This will be the case when soil gas velocities are on the order of 0.01 centimeters/second (10 meters/day). Sleep and Sykes (1989) have also modeled the density-driven natural velocities of a dense, trichloroethylene vapor through a high permeability (gravel) matrix, and obtained maximum vapor velocities on the order of 2 to 5 cm/day. To obtain velocities which will make hydrodynamic dispersion important, artificial pressure gradients are necessary. In such cases, the movement of soil gas will be towards extraction wells. The effect of hydrodynamic dispersion is not shown in the mass balance at any point in this kind of simulation because of the mechanism of dispersion. The mass is "smeared out," however the

center of mass is identical to a non-dispersed solution. For these reasons, and for purposes of creating a portable and easily solvable code, only diffusive flux is considered in the dispersion term in equation (4). This simplification will enable the simultaneous solution of the movement and phase interaction of many compounds in complex mixtures, without a sacrifice of mass balance accuracy.

It should be noted that the molar source/sink term (F_n) in equation (3) can incorporate a biologic degradation term, or expressions which simulate non-equilibrium (rate-limited) sorption of chemical compounds (Brusseau, 1991). These types of modifications pose no computational difficulties for simple kinetic expressions, and present themselves as possible future refinements of the computer model presented in this report. The utility of rate-limited sorption expressions has been disputed (Gierke, et al., 1992) because of the low vapor velocities observed at field sites, as opposed to the higher laboratory column velocities used by Brusseau (1991).

Calculation of Flow Regime

Conservation of mass gives the following equation, which describes the mass flux of soil gas in differential form:

$$-\nabla \cdot (\rho \mathbf{q}) = \frac{\partial(\epsilon \rho)}{\partial t} + \frac{F}{dx dy dz} \dots\dots\dots (5)$$

in which,

$$\mathbf{q} = - \frac{\rho g}{\mu} \mathbf{k} \nabla \phi \dots\dots\dots (6)$$

where,

- ρ = soil gas density (M/L³),
 \mathbf{q} = soil gas discharge vector (L/T),
 t = time,
 F = vapor mass flux source or sink (M/T),
 g = acceleration of gravity (L/T²),
 μ = soil gas viscosity (M/LT),
 \mathbf{k} = air permeability vector (L²), and
 ϕ = soil gas head (L).

An expression for the head of a compressible fluid is given by Hubbert, 1940, as:

$$\phi = z + \frac{1}{g} \int_{P_0}^P \frac{dP}{\rho} \dots\dots\dots (7)$$

and, by the ideal gas law,

$$\rho = \frac{P \cdot M_w}{RT} \dots\dots\dots (8)$$

where,

- z = elevation (L),
 P = soil gas pressure (M/LT²),
 P_0 = soil gas reference pressure (M/LT²),
 M_w = molecular weight of the soil gas (M/mole),
 R = universal gas constant (ML²/T²mole^oK), and
 T = temperature (^oK).

Because the elevation head is of small magnitude compared to the pressure head in studies involving the induced flow of soil gas (Baehr, et al., 1989), elevation head can be ignored in the formulation of head, so the solution of the integral (7) becomes:

$$\phi = \frac{RT}{Mw \cdot g} \ln \frac{P}{P_0} \dots\dots\dots (9)$$

Substitution of equation (9) into equation (6) yields:

$$\mathbf{q} = - \frac{P \cdot Mw \cdot g}{RT \mu} \mathbf{k} \nabla \frac{RT}{Mw \cdot g} \ln \frac{P}{P_0} \dots\dots\dots (10)$$

Within the subsurface, it is a reasonable assumption that the system is isothermal. In addition, the vapor molecular weight is not likely to vary significantly, with contaminant vapor concentrations below about ten percent. If P_0 (the soil gas reference pressure) is defined to equal to one atmosphere, then equation (10) reduces to:

$$\mathbf{q} = - \frac{\mathbf{k}}{\mu} P \nabla \ln(P) \dots\dots\dots (11)$$

And since $\nabla \ln(P)$ is equal to $\frac{1}{P} \nabla P$, then

$$\mathbf{q} = - \frac{\mathbf{k}}{m} \nabla P \dots\dots\dots (12)$$

Substitution of (12) into (5) gives the transient soil gas flow equation:

$$\nabla \cdot \left[\frac{P \cdot Mw \cdot \mathbf{k}}{RT \mu} \nabla P \right] = \frac{\partial \left[\frac{\varepsilon \cdot P \cdot Mw}{RT} \right]}{\partial t} + \frac{F}{dx \cdot dy \cdot dz} \dots\dots\dots (13)$$

The soil gas pressure distribution probably reaches an approximate steady-state configuration within several days (Johnson et al., 1990), while the duration of venting projects lasts many times as long. For this reason, the derivative with respect to time in equation (13) becomes zero, as no changes in soil gas storage take place. Additionally, the molecular weight, temperature, and viscosity of soil gas is constant in the spatial domain of the simulation, so equation (13) reduces to:

$$\nabla(\mathbf{Pk}\nabla P) = \frac{\mu F RT}{dx \cdot dy \cdot dz \cdot Mw} \dots\dots\dots (14)$$

And since $\nabla P^2 = 2P\nabla P$, equation (14) reduces further to:

$$\nabla(\mathbf{k}\nabla P^2) = \frac{2\mu F RT}{dx \cdot dy \cdot dz \cdot Mw} \dots\dots\dots (15)$$

Finite-Difference Formulation

The steady state flow equation embodied in equation (15) is solved using a finite-difference formulation. A two-dimensional differential representation of equation (15), assuming that the third dimension is a fixed length (b) is given by:

$$\frac{\partial}{\partial x} \left[k_x \frac{\partial P^2}{\partial x} \right] + \frac{\partial}{\partial y} \left[k_y \frac{\partial P^2}{\partial y} \right] = \frac{2\mu F RT}{dx \cdot dy \cdot b \cdot Mw} \dots\dots\dots (16)$$

A finite-difference solution of this partial differential equation is accomplished by approximating the space derivatives with defined lengths. In order to do this, an orthogonal grid system is used to discretize the model domain, and the pressures are calculated at the intersection of grid lines. Thus, the model domain is split into prisms which measure Dx by Dy by the thickness, b. Each of these prisms, or blocks, may be given unique physical properties, such as permeability or levels of contamination. By specifying the explicit values in each block, irregular geologic occurrences, such as stratification, can be simulated. In the equations which follow, the notation used to identify these blocks is with the subscripts i and j. For example, when describing a property of the i,j block, the adjacent block in the positive x-direction is referred to with the subscripts i+1,j. Similarly, the adjacent block in the negative y-direction is

given the subscripts $i,j-1$. If only one subscript is listed, then the unlisted subscript is understood to be i or j . The finite-difference form of the steady-state soil gas flow equation, assuming constant node spacing, can be written as:

$$\frac{k_{x(i+1/2)} \left(\frac{P_{i+1}^2 - P_i^2}{\Delta x} \right) - k_{x(i-1/2)} \left(\frac{P_i^2 - P_{i-1}^2}{\Delta x} \right)}{\Delta x} + \frac{k_{y(j+1/2)} \left(\frac{P_{j+1}^2 - P_j^2}{\Delta y} \right) - k_{y(j-1/2)} \left(\frac{P_j^2 - P_{j-1}^2}{\Delta y} \right)}{\Delta y}$$

$$= \frac{2\mu F RT}{\Delta x \cdot \Delta y \cdot b \cdot Mw} \dots\dots\dots (17)$$

Algebraic manipulation yields an equation in terms of the square of the pressure in the i,j node:

$$P_{i,j}^2 = \frac{(\Delta y)^2 (k_{x(i+1/2)} P_{i+1}^2 + k_{x(i-1/2)} P_{i-1}^2) + (\Delta x)^2 (k_{y(j+1/2)} P_{j+1}^2 + k_{y(j-1/2)} P_{j-1}^2) - \frac{2\mu F RT \Delta x \Delta y}{Mw \cdot b}}{(\Delta y)^2 (k_{x(i+1/2)} + k_{x(i-1/2)}) + (\Delta x)^2 (k_{y(j+1/2)} + k_{y(j-1/2)})}$$

(18)

The last term in the numerator represents the mass loss or gain by a cell, including pumpage and/or leakage from constant pressure sources. The mass flux term can incorporate a more usable pumping volume flux by realizing that the mass flux is equal to the volume flux multiplied by the gas density, as shown in the first term on the right side of the expanded mass flux term:

$$F = \frac{(Q_{i,j} \cdot P_{ATM} \cdot Mw)}{RT} + \frac{kz \cdot \Delta x \Delta y}{m \cdot z} (P_{ATM} - P_{i,j}) \frac{(Mw \cdot P_{i,j})}{RT} \dots\dots\dots (19)$$

where,

$Q_{i,j}$ = Extraction or injection volumetric pumping rate, measured at standard temperature and pressure (L^3/T),

P_{ATM} = atmospheric pressure (M/LT^2)

k_z = permeability of confining layer in the third dimension (L^2)

z = thickness of confining layer in the third dimension. (L)

The last term in the mass flux term expanded above represents leakage from an atmospheric source, as might be expected during forced venting from shallow soils beneath bare ground surfaces.

The permeability of a porous medium to a particular fluid is a function of the relative saturation of that fluid. For a given air pressure gradient, a greater air discharge would be expected through a dry soil than through a nearly water saturated soil. Because the volumes of liquid contaminant and soil moisture in the pore space are changing with time during a simulation, an expression must be found which relates the intrinsic permeability of the soil, the evacuated pore fraction, the total porosity, and the resultant air permeability. Several formulations of this type are documented by Brooks and Corey (1966), and Parker et al. (1987). The simplest relationship to implement is a modification of the Brooks-Corey relationship, described by Falta et al. (1989) in which:

$$k = k^*(\epsilon/v)^3 \dots\dots\dots (20)$$

where k^* is the intrinsic permeability of the soil, and v is the total porosity of the porous media. With this relationship, the permeability distribution (and the soil gas flow field) can be recalculated during the simulation to reflect the ongoing depletion of pore fluids in contaminated areas.

The finite difference approximation relies on the calculation of the average directional permeability between nodes. For example, $k_{x(i+1/2)}$ represents the

permeability in the x-direction between the i,j and the i+1,j nodes. Because the half-step permeability is used to calculate the vector flow directly between the nodes, it is appropriate to use the harmonic mean of the two permeabilities. In the model presented in this thesis, the Δx and Δy are constant throughout the model (although Δx does not have to equal Δy). The harmonic mean of the permeabilities in the x-direction are calculated thus:

$$k_{x(i+1/2)} = \frac{k_{xi} \cdot k_{xi+1}}{k_{xi} + k_{xi+1}} \dots\dots\dots (21)$$

The half-step permeabilities in the y-direction are similarly calculated. These half-step permeabilities are also used in the determination of inter-block soil gas discharges for use in the transport equation (described later in this report). The finite-difference form of equation (12) is given by:

$$q_{x(i+1/2)} = \frac{k_{x(i+1/2)} (P_i - P_{i+1})}{\mu \Delta x} \dots\dots\dots (22)$$

Phase Equilibrium

If the individual soil grains within the vadose zone are covered with at least a mono-layer of water, then chemical species will partition directly between the water phase (dissolved), and two other phases: the vapor phase, and the sorbed phase. If a sufficient quantity of contaminant is present, then these three phases will be simultaneously saturated, and a fourth, separate phase will be present. The exception to this rule would be a fluid which is perfectly miscible with water; in such a case the three-phase formulation is valid at all concentrations.

An expression which describes the total molar concentration of a chemical compound in the soil as the sum of the molar concentrations in the four phases is given by Johnson et al. (1990) as:

$$M_{cn} = \left[\frac{\varepsilon \cdot z_n \cdot P}{R \cdot T} + x_n \cdot M_c^{HC} + y_n \cdot M_C^{H_2O} + \frac{y_n \cdot K_{dn} \cdot \rho_{soil} \cdot \text{delwater}}{M_w^{H_2O}} \right] \dots\dots\dots (23)$$

where,

- M_{cn} = total molar concentration of the nth compound in soil (mole/L³),
- ε = air-filled void fraction (dimensionless),
- z_n = mole fraction of compound n in the vapor phase (M/M),
- P = soil gas pressure (ATM),
- R = universal gas constant (ML/T²mole^oK),
- T = temperature (°K),
- x_n = mole fraction in non-aqueous phase (dimensionless),
- M_c^{HC} = molar concentration of non-aqueous phase in soil (mole/L³),
- y_n = mole fraction of compound n in soil moisture (dimensionless),
- $M_C^{H_2O}$ = molar concentration of water in soil (mole/L³),
- K_{dn} = distribution coefficient of compound n (M/M),
- ρ_{soil} = soil density (M/L³),
- $M_w^{H_2O}$ = molecular weight of water (18 grams/mole),
- $\text{delwater} = 1$ when soil moisture is present, and
- $\text{delwater} = 0$ when soil moisture is not present.

The four terms on the right side of equation (23) represent the contribution to the total soil contamination of the vapor phase, the non-aqueous phase, the dissolved

soil moisture phase, and the solid-adsorbed phase, respectively. For equation (23) to be solvable, many of the terms must be consolidated into functions of one variable. Henry's law, Raoult's law, and the ideal gas law give the following relationships among the phases:

$$z_n \cdot P = x_n \cdot VP_n = \alpha_n \cdot y_n \cdot VP_n = C_n RT \dots\dots\dots (24)$$

where,

VP_n = pure component vapor pressure of compound n (ATM),

α_n = activity coefficient of compound n in water (dimensionless), and

C_n = molar concentration of compound n in vapor (mole/L³).

Equation (24) implies that the behavior of the vapor is described by an ideal gas, that the non-aqueous phase is an ideal mixture, and that the dissolved phase is non-ideal. Substitution of the phase relationships embodied in equation (24) into the mole balance equation (23), yields a mole balance in terms of just one of the phases. Because this model will be concerned with the movement of moles of each compound in the vapor phase, the mole balance is solved in terms of the soil vapor molar concentration:

$$Mc_n = C_n \left[\varepsilon + \frac{Mc^{HC} \cdot RT}{VP_n} + \frac{Mc^{H2O} \cdot RT}{\alpha_n \cdot VP_n} + \frac{Kd_n \cdot \rho_{soil} \cdot RT \cdot \text{delwater}}{\alpha_n \cdot VP_n \cdot Mw^{H2O}} \right] \dots\dots\dots (25)$$

The solution to this equation is trivial in the event that only three phases are present. When a separate phase is present, then an additional constraint arises; that the sum of the mole fractions of the non-aqueous phase liquid is equal to unity:

$$\sum_{i=1}^n x_i = 1 \dots\dots\dots (26)$$

The solution of equations (25) and (26) give an equilibrium-based mole balance of any number of contaminants with various chemical properties.

Solution of Phase Equilibria

Within the model, a solution scheme is employed to re-calculate the phase equilibria at discrete time steps. Between the time steps, moles of each compound have been moved into, and out of, finite-difference cells within the model domain. As a result, the vapor composition and concentration will change, and will be in disequilibrium with the remaining, stagnant phases. The equilibrium subroutine moves moles of each compound into or out of the three non-moving phases to come back to equilibrium with the vapor phase. This is accomplished by using the following procedure, outlined in Johnson et al., (1990).

First, the presence of a fourth phase is checked by determining whether the first three phases are over-saturated. This is done by checking if the product $\alpha_n \cdot y_n$ is less than 1.0 for all compounds. In other notation,

$$\alpha_n \cdot y_n \stackrel{?}{=} \frac{M_{c_n}}{\left[\frac{\epsilon \cdot VP_n}{RT} + \frac{M_{c_n}^{H_2O}}{\alpha_n} + \frac{K_{d_n} \cdot \rho_{soil} \cdot \rho_{water}}{\alpha_n \cdot M_{W}^{H_2O}} \right]} \dots\dots\dots (27)$$

If the right side of the expression in equation (27) is less than 1.0 for each of the n compounds, then there is not a non-aqueous phase present, and the soil gas concentration is directly solvable, by equation (24), from the expression $\alpha_n \cdot y_n$. If, on the other hand, the total number of moles of any one compound in soil (M_{c_n}) is greater than the moles of that compound that can be held in the other three phases (when the compound is at its solubility limit, $\alpha_n \cdot y_n = 1$), then a non-aqueous phase is present, and all compounds will partition into that phase.

The resultant calculation of the molar phase distribution is accomplished by realizing that equation (25) reduces to the following form for each compound:

$$Mc_n = \frac{C_n \cdot RT}{VP_n} [\text{Constants} + Mc^{HC}] \dots\dots\dots (28)$$

The set of equations for all compounds yields n equations and (n+1) unknowns. The constraint that the sum of all $\left[\frac{C_n \cdot RT}{VP_n} \right]$ is equal to unity makes the system solvable, through an iterative scheme in which:

1. Given the molar concentration of free-liquid in soil (Mc^{HC}) from the previous time step,
2. The vapor concentration of every compound (C_n) is calculated,
3. The sum of all $\left[\frac{C_n \cdot RT}{VP_n} \right]$ is calculated by Equation (28),
4. The value of Mc^{HC} is multiplied by the inverse of the sum of all $\left[\frac{C_n \cdot RT}{VP_n} \right]$, and the program returns to step 2 until convergence occurs.

Solution of Necessary Chemical Data

The previous section showed the need for several chemical properties of the simulated compounds. Among these are activity and distribution coefficients, and pure component vapor pressures. The following chemical relationships are

commonly known in the field of chemistry and are succinctly outlined in Johnson et al., 1990.

To arrive at values of activity coefficients, it is observed that the product $a_n \cdot y_n = 1$ at the solubility limit of a pure compound. For slightly soluble compounds, such as petroleum hydrocarbons and halogenated solvents, the activity coefficient can be calculated as:

$$\alpha_n = \frac{M_{wH_2O}}{\frac{M_{wn}}{S_n}} \dots\dots\dots (29)$$

where

M_{wn} = Molecular weight of compound n (M/mole)

S_n = Pure component solubility (M/L³)

If the compound is a gas at the temperature and atmospheric pressure, then the activity is defined as the activity calculated above times the quantity (1 ATM/VP_n).

Vapor pressures at the temperature of interest are calculated using the Clausius-Clapyron equation. This equation assumes that the logarithm of the vapor pressure varies linearly with the logarithm of the temperature. A linear interpolation is used between each compound's boiling point (where the vapor pressure is 1 ATM), and the vapor pressure at a fixed temperature. In this program, the vapor pressures are entered for a reference temperature of 20 degrees centigrade (°C). The resultant temperature dependant, pure component vapor pressure is given by:

$$VP_n = VP_{20} \cdot \exp \left[\frac{T_b \cdot 20^\circ}{(T_b - 20^\circ)} \left[\frac{1}{T} - \frac{1}{20^\circ} \right] \ln \left[\frac{VP_{20}}{1 \text{ ATM}} \right] \right] \dots\dots\dots (30)$$

where

VP_{20} = vapor pressure of compound n at 20° (ATM)

T_b = boiling point of compound n (°C)

T = temperature of interest (°C)

Estimation of the distribution coefficients (K_d) of the compounds is problematic for several reasons. Measurement of the distribution properties of many of the compounds in gasoline is not documented, and only estimations based on molecular structure are available (Johnson et al., 1990). Additionally, the movement of dissolved compounds onto solid particles is generally not linear with respect to concentration or the time derivative of concentration (sorption versus de-sorption). Further studies indicate that the distribution coefficient, in addition to being non-linear, is kinetically controlled, so that the time of non-equilibrium between the phases should be factored into calculating the molar concentrations in either phase.

Commonly, in groundwater contaminant transport experiments and models (Reynolds et al., 1982; Konikow and Bredehoeft, 1978), the distribution coefficient with respect to dissolved and sorbed species is assumed to be linear. Further refinements of the models (Goode and Konikow, 1989) have incorporated non-linear sorption, although the possibility of non-reversible (sorption versus de-sorption) reaction is not addressed. The more recent models allow the Langmuir and Freundlich non-linear sorption isotherms, which simulate much stronger sorption at low concentrations, and near-linear values of K_d at high concentrations. Using the non-linear isotherms within a transport code is more computationally difficult, due to the need to recalculate the distribution coefficient for each compound between every time step. Since K_d data for many compounds are unavailable, let alone non-linear equation coefficients, this model will use K_d's determined from the Karickhoff (1981) equation:

$$K_d = 0.63 \cdot K_{ow} \cdot F_{oc} \dots \dots \dots (31)$$

where,

K_{ow} = the octanol/water distribution coefficient (M/M), and

F_{oc} = the fraction of organic carbon in soil (dimensionless).

The use of the Karickhoff equation allows the model user to isolate the hydrophobic properties of the compounds and the sorption capacity of the porous media. Also, a larger database of octanol/water partition coefficients is available for organic compounds.

Transport of Vapor-Phase Compounds

Because the natural dispersion of the chemical species in the vapor phase is dominated by diffusion, and the calculation of the center of mass positions of the contaminants under forced venting is not affected by hydrodynamic dispersion, the dispersion will not be calculated as velocity-dependant. Therefore, the two-dimensional differential formulation of the transport equation can be expressed as:

$$\frac{\partial M_{cn}}{\partial t} = \frac{\partial \left[D_x \frac{\partial C_n}{\partial x} \right]}{\partial x} - \frac{\partial C_n \cdot q_x}{\partial x} + \frac{\partial \left[D_y \frac{\partial C_n}{\partial y} \right]}{\partial y} - \frac{\partial C_n \cdot q_y}{\partial y} - F_n \dots \dots \dots (32)$$

where

q_x, q_y = directional vapor discharges (L/T), and

F_n = the source/sink molar flux of compound n (mole/L³T).

As discussed previously, the dispersion coefficients (D_x and D_y) are functions of the free-air diffusion coefficient. The air-filled fraction of the porous media will also affect the diffusion of compounds. An expression relating the free-air diffusion and the diffusion characteristic of packed spheres (Millington and Quirk, 1961) is:

$$D_x = D_0 \frac{\epsilon^{10/3}}{v^2} \dots\dots\dots (33)$$

where,

D_x = directional diffusion coefficient (L^2/T), and

D_0 = free-air diffusion coefficient (L^2/T),

The chemical molar source/sink term incorporates the loss of vapor moles of each compound by pumping, or the injection or leakage of a known molar concentration (generally zero or atmospheric) into a model cell. The expanded chemical molar source/sink term takes the following form:

$$F_n = \frac{(Q_{i,j} C_p)}{\Delta x \Delta y b} + \frac{q_z C_l}{b} \dots\dots\dots (34)$$

where,

C_p = $C_{n,i,j}$ if $Q_{i,j}$ is negative,

C_p = the injection concentration (C_{inj}) if $Q_{i,j}$ is positive,

C_l = $C_{n,i,j}$ if q_z is negative, and

C_l = C_{inj} if q_z is positive.

An explicit finite-difference solution of the transport equation is given by:

$$\begin{aligned} \frac{Mcn^{k+1} - Mcn^k}{\Delta t} = & \frac{q_{x(i-1/2)} (C_{n,i,j} + C_{n,i-1,j}) - q_{x(i+1/2)} (C_{n,i+1,j} + C_{n,i,j})}{2\Delta x} + \\ & \frac{q_{y(j-1/2)} (C_{n,i,j} + C_{n,i,j-1}) - q_{y(j+1/2)} (C_{n,i,j+1} + C_{n,i,j})}{2\Delta y} + \\ & \frac{D_{x(i+1/2)} \left(\frac{(C_{n,i+1,j} - C_{n,i,j})}{\Delta x} \right) - D_{x(i-1/2)} \left(\frac{(C_{n,i,j} - C_{n,i-1,j})}{\Delta x} \right)}{\Delta x} + \\ & \frac{D_{y(j+1/2)} \left(\frac{(C_{n,i,j+1} - C_{n,i,j})}{\Delta y} \right) - D_{y(j-1/2)} \left(\frac{(C_{n,i,j} - C_{n,i,j-1})}{\Delta y} \right)}{\Delta y} - F_n \dots\dots (35) \end{aligned}$$

where the superscripts k and $k+1$ are time step indices, and the subscripts n , i , and j indicate, respectively, the compound number, and the nodal positions in the x and y -directions. Rearrangement of terms gives the solution of the total molar concentration of compound n in soil at the next $(k+1)$ time step:

$$\begin{aligned}
 M_{Cn}^{k+1} = & \left[\left[\frac{(-D_{x(i+1/2)} - D_{x(i-1/2)})}{\Delta x^2} + \frac{(-D_{y(j+1/2)} - D_{y(j-1/2)})}{\Delta y^2} + \frac{(q_{x(i-1/2)} - q_{x(i+1/2)})}{2\Delta x} + \right. \right. \\
 & \left. \left. \frac{(q_{y(j-1/2)} - q_{y(j+1/2)})}{2\Delta y} \right] \cdot C_{n,i,j} + \left[\frac{D_{x(i+1/2)}}{\Delta x^2} - \frac{q_{x(i+1/2)}}{2\Delta x} \right] \cdot C_{n,i+1,j} + \right. \\
 & \left. \left[\frac{D_{x(i-1/2)}}{\Delta x^2} + \frac{q_{x(i-1/2)}}{2\Delta x} \right] \cdot C_{n,i-1,j} + \left[\frac{D_{y(j+1/2)}}{\Delta y^2} - \frac{q_{y(j+1/2)}}{2\Delta y} \right] \cdot C_{n,i,j+1} + \right. \\
 & \left. \left[\frac{D_{y(j-1/2)}}{\Delta y^2} + \frac{q_{y(j-1/2)}}{2\Delta y} \right] \cdot C_{n,i,j-1} - F_n \right] \cdot \Delta t + M_{Cn}^k \dots\dots\dots(36)
 \end{aligned}$$

To simplify, let

$$A = \left[\frac{D_{x(i+1/2)}}{\Delta x^2} - \frac{q_{x(i+1/2)}}{2\Delta x} \right], \dots\dots\dots(37a)$$

$$B = \left[\frac{D_{x(i-1/2)}}{\Delta x^2} + \frac{q_{x(i-1/2)}}{2\Delta x} \right], \dots\dots\dots(37b)$$

$$C = \left[\frac{D_{y(j+1/2)}}{\Delta y^2} - \frac{q_{y(j+1/2)}}{2\Delta y} \right], \text{ and} \dots\dots\dots(37c)$$

$$D = \left[\frac{D_{y(j-1/2)}}{\Delta y^2} + \frac{q_{y(j-1/2)}}{2\Delta y} \right] \dots\dots\dots(37d)$$

Then the finite difference formulation of the vapor transport and resultant soil molar concentration equation is expressed as:

$$\begin{aligned}
 \mathbf{M}\mathbf{c}_n^{k+1} = \Delta t \left[\right. & \left[A + B + C + D - \frac{2D_{x(i+1/2)}}{\Delta x^2} - \frac{2D_{x(i-1/2)}}{\Delta x^2} - \frac{2D_{y(j+1/2)}}{\Delta y^2} - \frac{2D_{y(j-1/2)}}{\Delta y^2} \right] \mathbf{C}_{n,i,j} + A\mathbf{C}_{n,i+1,j} \\
 & \left. + B\mathbf{C}_{n,i-1,j} + C\mathbf{C}_{n,i,j+1} + D\mathbf{C}_{n,i,j-1} - F_n \right] \mathbf{M}\mathbf{c}_n^k \dots\dots\dots (38)
 \end{aligned}$$

CHAPTER III

SOLUTION OF EQUATIONS

Model Structure

The basis of the finite-difference solution is the creation of an orthogonal grid. This grid represents a physical slice of soil material which is subdivided into imaginary elements which may have unique physical and chemical properties. This grid can be configured to represent a horizontal (plan-view) layer of porous material, or a vertical cross-section of many layers of different soil types. Within the grid, a certain number of elements must have fixed values of pressure, concentration, or flux to enable a solution. These elements, or cells, are termed "inactive" due to the fact that the properties do not change and are not calculated. Specifically, because changing values (such as vapor concentration) within one cell are dependant on values in cells on all four sides, the "active" region of the model must be surrounded by inactive cells. A schematic representation of a plan view model is shown in Figure1.

For the purposes of this model, the outer 2 columns and rows are always inactive, while all others are active. In this model, the number of elements is limited to a maximum of 20 rows by 20 columns, with the exterior 2 rows and columns being inactive. The maximum number of rows and columns in the computer program can easily be increased, based on the amount of memory addressable by the host computer and FORTRAN compiler. A listing of the source FORTRAN code is given in Appendix A. Within this model, the size of the elements are equal; however,

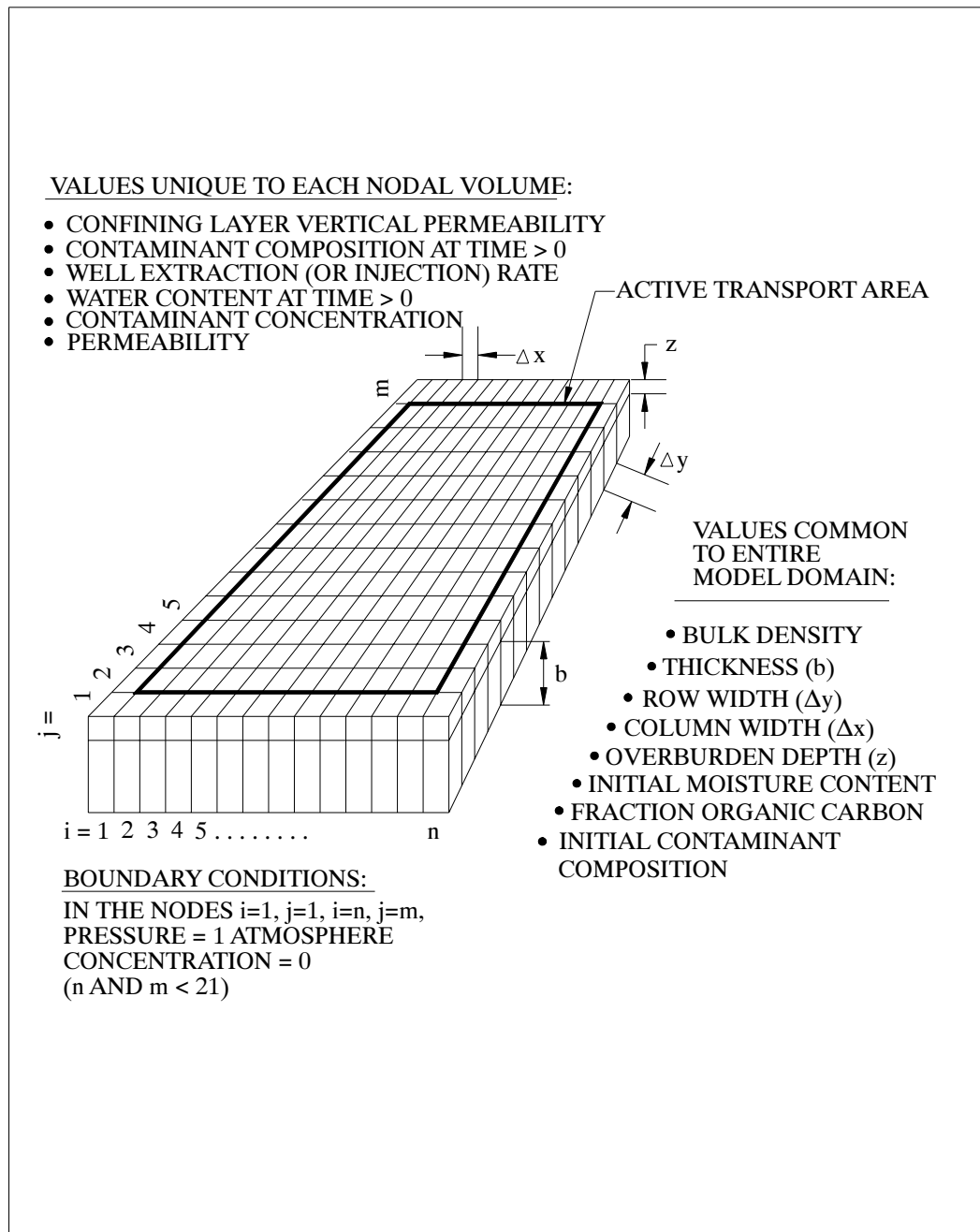


Figure 1. Schematic representation of model structure.

the row height (Δx) does not have to equal the column width (Δy).

In the third dimension, which would represent the vertical direction in a plan-view simulation, the elements have a user-input thickness. This thickness (b) is constant throughout the model. The model allows leakage of gasses from the third dimension into, or out of, the elements, as might be expected during near-surface vacuum extraction remedial schemes. The model requires the specification of the permeability and thickness of a confining layer which separates the model elements from the atmosphere (Figure 1). Leakage from the third dimension can, of course, be set to zero.

Calculation of Pressure Distribution

The solution to equation (18) is facilitated by a successive over-relaxation (SOR) iterative routine. In this technique, the pressure in all cells begins as atmospheric. The pressure in each cell is then recalculated, based on the pressure in the four adjacent cells, the nodal well extraction or injection rate, and the leakage rate. After the first pass through the array of elements, some of the cell pressure values will have changed, and will, on the next pass through the array, have an effect on the adjacent cells. Each pass, or iteration, brings the pressure distribution of the model as a whole closer to the "real" solution. Eventually, the model will achieve closure on the solution, when each additional iteration will not change the pressure values significantly. The SOR technique hastens this process by calculating the change in pressure in a given cell during each iteration and increases that change by a factor between 1 and 2. This acceleration factor (ω) is specified by the model user, and will shorten the run-time as a function of the geometry of the model.

The user also specifies the closure criteria for calculating the pressure distribution. When no cell within the model changes more than the specified percentage of the pressure at the previous iteration step, then the model is considered to have reached closure, and iteration is stopped. The number of iterations needed to reach closure is a complex function of ω . As ω tends toward 2.0, the solution will over-accelerate and oscillate, until the solution becomes unstable when ω is greater than or equal to 2. A choice of ω between 1.3 and 1.7 will generally provide an adequately low number of iterations required for closure. If 500 iterations are reached, then a solution is probably not possible (or representative of real-world conditions), and the simulation is terminated. An example of a nonrepresentative problem may be trying to simulate the extraction of large volumes of soil gas from soil with very low permeabilities, which may (mathematically) produce negative pressures in the simulation.

As the model simulates the volumetric changes of separate phase contaminants and water within the active cells, the permeability of the cells will be changing as well. The model must recalculate the flow field to reflect these changes; however, since the calculation is time consuming, the flow field is only recalculated when 10 percent or more of the active cells' permeability has changed by 25 percent or more.

Movement of Compounds

In a strict finite-difference formulation of the transport equation (35), the concentration of soil gas moving into or out of a cell is taken as the average of the concentration within the cell and the concentration within the adjacent cell. In the notation used thusfar, this is represented by:

$$C_{n_{i\pm 1/2}} = \frac{(C_{n_i} + C_{n_{i\pm 1}})}{2} \dots\dots\dots (39)$$

This formulation can cause problems with oscillation and the creation of either negative concentrations or mass balance errors. Such an occurrence is illustrated in the three active cells shown in Figure 2. The configuration shown in Figure 2 represents three cells that might be found on the edge of a contaminant plume. The flow of soil gas is toward the cell with the higher vapor concentration (for the sake of argument, 500 units), while the central cell and its neighbor on the other side are devoid of contamination. If the soil gas discharge into and out of the cell are equal (call this value q), then the following expression for the molar change in the central cell will give a negative concentration in the central cell:

$$\frac{\Delta M c_n}{\Delta t} = \frac{q(0 - 0)}{2\Delta x} - \frac{q(500 - 0)}{2\Delta x} = \frac{-250q}{\Delta x}.$$

To alleviate this problem, the concentrations used in the calculation of the molar fluxes in the model are a function of the sign (or direction) of the soil gas discharge. If the discharge is into the cell of interest, then the vapor concentration of the "donor" cell is used in the flux calculation. If, however, the flow is out of the cell of interest, then the concentration within that cell is used in the same calculation. The example illustrated above would then become:

$$\frac{\Delta M c_n}{\Delta t} = \frac{q(0)}{\Delta x} - \frac{q(0)}{\Delta x} = 0$$

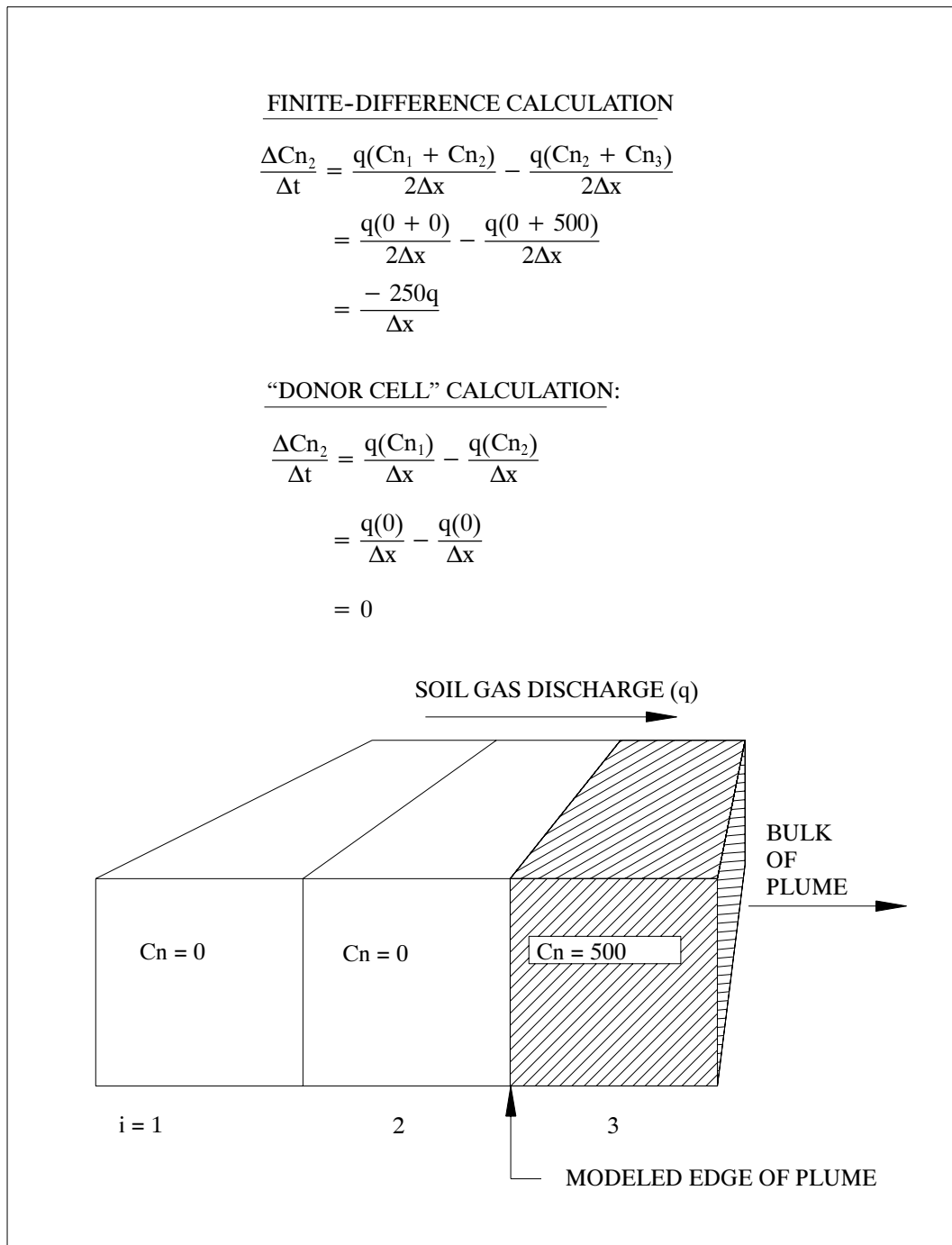


Figure 2. Elimination of negative concentrations by using a “donor cell” calculation of soil gas movement.

Time Step Size Determination

The user of the model specifies length of time in the simulation, as well as the minimum number of time steps to be used within that time period. This time step size is very likely to be much larger than necessary for solution stability and reasonable accuracy of the finite time difference. For these reasons, the model calculates an internal time step size to maintain stability and low mass balance errors. Three different methods are used to calculate the time step size, based on the diffusion rate, the pumping term, and the maximum soil gas velocity.

The time step size that will allow stability of the explicit solution of the dispersive flux is reported by Konikow and Bredehoeft, 1978 as:

$$\Delta t \leq \frac{1}{\left[\frac{D_x}{\Delta x^2} + \frac{D_y}{\Delta y^2} \right]} \dots\dots\dots (40)$$

where D_x and D_y are the maximum values observed within the entire model domain. This time step size will generally only become the limiting size when the grid dimensions are very small, as might be expected in shallow diffusion studies.

The second method of time step determination is based on the vapor removal by pumping, and is not employed for stability's sake. Rather, this time step size is calculated to improve the accuracy of the chemical mass balance. Because the composition of the soil gas will change with each incremental removal of a certain volume of vapor, it is more accurate to recalculate the composition after many, smaller withdrawals; however, this accuracy is achieved at the expense of computational time. The time step criterion can be calculated several ways, all of

which depend on the ratio of moles in the vapor phase being withdrawn and the moles in the residual phases.

If, for example, the mass of a single compound in the dissolved and separate phases within a pumped cell is many orders-of-magnitude greater than in the vapor phase, then a longer time step can be utilized while maintaining an accurate mass balance for that compound. The converse is easily imagined, when an extended pumping period extracts more moles of an extremely volatile compound in a mixture than are initially present in all of the phases.

For the purposes of this model, the time step size is calculated at each pumped cell according to the equation:

$$\Delta t = \frac{\text{-wellcrit} \cdot Q_{(i,j)} \cdot \sum M_{cn}}{\sum C_{n(i,j)}} \dots\dots\dots (41)$$

where,

wellcrit = a user-input criterion multiplier (dimensionless),

$Q_{(i,j)}$ = Volumetric soil gas extraction rate at the i,j node (L^3/T),

$\sum M_{cn}$ = total contaminant moles in the model domain, and

$\sum C_{n(i,j)}$ = total contaminant vapor moles in the i,j node.

By comparing the sums of all compounds in the above equation, the time step size isn't made too small by one or more extremely volatile compounds that may comprise only a tiny fraction of the contaminant mass. In addition, the vapor concentration in each pumped node is compared to the contaminant mass as a whole, to avoid similar effects of pumping a node exterior to the contaminant mass, where vapors are drawn toward the node without the large mass associated with the stagnant phases within that node. If the vapor to total soil mass ratio for such a node were used in the time step size calculation, an inordinately small size would be calculated.

The final measure of the maximum allowable time step size is a function of the largest vapor discharges (hence velocities). In a manner similar to that used in the MOC code (Konikow and Bredehoeft, 1978), the time step is held to a size such that a parcel of soil gas may not traverse a distance greater than the size of one cell. In doing so, the program prevents the over-accumulation (or depletion) of compounds in a cell in any one time step, without transferring compounds to the next cell in a timely fashion. This time step size is calculated thus:

$$Dt = \frac{\text{celldis}}{\left[\frac{q_i}{\varepsilon \cdot \Delta x_i} \right]} \dots\dots\dots (42)$$

where,

celldis = user-defined fraction of cell travel distance allowed (L/L),

q_i = maximum velocity vector within the entire model domain (L/T),

and

Δx_i = distance in the direction of maximum velocity (L).

The smallest of the three time steps determined by equations (40) through (42) is used in the chemical transport solution. After the movement of the compounds, the time step size is calculated again, until the simulation is completed.

Mass Balance Calculation

The mass of each contaminant compound remaining within the model domain has the potential of changing with every time step. The mass can be removed from any number of cells by two mechanisms: by induced pumping, or by the simulation of zero concentration cells. In the case of the zero concentration cells, which may simulate the ground surface in a diffusion-only simulation, mass moves into these

cells under the force of molecular diffusion. The mass of each compound in these cells is stored in memory, and subsequently removed before the next time step, so that diffusion will once again drive compounds toward any zero concentration boundaries.

The mass balance within the program is a measure of the accuracy of the simulation. It is a comparison, for each compound, of the mass removed, the mass remaining, and the initial mass within the model domain. The mass balance is calculated in two ways, to avoid misleading values of error due to either very small or very large mass withdrawals. The mass balance equations have been taken from Konikow and Bredehoeft, 1978:

$$\text{Error1} = \frac{100(M_{\text{out}} - \Delta M_{\text{stor}})}{(M_{\text{init}} - M_{\text{out}})} \dots\dots\dots (43)$$

$$\text{Error2} = \frac{100(M_{\text{out}} - \Delta M_{\text{stor}})}{0.5(M_{\text{out}} + \Delta M_{\text{stor}})} \dots\dots\dots (44)$$

where,

M_{out} = mass removed from the model domain by pumping or diffusion,

ΔM_{stor} = change in mass stored within the model domain, and

M_{init} = initial mass stored within the model.

These equations are applied to each of the compounds in the simulation and to the sum of all contaminant compounds, for two measures of simulation accuracy. The numerator in both error terms is a comparison of the difference in removed mass to the change in mass stored, which should be equal. The first error term (Error1) is more sensitive after the removal of large contaminant masses from the model domain, while the second error term (Error2) is a more stringent indicator at the beginning of model runs.

Data Requirements

In order to obtain the necessary parameters to define a particular simulation, the computer program reads a user-prepared data file. Information contained in this data file include the dimensions of the model, soil physical constants, well locations and discharge rates, convergence criteria, time step size modifiers, the contaminant composition and the physical characteristics of each compound, and arrays of the distribution of permeability, surface leakage, and contaminant concentration. The arrays are structured in a manner similar to the MOC input file (Konikow and Bredehoeft, 1978), where a single value can be substituted for the array to represent a homogeneous distribution. A description of each data element in the required input file is included in Appendix B. A sample input file and the resultant output file from the model is given in Appendix C.

CHAPTER IV

RESULTS OF SIMULATIONS

Model Verification

The model has three basic functions, and the proper operation of each can be independently verified. These functions are the calculation of phase equilibria, the advective movement of compounds, and the diffusive movement of compounds. In order to isolate the phase equilibria calculations, the model was run with a single active node using the same input parameters as were listed in Johnson, et al., 1989. In this simulation, no mass transfer occurs among any of the cells, so the simulations should be identical, with the possible exception of time step size determination. Figure 3 shows the agreement between the two solutions with respect to several compounds within a measured 37 component gasoline mixture listed by Johnson et al. (1990).

Other parameters common to the two simulations included an initial soil gasoline concentration of 20,000 mg/kg within 60,000 kg (40 m³) of soil, a total porosity of 40 percent, a constant moisture content of 10 percent, and an organic carbon fraction of 0.01. The vapor extraction rate used in the simulations was 5 cfm, and the system temperature was held at 60° F.

The advective transport portion of the code is composed of soil gas velocity (flow) and resultant concentration propagation (transport). To check the validity of the flow portion of the of the code, the iterated steady-state pressure distribution

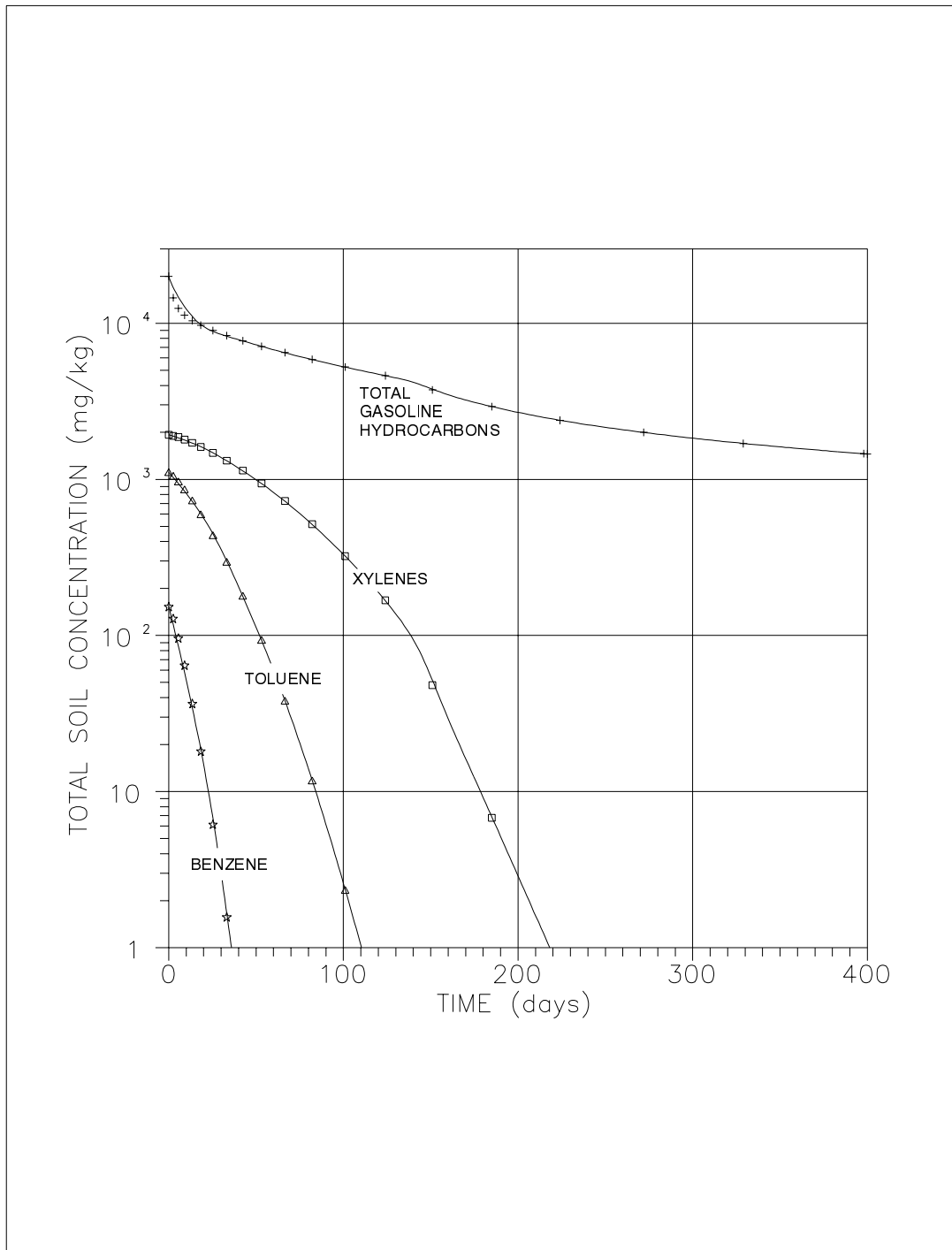


Figure 3. Comparison of venting simulations using Johnson et al. (1990) model (solid lines) and the present work in a non-transport mode (symbols).

can be checked against analytic solutions. Soil gas flows according to Darcy's law (equation 12), so the Thiem equation for conservation of mass within an aquifer can be used for comparison. In the Thiem equation for steady-state radial flow within a fixed-thickness (b) porous media, an equal amount (Q) of fluid moves through concentric rings around an extraction well, or

$$Q = \frac{2\pi r b k}{\mu} \cdot \frac{dP}{dr} \dots\dots\dots (45)$$

Integrating the above equation and assuming that the pressure is unchanged at a given radius ($P = 1$ ATM at r_0), then the measured change in pressure is the following function of the radius from a pumping well:

$$P(r) = \frac{Q\mu}{2\pi b k} \ln \frac{r}{r_0} \dots\dots\dots (46)$$

Figure 4 is a plot of the Thiem equation pressures and the modeled pressures along model axes and within nodes along a 45° angle to the axes. The dual comparison is warranted because of the fact that the Thiem equation assumes a constant radius to no influence, while the model uses a rectangular boundary. The subtle deviations of the model and analytic solutions are due to the irregular boundary and the need to numerically simulate the pumping well as an entire nodal area. As shown by the modeled pressure gradients, the simulation provides suitable values of inter-block soil gas discharge.

To further validate the retarded transport of chemical compounds, the model has been run in a one-dimensional mode (using a single row of active cells) using a chemical concentration low enough to ensure a three-phase system only. By doing this, the vapor concentration is a linear function of the total soil concentration, and retardation (R) can be represented by a constant value (Mendoza and Frind, 1990).

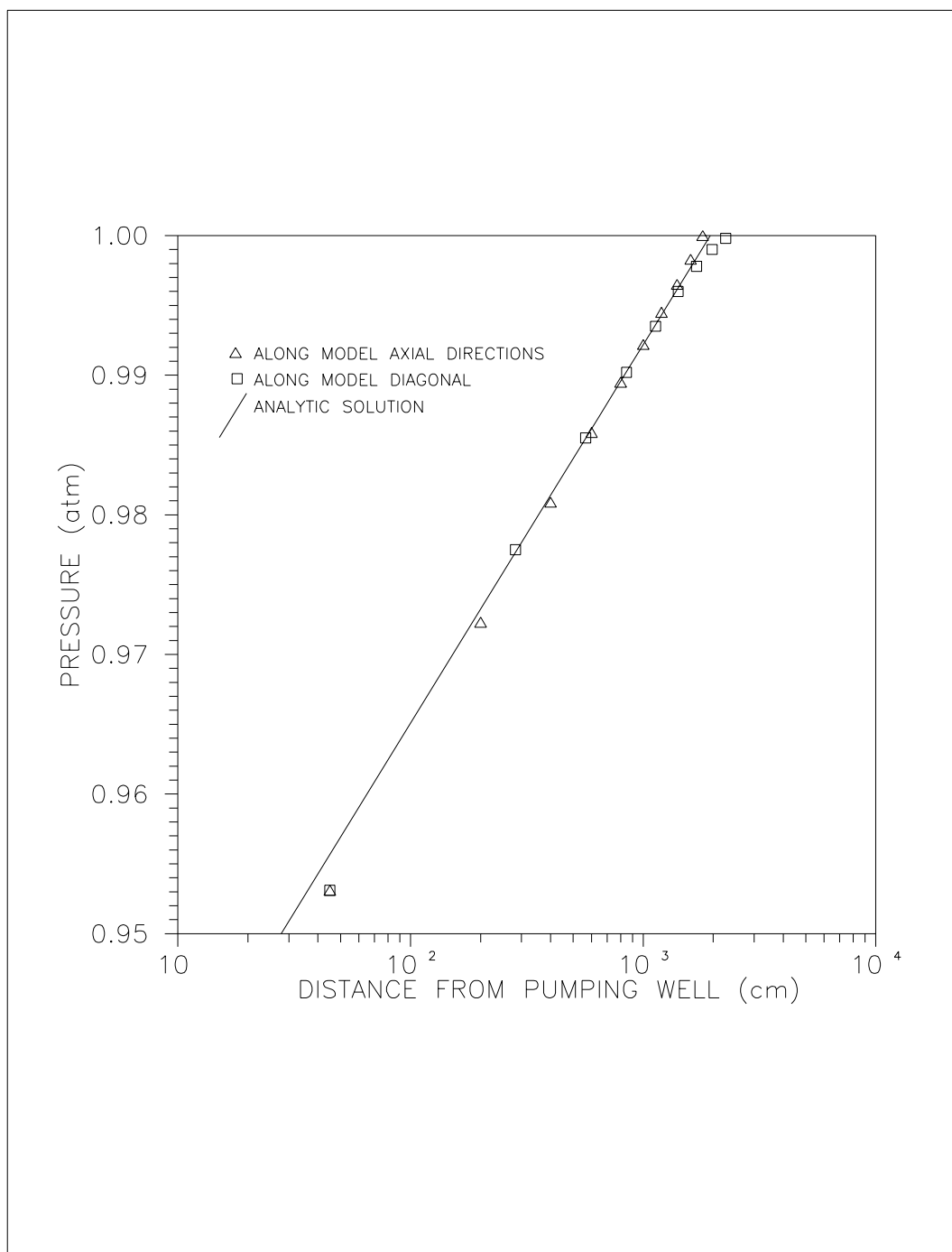


Figure 4. Comparison of modeled pressure distribution (symbols) and the radial analytic solution.

In this way, the value of R is the same at all locations in the simulation, since no separate phase is present in any cell during the entire model run. In order to simulate a constant velocity field, the model required modification allowing the input of a user-defined discharge in one direction.

Figure 5 shows the movement of three gaseous compounds with different solubilities and distribution coefficients. The non-retarded compound has no solubility and a distribution coefficient of zero, while the other two compounds were given solubilities of 1000 and 2000 mg/l, and Kow's of 500 and 1000, respectively. Given a porosity of 0.4, and a soil moisture content of 0.1, these numbers correspond to R values of 3.34 and 1.67. The positions of the center of mass of each of the simulated dispersed contaminant slugs were calculated, and are indicated in Figure 5. The distances travelled by the retarded slugs is within 0.5 percent of the distances predicted by dividing the non-retarded distance by 3.34 and 1.67, thereby validating the functionality of the transport and phase distribution portions of the code.

Hypothetical Remediation Simulations

In order to investigate the utility of the model described within this report, a number of varied physical systems have been simulated. In most cases, the simulations have been constructed to illustrate a shortcoming of an available model or technique. Where possible, the results of both methods are presented for comparison.

Irregular Contaminant Distribution

In non-dimensional, four-phase equilibrium models, it is assumed that the geometry of the contaminant plume will not effect the concentrations or

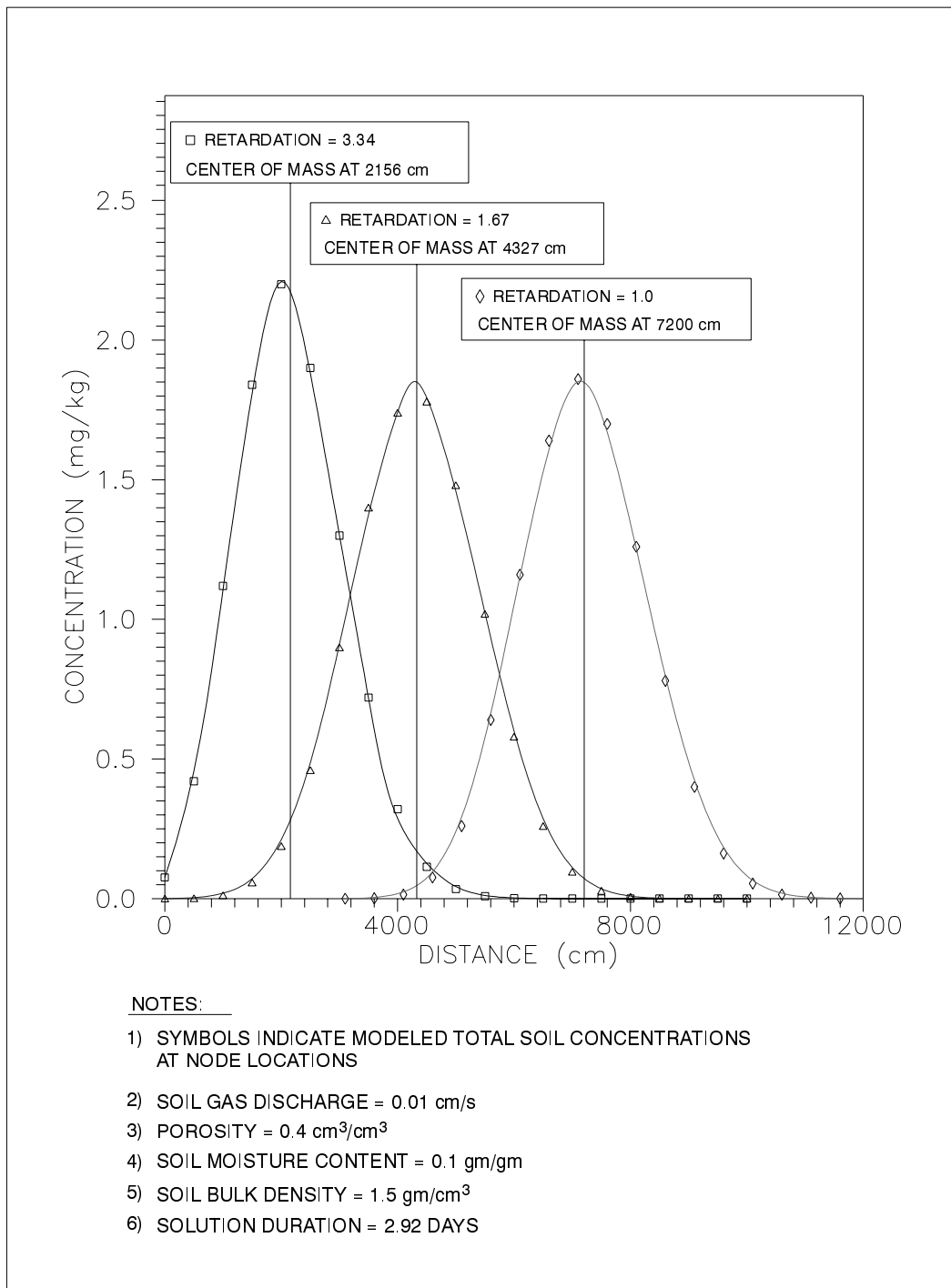


Figure 5. One-dimensional transport of retarded compounds.

composition of extracted soil gas. These models (Johnson, et al., 1990; Marley and Hoag, 1984) assume that a volume of soil has a single level of contamination, and that the soil vapor is in equilibrium with that contaminant mass. A scenario is easily imagined in which varying degrees of contamination are present in different directions around one or more extraction wells. The composition of the extracted vapor will be a function of the relative contributions from these areas, making prediction of clean-up time or optimal placement of extraction wells impractical without accounting for the distribution of the contaminant.

To illustrate such an occurrence, two simplified, hypothetical spills have been simulated in which equal masses of gasoline have been placed into equal, but differently shaped, volumes of soil. Cleanup was simulated with one central venting well, and the flow fields throughout the model domains were identical. The simulations were run with all other parameters held constant. The first solution was for an elongated spill, represented by 10,000 mg/kg gasoline in 3 rows by 10 columns. The second simulation contained 5 rows and 6 columns with the same levels of contamination. This second simulation, because of its near-symmetry, will be close to the solution using the model of Johnson et al., (1990).

The simulated depletion of the total soil mass of toluene, xylenes, and total gasoline compounds in both models is shown in Figure 6. The anticipated effect of nearby clean areas is shown in the slowed cleanup of the elongated spill. If it is desired to predict the time to reach a cleanup level of 90 percent (for an average concentration of 1,000 mg/kg), the difference in the two simulations is roughly 75 percent (130 days versus 225 days). As seen in Figure 6, the time difference for some of the more volatile compounds in the mixture (toluene and xylene) is even greater.

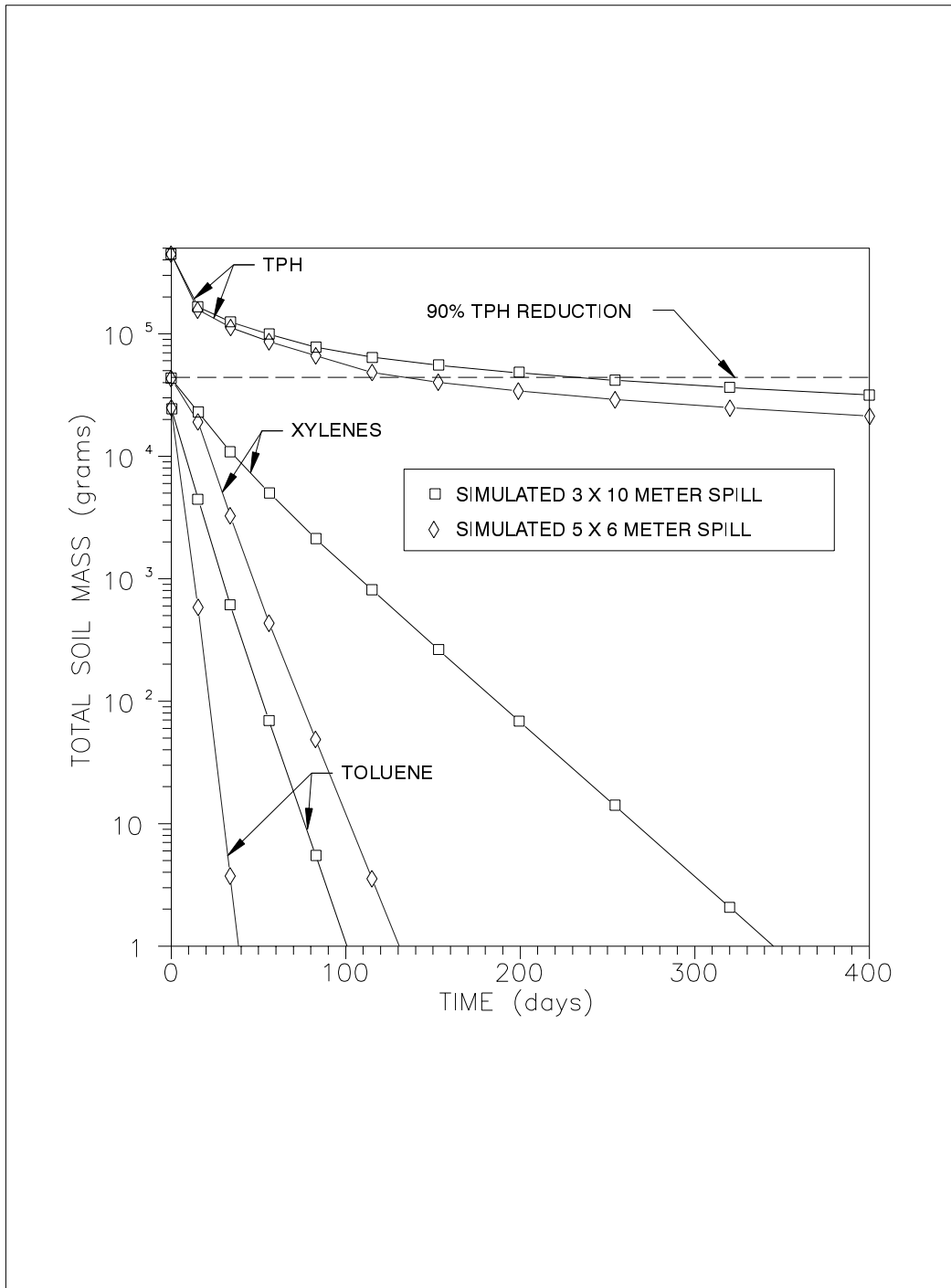


Figure 6. Comparison of remediation time for different plume geometry.

Diffusion-Limited Scenario

A practical problem of particular interest is embodied in the remediation of layered soils. It is relatively straightforward to determine how to vent massive thicknesses of coarse-grained soils, but oftentimes the coarser layers are separated by significant thicknesses of contaminated fine-grained material. This finer material may present itself as a long-term source of contamination because of the inability to create sufficient vapor velocity through such a zone. In clayey soil material, the chemical flux due to artificially induced soil gas velocities is likely to be much less than the flux due to vapor-phase diffusion (Johnson, et al. 1990). Given the fact that governmental regulatory agencies are often interested in the areas of highest residual contamination, it would be advantageous to predict the rate of diffusive movement of all compounds within a mixture in the low permeability zones.

Two models were constructed to simulate the movement of vapors in a vertical cross-section. In each model, 10,000 mg/kg of gasoline were distributed in an array of 5 rows (layers) by 7 columns of active cells. In one model, a homogeneous, high permeability media is simulated, while in the second, a low permeability layer 2 rows thick (50 centimeters) has been added. Soil gas is extracted from cells on one side of the model, so the calculated primary advective transport direction (by many orders of magnitude) through the higher permeability layers is parallel to the layers. The higher permeability layer is modeled as 75 cm thick, and the intrinsic permeability of the contrasting soil types were simulated as 100 and 0.00001 darcys. The iterated soil gas velocities within the 2 low permeability layers are negligible; therefore, transport of chemical compounds within these layers is by diffusion toward the "cleaner" higher permeability layers.

Figure 7 shows the decline of total contaminant mass in the two simulations. In both models, a large portion of the contaminant mass is relatively quickly removed; however, the low permeability layer acts as a long term source of vapor hydrocarbons, roughly doubling the time needed to achieve a desired average cleanup level. Another measure of the cleanup is the maximum nodal contaminant concentration that is left within the model domain during the modeled remediation. Figure 8 shows a graph of this measurement in the two simulations, and demonstrates how much extra time must be allotted within a typical remedial operation in layered system before samples can be obtained for confirmation of cleanup.

Three-Phase Versus Four-Phase Formulation

The assumption that the vapor concentration of a compound is independent of the presence of other volatile compounds is often made when conducting vapor transport modeling for risk assessment. This may result from the assumption of either a four-phase, single compound environment, or a multi-compound, three-phase environment. If a NAPL phase is present, then the vapor concentration of each chemical in the mixture will be changing with time as a function of the diffusive loss of compounds with variable vapor pressures. Because the compound of interest in gasoline spills is generally benzene, it is of interest to determine whether a single-compound formulation is conservative in the calculation of human exposure to vaporous benzene.

Two simulations have been constructed in the diffusion-only mode of the model, each with initial concentrations of benzene in the soil of 150 mg/kg. In one simulation, the benzene is not mixed with any compounds, while in the other simulation, the benzene is present within a gasoline mixture of the same composition

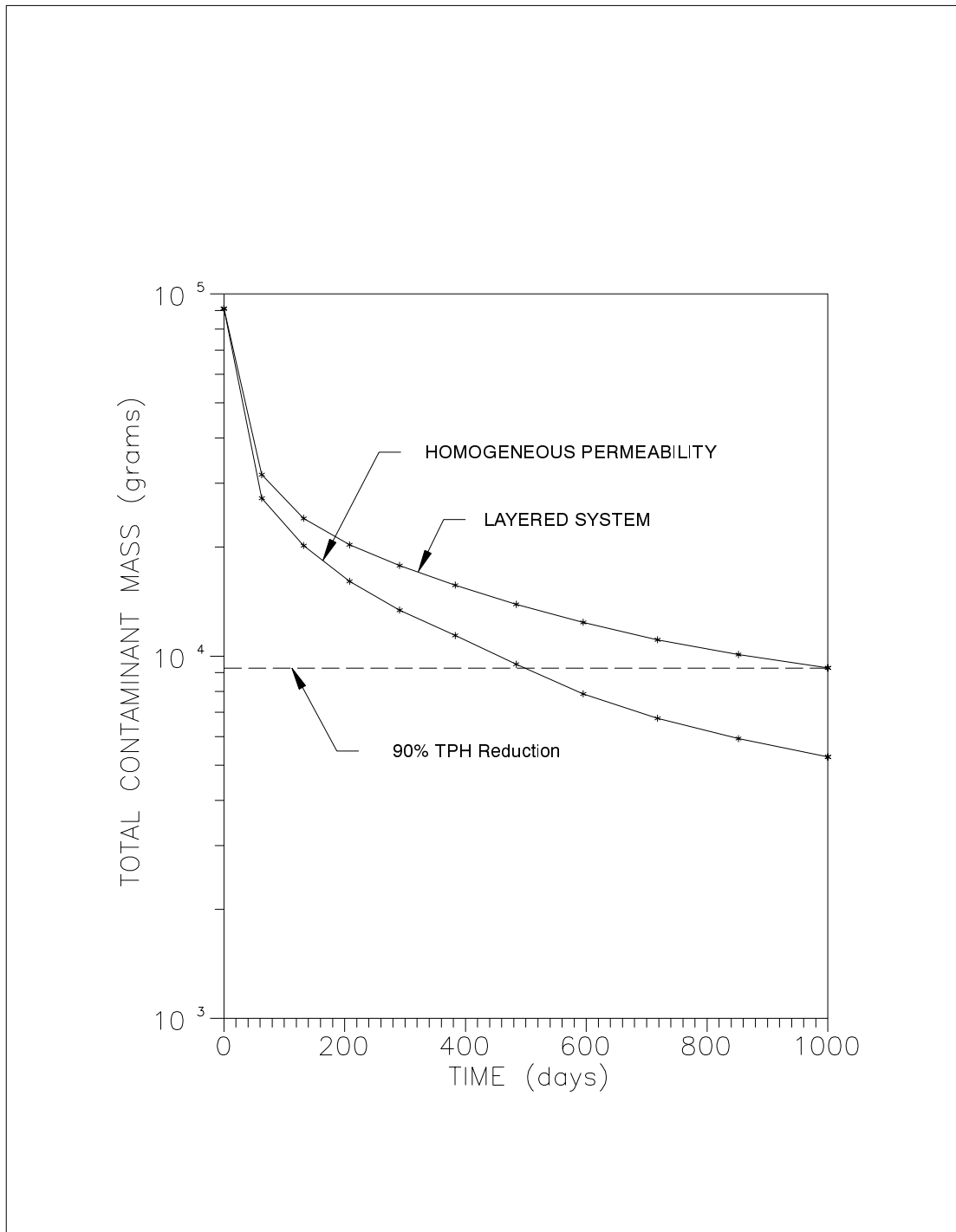


Figure 7. Comparison of residual gasoline mass during venting of homogeneous versus layered permeability models.

listed by Johnson et al. (1990). The contaminant mass is initially located between 135 and 165 centimeters (4.4 to 5.4 feet) below a bare ground surface, and the mass flux is calculated at the ground surface by the model. A graph of the benzene flux, as calculated by each simulation, is shown in Figure 9. It appears that the single-compound simulation over-predicts vapor concentrations (hence a maximum flux which is about 3 times greater), and also accordingly under-predicts the longevity of benzene emanation from the ground surface.

Surface Leakage

The amount of atmosphere which is pulled into the subsurface is a function of the amount of vacuum directly below the ground surface. The amount of leakage will be greatest near the source of the vacuum (extraction wells), and the flow of soil gas from the contaminated interval distant from the wells will be decreased. This has the effect of increasing the rate of remediation near extraction wells, and decreasing the ability of each well to remediate soils located radially distant from the well (radius-of-influence). In the design of remedial systems, such an occurrence needs to be simulated to arrive at the appropriate number of extraction wells. Figure 10 shows a map view of the simulated TPH concentrations after 200 days of venting in two models. The contours shown in Figure 10a were produced by a model which included atmospheric leakage through a 1-meter thickness of sandy (permeability = 50 darcys) soil. The contours in Figure 10b were produced by a simulation that included no leakage. The two models consisted of 20,000 mg/kg of gasoline in a 6 row by 5 column grid, and a soil gas extraction rate of 20 cfm from one well. Every grid element measured 1 meter on each side, and each had an intrinsic permeability of 50 darcy.

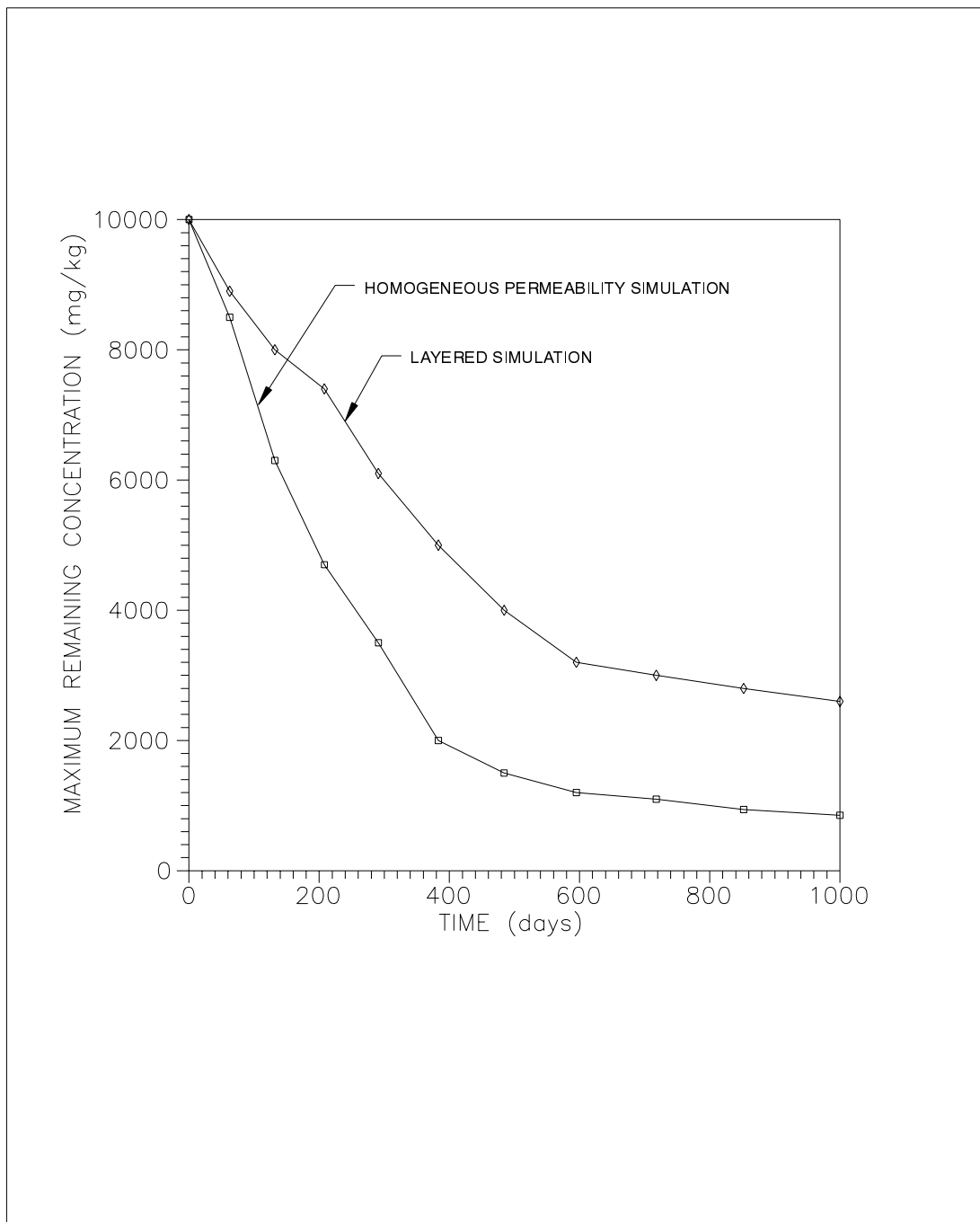


Figure 8. Residual “hot-spot” maximum observed gasoline concentrations during venting of homogeneous versus layered permeability models.

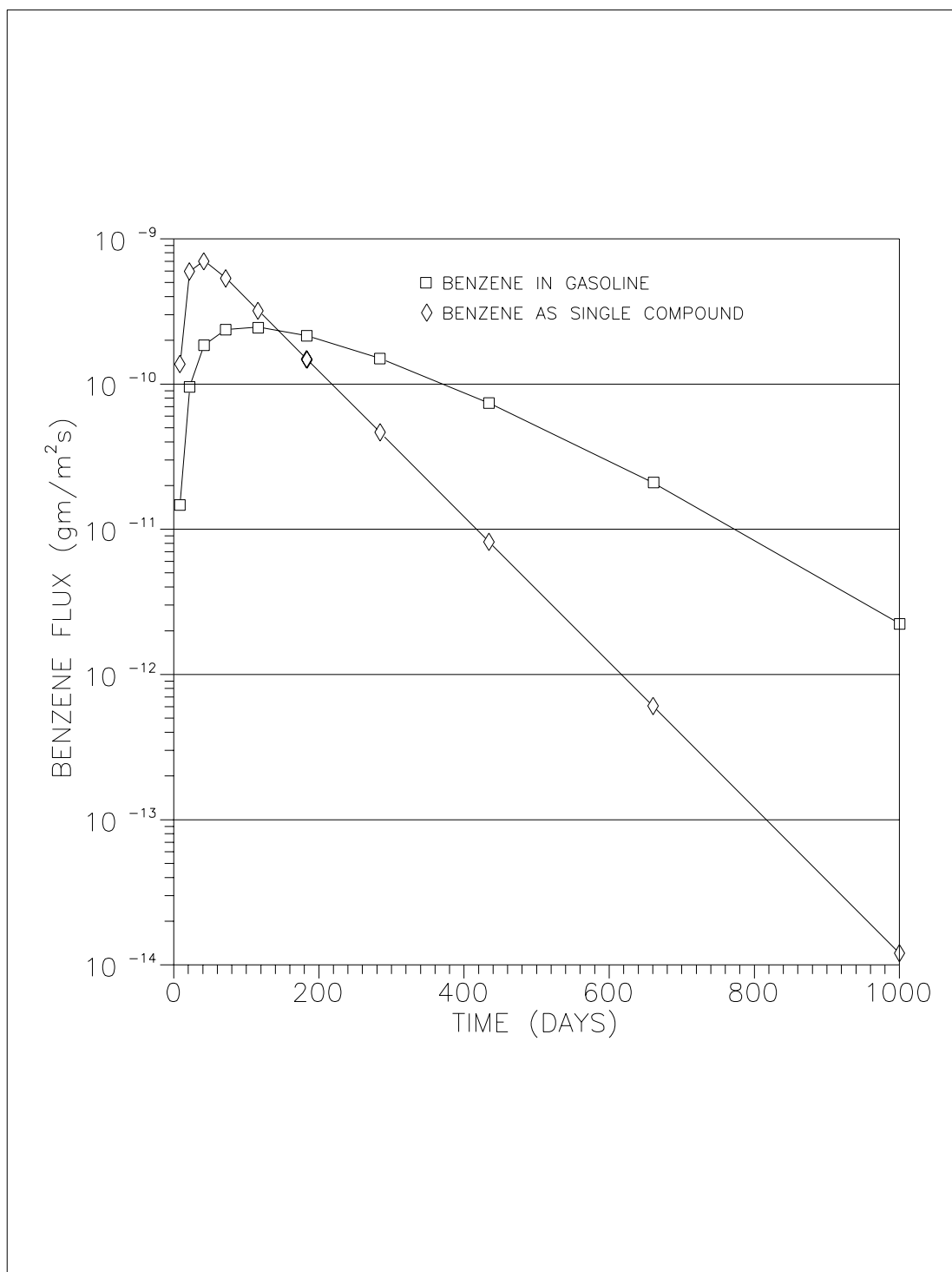
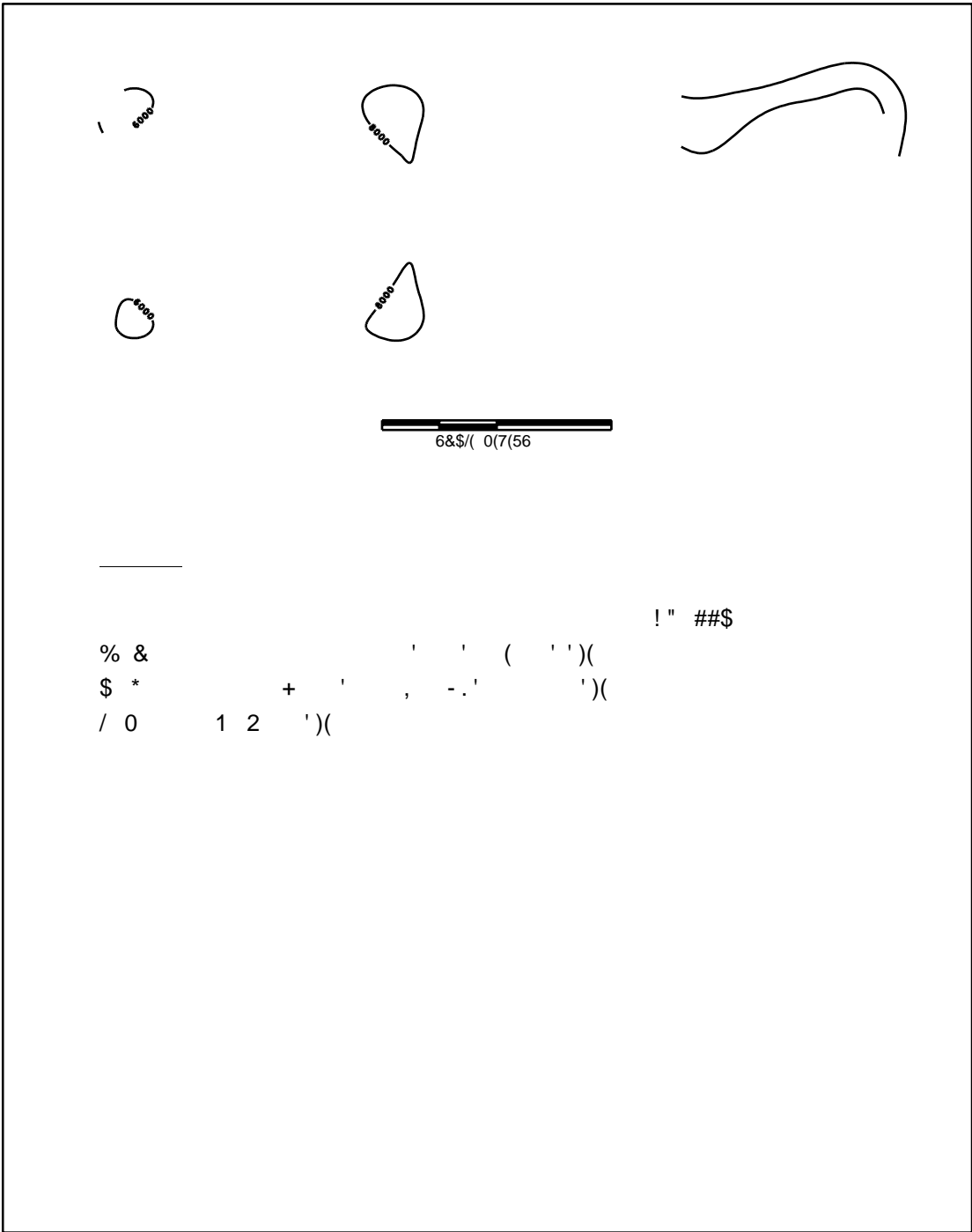


Figure 9. Comparison of benzene flux using single component or gasoline mixture formulation.



3 ' + % , 1 '
 (4 + (

CHAPTER V

SUMMARY AND CONCLUSIONS

A computer program has been generated to fill a gap in the tools used for remedial simulation. Just as non-ideal groundwater aquifer conditions warrant the use of higher-order solute transport models, similar conditions in the unsaturated zone indicate the same treatment with vapor transport simulation. Some additional parameters in the unsaturated zone, including a variable number of phases and continually changing pneumatic conductivity, make such simulations somewhat more complex. However, with diffusion coefficients of most vapors being so much higher than water diffusion coefficients, dispersion can be handled without velocity dependence. This simplification enables creating a program that can be easily used on a 32-bit personal computer. For example, a 400 node, 50 chemical compound version of the code compiles in less than 300 kilobytes. Further, the addition of a third dimension poses no real computational difficulties, if more representative free-product layer simulation is desired. A side benefit of the model happens to be the ability to more accurately track the natural diffusion of compounds in fate and transport simulation for risk assessment.

The utility of the model has been demonstrated by simulating several hypothetical vapor extraction remediation scenarios. In each of the highly simplified examples, previous models were unconservative in their estimation of time needed to reach cleanup by up to 100 percent. Virtually any deviation from a symmetrical contaminant spill within soil of homogeneous permeability will produce longer

remediation time. A number of deviations can be imagined that were not investigated in this paper, such as the effect of multiple wells producing "dead-spots" of little or no advective vapor flow. In such a simulation it can be seen and whether diffusion from these zones will offset that single drawback of adding more wells, or if air-injection wells are needed.

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REFERENCES

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APPENDICES

APPENDIX A

FORTRAN PROGRAM LISTING

FORTRAN PROGRAM LISTING

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```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C          P R O G R A M       V E N T 2-D
C
C          DAVID A. BENSON       02/28/91
C
C      THIS PROGRAM IS DESIGNED TO SOLVE THE 2-D VAPOR PHASE
C      ADVECTIVE AND DIFFUSIVE FLUX OF MIXTURES OF COMPOUNDS.
C      IN DOING SO, THE FLOW FIELD IS SOLVED FOR A 20 BY 20
C      ORTHOGONAL GRID. WITHIN THE GRID, ANY NUMBER OF VAPOR
C      EXTRACTION AND INJECTION WELLS CAN BE SIMULATED, AND
C      GRID-VARIABLE INITIAL PERMEABILITY AND CONTAMINANT DIST-
C      RIBUTION IS SIMULATED. THE EQUILIBRIUM 4-PHASE OCCURRENCE
C      OF EACH COMPOUND IN THE MIXTURE IS SOLVED BETWEEN
C      VAPOR PHASE MOVING PERIODS. THE COMPOUNDS ARE MOVED
C      USING A FORWARD EXPLICIT SOLUTION. THE MOVEMENT
C      OF SOIL MOISTURE IS SIMULATED, AND PERMEABILITY IS TIME-
C      AND-GRID-VARIABLE AS A FUNCTION OF FLUID SATURATION.
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      MAKE NC THE NUMBER OF COMPOUNDS + 1 (THE EXTRA IS FOR WATER)
C
C      PARAMETER (NC=50)
C
C      CHARACTER*30 LCNAME(NC), LTITLE*80, NUL*1, ESC*1
C      REAL MC(20,20,NC), MCHC(20,20), MCWAT(20,20), MASSF(NC), MW(NC),
1      KD(NC), INTRK(20,20), B, DELT, RUNTIME, TMULT, MOIST
C      COMMON NX, NY, DX, DY, THCK, POR, MOIST, NCOMP, SDENS, DELH2O, RUNTIME,
1      DELT, TMULT, TEMP, QX(20,20), QY(20,20), VOID(20,20), P(20,20),
2      PERM(20,20), PERMX(20,20), PERMY(20,20), MC, CI(20,20,NC),
3      PUMPMOLE(NC), W(20,20), C(20,20), MCWAT, TOTMOLE(NC), INTRK,
4      TOTMASS, NSTEPS, IFLAGIMP, ICOMPFL(NC), CELLDIS, WELLCRIT,
5      VPERM(20,20), NWELLS, NZEROC, ZEROC(20,20), DIFFLOSS(NC),
6      FLUXMASS(NC), DENSLIQ, DIFFMAX, DIFFMAXJ
C      COMMON /STRINGS/LCNAME, LTITLE
C      COMMON /VELO/VISC, OMEGA, CRIT, QXMAX, QYMAX
C      COMMON /EQ/MASSF, MW, KD, MCHC, VPWAT, BP(NC), ACT(NC), SOL(NC), VP(NC),
1      FOC, NPHASE(20,20), RETARD(NC)
C      COMMON /MOVE/RH, RHINJ, CINJ, AIRDIFF
C      COMMON /OUT/IFLAGM, IFLAGC, NGRAPH, GRAPH(50,10)
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      THINGS TO DO IN THE MAIN PROGRAM:
C      DO THE TIME LOOP, KEEP TRACK OF OUTPUT NEEDS,

```

```

C      FIGURE MOISTURE CONTENT BEFORE PASSING TO EQ.
C      KEEP TRACK OF CHANGING k/VISC, AND DO MASS BALANCE
C
C      BUT FIRST, INPUT THE DATA FILE AND LOAD THE NECESSARY PARAMETERS
C
C      CALL GETIN
C
      TIME=0.0
      NTSTEPS=0
      FTIME=0.0
      FDELTA=DELTA
      NFSTEPS=0
      NUL=CHAR(0)
      ESC=CHAR(27)
      FTIME=FTIME+DELTA
777 CALL FLOW(TIME)
      NFLOWS=0
888 WRITE(6,400)NUL,ESC
      WRITE(6,*)NFSTEPS,' STEPS HAVE BEEN COMPLETED OF ', NTSTEPS
      TMOLE=0.0
      DO 10 I=1,NX
        DO 10 J=1,NY
          C(I,J)=0.0
          DO 11 N=1,NCOMP
            C(I,J)=C(I,J)+(MC(I,J,N)*MW(N)*1.0E06)/SDENS
            TMOLE=TMOLE+MC(I,J,N)
11      CONTINUE
          IF(C(I,J).GT.0.0) THEN
            VOID(I,J)=POR-(C(I,J)*SDENS/(1.0E06*DENS LIQ))-
1          MC(I,J,NCOMP+1)*18.0
          ELSE
            VOID(I,J)=POR-MC(I,J,NCOMP+1)*18.0
          ENDIF
          EVAC=VOID(I,J)
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALL THE SUBROUTINE TO ITERATE THE CHEMICAL EQUILIBRIUM
C      AT THIS NODE
C      CALL EQUIL(I,J,EVAC,NTSTEPS)
10 CONTINUE
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALCULATE TOTAL VAPOR MOLES AT EACH NODE FOR USE
C      IN THE DETERMINATION OF ACTUAL TIME STEP SIZE
C
      DO 13 I=1,NX
        DO 13 J=1,NY
          GMOLE=0.0
          IF(W(I,J).LT.0.0) THEN
            DO 14 N=1,NCOMP
              GMOLE=GMOLE+CI(I,J,N)
14      CONTINUE
          DT1=-1.0*WELLCRIT*TMOLE*DX*DY*THCK/(GMOLE*W(I,J))
          IF((DT1.GT.0.0).AND.(DT1.LT.DELTA)) THEN
            DELTA=DT1
            WRITE(6,340)DELTA/(60.0*1440.0),TIME/(60.0*1440.0)
            WRITE(6,401)NUL,ESC
          ENDIF
        ENDIF
      ENDIF

```

```

13 CONTINUE
C
C-----DETERMINE TIME STEP SIZE FOR EXPLICIT SOLUTION
C      AND SET UP ANSI.SYS ROUTINE
C
      if((nwells).gt.0) then
          DTTEMP=CELLDIS*evac*(MIN((DX/QXMAX),(DY/QYMAX)))
          IF(DTTEMP.LT.DELT) THEN
              DELT=DTTEMP
              WRITE(6,350)DELT/(60.0*1440.0),TIME/(60.0*1440.0)
              WRITE(6,401)NUL,ESC
          ENDIF
      endif
      if(airdiff.gt.0.0) then
          dttemp=0.5/((airdiff/dx**2.0)+(airdiff/dy**2.0))
          if(ntsteps.gt.0) DTTEMP=0.45/DIFFMAX
          IF(DTTEMP.LT.DELT) THEN
              DELT=DTTEMP
              WRITE(6,370)DELT/(60.0*1440.0),TIME/(60.0*1440.0)
              WRITE(6,401)NUL,ESC
          ENDIF
      endif
      IF((TIME+DELT).GT.FTIME) THEN
          DELT=FTIME-TIME
          FDELT=FDELT*TMULT
          FTIME=FTIME+FDELT
          NFSTEPS=NFSTEPS+1
          WRITE(6,360)DELT/(60.0*1440.0),TIME/(60.0*1440.0)
          WRITE(6,401)NUL,ESC
          CALL OUTPUT(NFLOWS,NFSTEPS,TIME)
      elseif(time.eq.0.0) then
          WRITE(6,360)DELT/(60.0*1440.0),TIME/(60.0*1440.0)
          WRITE(6,401)NUL,ESC
          CALL OUTPUT(NFLOWS,NFSTEPS,TIME)
      ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALL THE DESIRED SUBROUTINE TO MOVE THE COMPOUNDS AND WATER
C
      IF(IFLAGIMP.LT.1) THEN
          CALL MOVEIMP(NFLOWS)
      ELSE
          CALL MOVEEXP(NFLOWS)
      ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      INCREMENT THE TIME COUNTER AND RESET DELTA TIME
C
      TIME=TIME+DELT
      DELT=FDELT
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      RECALCULATE THE RELATIVE GAS PERMEABILITY, AND IF 10 PERCENT
C      OF THE CELLS HAVE CHANGED 25% OR MORE, RECALCULATE THE FLOW
C      PARAMETERS.
C
      IF(TIME.LT.RUNTIME) THEN

```

```

NFLOWS=NFLOWS+1
NTSTEPS=NTSTEPS+1
DO 25 I=1,NX
  DO 25 J=1,NY
    SATGAS=VOID(I,J)/POR
    PERMNEW=INTRK(I,J)*SATGAS**3.0
    IF (ABS(PERMNEW-PERM(I,J))/PERM(I,J).GT.0.25) THEN
      NRECALC=NRECALC+1
    ENDIF
    PERM(I,J)=PERMNEW
25  CONTINUE
    IF(NRECALC.GT.(NX*NY/10)) GO TO 777
    GO TO 888
  ELSE
    CALL OUTPUT(NFLOWS,NFSTEPS,TIME)
  STOP
  ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   FORMATS
C
300 FORMAT(' MOLE BALANCE CALCUALATIONS AT TIME = ', F7.2,' DAYS'
1      /' COMPOUND #          PERCENT ERROR')
310 FORMAT(1X,I5,14X,F7.2)
320 FORMAT(' MASS BALANCE CALCUALATIONS AT TIME = ', F7.2,' DAYS'/
1      ' NET PUMPED MASS  MASS REMAINING  INITIAL MASS  MASS',
2      ' ERROR (%)',' ERROR (%)')
330 FORMAT(1X,G10.4,6X,G10.4,10X,G10.4,6X,G10.4,6X,G10.4)
340 FORMAT(1X,'TIME STEP SIZE = ',G10.4,' AT TIME:',
1      G10.4,' DAYS, DUE TO PUMP TERM')
350 FORMAT(1X,'TIME STEP SIZE = ',G10.4,' AT TIME:',
1      G10.4,' DAYS, DUE TO MAX VELOCITY')
360 FORMAT(1X,'TIME STEP SIZE = ',G10.4,' AT TIME:',
1      G10.4,' DAYS, TO ADJUST TO PRINTOUT TIME')
370 FORMAT(1X,'TIME STEP SIZE = ',G10.4,' AT TIME:',
1      G10.4,' DAYS, DUE TO DIFFUSION TERM')
C
C-----THIS FORMAT STATEMENT REQUIRES ANSI.SYS
C
400 FORMAT(2A1,' [2A')
401 FORMAT(2A1,' [2A')
  END
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C          S U B R O U T I N E   G E T I N          C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   THIS SUBROUTINE READS IN ALL OF THE GRID, SOIL, AND CHEMICAL
C   PARAMETERS. VALUES WHICH DO NOT CHANGE DURING THE SIMULATION
C   (ACTIVITIES, PURE COMPONENT VAPOR PRESSURES, ETC.) ARE
C   INITIALIZED HERE.
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
SUBROUTINE GETIN
PARAMETER (NC=50)
CHARACTER*40 FILEIN,FILEOUT,FILEGR
CHARACTER*30 LCNAME(NC),LTITLE*80
REAL MC(20,20,NC),MCHC(20,20),MCWAT(20,20),MASSF(NC),MW(NC),
1  KD(NC),INTRK(20,20),B,DELT,RUNTIME,TMULT,MOIST
COMMON NX,NY,DX,DY,THCK,POR,MOIST,NCOMP,SDENS,DELH2O,RUNTIME,

```

```

1      DELT, TMULT, TEMP, QX(20,20), QY(20,20), VOID(20,20), P(20,20),
2      PERM(20,20), PERMX(20,20), PERMY(20,20), MC, CI(20,20,NC),
3      PUMPMOLE(NC), W(20,20), C(20,20), MCWAT, TOTMOLE(NC), INTRK,
4      TOTMASS, NSTEPS, IFLAGIMP, ICOMPFL(NC), CELLDIS, WELLCRIT,
5      VPERM(20,20), NWELLS, NZEROC, ZEROC(20,20), DIFFLOSS(NC),
6      FLUXMASS(NC), DENSLIQ
COMMON /STRINGS/LCNAME, LTITLE
COMMON /VELO/VISC, OMEGA, CRIT, QXMAX, QYMAX
COMMON /EQ/MASSF, MW, KD, MCHC, VPWAT, BP(NC), ACT(NC), SOL(NC), VP(NC),
1      FOC, NPHASE(20,20), RETARD(NC)
COMMON /MOVE/RH, RHINJ, CINJ, AIRDIFF
COMMON /OUT/IFLAGM, IFLAGC
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      FIND OUT THE INPUT AND OUTPUT FILENAMES AND READ DATA
C
WRITE(6,*) 'ENTER THE INPUT FILENAME: '
READ(5,10) FILEIN
WRITE(6,*) 'ENTER THE OUTPUT FILENAME: '
READ(5,10) FILEOUT
WRITE(6,*) 'ENTER TIME V. CONC. OUTPUT FILENAME: '
READ(5,10) FILEGR
10  FORMAT(A40)
OPEN(UNIT=9, FILE=FILEIN, STATUS='OLD')
OPEN(UNIT=8, FILE=FILEOUT, STATUS='UNKNOWN')
OPEN(UNIT=10, FILE=FILEGR, STATUS='UNKNOWN')
READ(9,11) LTITLE
11  FORMAT(A80)
READ(9,*) NX, DX, NY, DY, THCK, POR, MOIST, NWELLS, NZEROC
READ(9,*) SDENS, TEMP, OMEGA, CRIT, RH, RHINJ, CINJ
READ(9,*) NCOMP, DENSLIQ, AIRDIFF, FOC
READ(9,*) RUNTIME, NSTEPS, TMULT, CELLDIS, WELLCRIT
READ(9,*) IFLAGM, IFLAGC, IFLAGIMP
DO 15 I=1, NX
DO 15 J=1, NY
W(I,J)=0.0
P(I,J)=1.013E6**2.0
ZEROC(I,J)=-999.9
15  CONTINUE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      READ IN THE WELL LOCATIONS AND FLOWRATES (EXTRACT=NEGATIVE)
C      CONVERT L/MIN TO CC/SEC
C
IF(NWELLS.GT.0) THEN
DO 20 N=1, NWELLS
READ(9,*) I, J, W(I,J)
WRITE(6,*) 'WELL AT NODE', I, ', ', J, ' FLOWRATE:', W(I,J), ' L/MIN'
W(I,J)=W(I,J)*1000.0/60.0
20  CONTINUE
ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      READ IN THE LOCATION OF CONSTANT CONCENTRATION NODES
C      FOR USE IN DIFFUSION ONLY SIMULATIONS
C
IF(NZEROC.GT.0) THEN
DO 30 N=1, NZEROC

```

```

          READ (9,*) I,J
          ZEROC (I,J)=0.0E-33
30    CONTINUE
      ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      READ IN AQUIFER INTRINSIC PERMEABILITIES IN DARCIES
C      CONVERT TO k/VISC IN CM**3*S/GM
C
      VISC=1.8E-04
      READ (9,*) INFLAG,FACTOR
      DO 40 J=NY,1,-1
        IF (INFLAG.EQ.1) READ (9,*) (INTRK(I,J),I=1,NX)
      DO 40 I=1,NX
        IF (INFLAG.NE.1) THEN
          INTRK(I,J)=(FACTOR*1.0E-08)/VISC
        ELSE
          INTRK(I,J)=(INTRK(I,J)*FACTOR*1.0E-08)/VISC
        ENDIF
      40 CONTINUE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      READ IN THE VERTICAL LEAKANCE ARRAY IN, YES, DARCY/FEET
C      AND CONVERT TO CM**2*S/GM
C
      READ (9,*) INFLAG,FACTOR,OVERBRDN
      DO 50 J=NY,1,-1
        IF (INFLAG.EQ.1) READ (9,*) (VPERM(I,J),I=1,NX)
      DO 50 I=1,NX
        IF (INFLAG.NE.1) THEN
          VPERM(I,J)=(FACTOR*1.0E-08)/(VISC*(OVERBRDN*12.0*2.54))
        ELSE
          VPERM(I,J)=(VPERM(I,J)*FACTOR*1.0E-08)/
1          (VISC*(OVERBRDN*12.0*2.54))
        ENDIF
      50 CONTINUE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      READ IN THE INITIAL CONCENTRATION ARRAY IN MG/KG UNITS
C
      READ (9,*) INFLAG,FACTOR
      DO 60 J=NY,1,-1
        IF (INFLAG.EQ.1) READ (9,*) (C(I,J),I=1,NX)
      DO 60 I=1,NX
        IF (INFLAG.NE.1) THEN
          C(I,J)=FACTOR
        ELSE
          C(I,J)=C(I,J)*FACTOR
        ENDIF
        TOTMASS=TOTMASS+C(I,J)
      60 CONTINUE
      TOTMASS=TOTMASS*DX*DY*THCK*SDENS*1.0E-6
      WRITE(6,*) 'TESTING 1 - TOTAL MASS (GRAMS) = ',TOTMASS
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      READ IN THE COMPOUND PARAMETERS
C

```

```

    NGRAPH=0
    DO 70 I=1,NCOMP
        write(6,*) I,NCOMP,MASSF(I),MW(I),BP(I),VP(I),SOL(I),KD(I),
1          ICOMPFL(I)
        READ(9,*)MASSF(I),MW(I),BP(I),VP(I),SOL(I),KD(I),
1          ICOMPFL(I)
        write(6,*) I,NCOMP,MASSF(I),MW(I),BP(I),VP(I),SOL(I),KD(I),
1          ICOMPFL(I)
        NGRAPH=NGRAPH+ICOMPFL(I)
70 CONTINUE
    DO 71 N=1,NCOMP
        READ(9,110)LCNAME(N)
71 CONTINUE
        MW(NCOMP+1)=18.0
        LCNAME(NCOMP+1)='WATER'
        ICOMPFL(NCOMP+1)=1
110 FORMAT(A30)
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C    CALCULATE NEEDED PARAMETERS OF VAPOR PRESSURE AT TEMP,
C    PARTITIONING COEFFICIENT, AND ACTIVITY COEFFICIENTS
C
    TEMP=TEMP+273.0
    REF=293.0
    DO 80 I=1,NCOMP
        BPK=BP(I)+273.0
        VP(I)=VP(I)*EXP((BPK*REF/(BPK-REF))*(1.0/TEMP-1.0/REF))*
1          LOG(VP(I))
        ACT(I)=55.55*MW(I)/(SOL(I)/1000.0)
        IF(VP(I).GE.1.0) ACT(I)=ACT(I)/VP(I)
        KD(I)=0.63*KD(I)*FOC
80 CONTINUE
        VPWAT=0.023*EXP((373.*293./(373.-293.))*(1./TEMP-1./293.))*
1          LOG(0.023)
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C    CONVERT MASS FRACTIONS TO MOLE FRACTIONS
C    AND PLACE THIS COMPOSITION INTO EACH GRID CELL.
C    EACH CELL CARRIES THE MOLES OF EACH COMPOUND PER VOLUME SOIL.
C
    TOTMASS=0.0
    DO 95 N=1,NCOMP
        TOTMOLE(N)=0.0
        DO 96 I=1,NX
            DO 96 J=1,NY
                MC(I,J,N)=(C(I,J)*SDENS/1.0E06)*MASSF(N)/MW(N)
                TOTMOLE(N)=TOTMOLE(N)+MC(I,J,N)*THCK*DX*DY
                IF((ZEROC(I,J).GT.-1.0).AND.(C(I,J).GT.0.0)) THEN
                    WRITE(6,*)'BIG PROBLEM: POSITIVE CONCENTRATIONS SPECIFIED
1          IN ZERO CONC. NODE!'
                ENDIF
96 CONTINUE
        TOTMASS=TOTMASS+(TOTMOLE(N)*MW(N))
95 CONTINUE
        WRITE(6,*)'TESTING - TOTAL CONTAMINANT MASS:',TOTMASS,' GRAMS'
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C    NOW FIGURE THE IMPORTANT INITIAL VALUES OF EACH CELL

```

```

C
TOTMOLE (NCOMP+1)=0.0
TEMPSAT=POR-SDENS*MOIST
DO 97 I=1,NX
  DO 98 J=1,NY
    IF ( (I.EQ.1) .OR. (I.EQ.NX) .OR. (J.EQ.1) .OR. (J.EQ.NY) ) THEN
      MC (I,J,NCOMP+1)=0.0
    ELSE
      MC (I,J,NCOMP+1)=SDENS*MOIST/18.0
    ENDIF
    VOID (I,J)=POR- (C (I,J)*SDENS/ (1.0E06*DENS LIQ) ) -
1      MC (I,J,NCOMP+1)*18.0
    SATGAS=VOID (I,J)/POR
    PERM (I,J)=INTRK (I,J)*SATGAS**3.0
    VPERM (I,J)=VPERM (I,J)*TEMPSAT**3.0
    TOTMOLE (NCOMP+1)=TOTMOLE (NCOMP+1)+MC (I,J,NCOMP+1)*DX*DY*THCK
98    CONTINUE
97 CONTINUE

C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   FIGURE SOME OF THE RUN PARAMETERS - DELT IS IN SECONDS,
C   WHILE RUNTIME IS INPUT IN DAYS
C
    SUMTEMP=1.0
    SUMTEMP2=1.0
    DO 99 M=1,NSTEPS-1
      SUMTEMP2=SUMTEMP2*TMULT
      SUMTEMP=SUMTEMP+SUMTEMP2
99 CONTINUE
    DELT=RUNTIME*1440.0*60.0/SUMTEMP
    RUNTIME=RUNTIME*1440.0*60.0
    RETURN
    END

C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   S U B R O U T I N E   F L O W   C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   THIS SUBROUTINE CALCULATES PRESSURE DISTRIBUTION
C   AND INTERBLOCK SOIL GAS DISCHARGES
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
SUBROUTINE FLOW (TIME)
PARAMETER (NC=50)
REAL MC (20,20,NC) , MCHC (20,20) , MCWAT (20,20) , MASSF (NC) , MW (NC) ,
1 KD (NC) , INTRK (20,20) , B , DELT , RUNTIME , TMULT , MOIST
COMMON NX , NY , DX , DY , THCK , POR , MOIST , NCOMP , SDENS , DELH2O , RUNTIME ,
1 DELT , TMULT , TEMP , QX (20,20) , QY (20,20) , VOID (20,20) , P (20,20) ,
2 PERM (20,20) , PERMX (20,20) , PERMY (20,20) , MC , CI (20,20,NC) ,
3 PUMPMOLE (NC) , W (20,20) , C (20,20) , MCWAT , TOTMOLE (NC) , INTRK ,
4 TOTMASS , NSTEPS , IFLAGIMP , ICOMPFL (NC) , CELLDIS , WELLCRIT ,
5 VPERM (20,20) , NWELLS , NZEROC , ZEROC (20,20)
COMMON /VELO/VISC , OMEGA , CRIT , QXMAX , QYMAX
AIRDENS=1.2E-03
IF (NWELLS.EQ.0) THEN
  DO 4 I=1,NX
    DO 4 J=1,NY
      QX (I,J)=0.0
      QY (I,J)=0.0
4 CONTINUE

```

```

ELSE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      COMPUTE INTERBLOCK k'S USING HARMONIC MEAN
C
DO 5 I=1,NX-1
  DO 5 J=1,NY-1
    PERMX(I,J)=PERM(I,J)*PERM(I+1,J)*2.0/(PERM(I,J)+PERM(I+1,J))
    PERMY(I,J)=PERM(I,J)*PERM(I,J+1)*2.0/(PERM(I,J)+PERM(I,J+1))
  5 CONTINUE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      INITIALIZE OMEGA AND ITERATE STEADY STATE
C      PRESSURE DISTRIBUTION, ADJUSTING OMEGA ON THE FLY.
C      REMEMBER THAT THE P ARRAY HOLDS VALUES OF P**2
C
OM=OMEGA
NIT=0
10 NIT=NIT+1
ERRMAX=0.0
PMAX=0.0
PMIN=1.0E25
DIM=(DX*DY)**2.0/THCK
DO 100 I=2,NX-1
  DO 110 J=2,NY-1
    C1=DY*DY*(PERMX(I,J)*P(I+1,J)+PERMX(I-1,J)*P(I-1,J))
    C2=DX*DX*(PERMY(I,J)*P(I,J+1)+PERMY(I,J-1)*P(I,J-1))
    C3=DY*DY*(PERMX(I,J)+PERMX(I-1,J))
    C4=DX*DX*(PERMY(I,J)+PERMY(I,J-1))
    GAUSS=(C1+C2+2.0*W(I,J)*1.013E06*DX*DY/THCK)/(C3+C4)
    VLEAK=2.0*DIM*VPERM(I,J)*(1.013E6*SQRT(P(I,J))-P(I,J))/(C3+C4)
    WRITE(6,*)I,J,GAUSS,VLEAK
    GAUSS=GAUSS+VLEAK
    PNEW=(1.0-OM)*P(I,J)+(OM*GAUSS)
    PERER=((PNEW-P(I,J))/PNEW)*100.0
    IF(ABS(PERER).GT.ERRMAX) ERRMAX=ABS(PERER)
C-----THWART SOME OSCILLATION PROBLEMS:
    IF(PNEW.LT.0.0) PNEW=0.1
    P(I,J)=PNEW
    IF(PNEW.GE.PMAX) PMAX=PNEW
    IF(PNEW.LE.PMIN) PMIN=PNEW
  110 CONTINUE
100 CONTINUE
IF((ERRMAX.LT.CRIT).OR.(NIT.GT.500)) THEN
  GOTO 200
ELSEIF((ERRMAX.LT.(CRIT*5.0)).AND.(OM.LE.1.80)) THEN
  OM=OM+0.05
  WRITE(6,*)ERRMAX,NIT,OM
  GOTO 10
ELSE
  WRITE(6,*)ERRMAX,NIT,OM
  GOTO 10
ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C      PRINT PRESSURE ARRAY AND
C      FIGURE OUT THE INTERBLOCK DISCHARGES
C
200 WRITE(6,*)'CALCULATING FLOW FIELD AT TIME = ',TIME

```

```

QXMAX=0.0
QYMAX=0.0
DO 220 J=1,NY-1
  DO 230 I=1,NX-1
    QX(I,J)=PERMX(I,J)*(SQRT(P(I+1,J))-SQRT(P(I,J)))/DX
    QY(I,J)=PERMY(I,J)*(SQRT(P(I,J+1))-SQRT(P(I,J)))/DY
    IF (ABS(QX(I,J)).GT.QXMAX) THEN
      QXMAX=ABS(QX(I,J))
      IQXMAX=I
      JQXMAX=J
    ENDIF
    IF (ABS(QY(I,J)).GT.QYMAX) THEN
      QYMAX=ABS(QY(I,J))
      IQYMAX=I
      JQYMAX=J
    ENDIF
  230 CONTINUE
220 CONTINUE
  WRITE(6,*)'MAXIMUM X DISCHARGE (CM/S) OF ',QXMAX,' AT NODE ',
1          IQXMAX,' ',',',JQXMAX
  WRITE(6,*)'MAXIMUM Y DISCHARGE (CM/S) OF ',QYMAX,' AT NODE ',
1          IQYMAX,' ',',',JQYMAX
  ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
  RETURN
  END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C          S U B R O U T I N E      E Q U I L          C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C          THIS SUBROUTINE CALCULATES THE EQUILIBRIUM PHASE
C          DISTRIBUTION OF EACH COMPOUND IN THE MIXTURE, AND
C          CALCULATES THE SUBSEQUENT MOLAR VAPOR CONCENTRATIONS
C          FOR INTERBLOCK MOVEMENT IN ANOTHER SUBROUTINE
C          CALLED MOVE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
  SUBROUTINE EQUIL(I,J,EVAC,NTSTEPS)
  PARAMETER (NC=50)
  REAL MC(20,20,NC),MCHC(20,20),MCWAT(20,20),MASSF(NC),MW(NC),
1      KD(NC),INTRK(20,20),B,DELT,RUNTIME,TMULT,MOIST
  COMMON NX,NY,DX,DY,THCK,POR,MOIST,NCOMP,SDENS,DELH2O,RUNTIME,
1      DELT,TMULT,TEMP,QX(20,20),QY(20,20),VOID(20,20),P(20,20),
2      PERM(20,20),PERMX(20,20),PERMY(20,20),MC,CI(20,20,NC),
3      PUMPMOLE(NC),W(20,20),C(20,20),MCWAT,TOTMOLE(NC),INTRK,
4      TOTMASS,NSTEPS,IFLAGIMP,ICOMPFL(NC),CELLDIS,WELLCRIT,
5      VPERM(20,20),NWELLS,NZEROC,ZEROC(20,20),DIFFLOSS(NC),
6      FLUXMASS(NC),DENSLIQ
  COMMON /EQ/MASSF,MW,KD,MCHC,VPWAT,BP(NC),ACT(NC),SOL(NC),VP(NC),
1      FOC,NPHASE(20,20),RETARD(NC)
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C          CHECK FOR FREE PHASE IN ANY OF THE COMPOUNDS.
C          IF ALL ARE 3-PHASE, CALCULATE VAPOR CONC. OF EACH
C          COMPOUND AND RETURN. IF 4-PHASE, ITERATE TO THE PHASE
C          DISTRIBUTION
C
CONCMASS=0.0

```

```

CONCMOLE=0.0
IF (MC (I, J, NCOMP+1) .LE. 0.0) THEN
  MC (I, J, NCOMP+1) = 0.0
  DELWAT = 0.0
ELSE
  DELWAT = 1.0
ENDIF
NUMPHASE = 3
DO 10 N = 1, NCOMP
  CONCMASS = CONCMASS + MC (I, J, N) * MW (N)
  CONCMOLE = CONCMOLE + MC (I, J, N)
  C1 = VP (N) * EVAC / (82.1 * TEMP)
  C2 = MC (I, J, NCOMP+1) / ACT (N)
  C3 = KD (N) * SDENS * DELWAT / (18.0 * ACT (N))
  C4 = MC (I, J, N) / (C1 + C2 + C3)
  IF (C4 .GE. 1.000) NUMPHASE = 4
  CI (I, J, N) = C4 * VP (N) / (82.1 * TEMP)
  IF ((ntsteps .lt. 1) .and. (mc (i, j, n) .gt. 0.0)) THEN
    RETARD (N) = mc (i, j, n) / (ci (i, j, n) * evac)
  ENDIF
10 CONTINUE
IF ((NUMPHASE .EQ. 3) .OR. (CONCMASS .LT. 1.0E-08)) THEN
  NPHASE (I, J) = 3
  RETURN
ELSE
  NPHASE (I, J) = 4
ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   IF THERE IS A SEPARATE PHASE, MAKE A FIRST GUESS THAT
C   THE SEPARATE PHASE MOLE FRACTION (X(N)) EQUALS THE TOTAL
C   MOLES OF N DIVIDED BY THE TOTAL CONTAMINANT MOLES, OR
C    $CI * RT / VP (N) = MI / CONCMOLE.$ 
C
  DO 20 N = 1, NCOMP
    CI (I, J, N) = MC (I, J, N) * VP (N) / (CONCMOLE * 82.1 * TEMP)
20 CONTINUE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   THIS IS THE ITERATIVE LOOP WHERE, ESSENTIALLY,
C    $MI (N) = (CONST + MCHC) CI (N).$  SO SOLVE FOR MCHC, THEN CI (N), ETC.
C   UNTIL  $SUM (CI (N) * R * T / VP (N)),$  WHICH =  $SUM (X (N)) = 1.000$ 
C
  PHASE3 = 0.0
  DO 30 NN = I, NCOMP
    C1 = EVAC
    C2 = MC (I, J, NCOMP+1) * TEMP * 82.1 / (ACT (NN) * VP (NN))
    C3 = KD (NN) * SDENS * DELWAT * 82.1 * TEMP / (ACT (NN) * VP (NN) * 18.0)
    PHASE3 = PHASE3 + (CI (I, J, NN) * (C1 + C2 + C3))
30 CONTINUE
  MCHC (I, J) = CONCMOLE - PHASE3
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   WITH NEW MCHC, RECALCULATE CI (N), AND CHECK THE SUM OF X (N)
C
200 NUMITER = NUMITER + 1
  DO 40 N = 1, NCOMP
    C1 = 82.1 * TEMP / VP (N)

```



```

C
C      DON'T ALLOW TRANSPORT OUTSIDE THE BOUNDARIES
C
      IF(I.EQ.2) A=0.0
      IF(I.EQ.(NX-1)) A1=0.0
      IF(J.EQ.2) B=0.0
      IF(J.EQ.(NY-1)) B1=0.0
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      DO 220 N=1, NCOMP+1
          VAL=CI(I, J, N)
c          mc(I, J, N)=-1.0*(A+B+A1+B1)*CI(I, J, N)+A1*CI(I+1, J, N)+
c          1 A*MOLDCOL(J, N)+B1*CI(I, J+1, N)+B*MOLDCOL(J-1, N)+mc(I, J, N)
          CI(I, J, N)=(-1.0*(A+B+A1+B1)*CI(I, J, N)+A1*CI(I+1, J, N)+
          1 A*MOLDCOL(J, N)+B1*CI(I, J+1, N)+B*MOLDCOL(J-1, N))/void(i, j)
          2 +CI(I, J, N)
          MOLDCOL(J, N)=VAL
          IF(NZEROC.GT.0) THEN
              IF(ZEROC(I, J).GT.-1.0) THEN
c                  DIFFLOSS(N)=DIFFLOSS(N)-mc(I, J, N)*DX*DY*THCK
c                  FLUXMASS(N)=mc(I, J, N)*MW(N)*DX*DY*THCK/DELT
                  DIFFLOSS(N)=DIFFLOSS(N)-CI(I, J, N)*DX*DY*THCK*VOID(I, J)
                  FLUXMASS(N)=CI(I, J, N)*MW(N)*DX*DY*THCK*VOID(I, J)/DELT
                  MC(I, J, N)=0.0E-1
                  CI(I, J, N)=0.0E-1
              ENDIF
          ENDIF
          MC(I, J, N)=MC(I, J, N)+VOID(I, J)*CI(I, J, N)
C 11/27      CONTINUE
          220 CONTINUE
          210 CONTINUE
          200 CONTINUE
C-----IF THERE ARE NO WELLS, QUIT. ELSE, FIGURE ADVECTIVE MOVEMENT
          IF(NWELLS.EQ.0) GO TO 400
          DO 97 J=1, NY
              DO 97 N=1, NCOMP+1
                  MOLDCOL(J, N)=CI(1, J, N)
          97 CONTINUE
              DO 100 I=2, NX-1
                  DO 110 J=2, NY-1
                      CPUMP=W(I, J)*DELT/(THCK*DX*DY)
                      QLEAK=DELT*VPERM(I, J)*(1.013E6-SQRT(P(I, J)))/THCK
                      DO 20 N=1, NCOMP+1
                          MOLDCOL(1, N)=CI(I, 1, N)
                          IF(QX(I-1, J).LT.0.0) THEN
                              C1=QX(I-1, J)*MOLDCOL(J, N)/DX
                          ELSE
                              C1=QX(I-1, J)*CI(I, J, N)/DX
                          ENDIF
                          IF(QX(I, J).GT.0.0) THEN
                              C2=QX(I, J)*CI(I+1, J, N)/DX
                          ELSE
                              C2=QX(I, J)*CI(I, J, N)/DX
                          ENDIF
                          IF(QY(I, J-1).LT.0.0) THEN
                              C3=QY(I, J-1)*MOLDCOL(J-1, N)/DY
                          ELSE
                              C3=QY(I, J-1)*CI(I, J, N)/DY
                          ENDIF
                          IF(QY(I, J).GT.0.0) THEN
                              C4=QY(I, J)*CI(I, J+1, N)/DY
                          ELSE
                              C4=QY(I, J)*CI(I, J, N)/DY
                      END DO
                  END DO
              END DO
          END IF

```



```

DO 5 N=1, NCOMP
WRITE (8, 305) LCNAME (N) , MASSF (N) , BP (N) , VP (N) , SOL (N) , KD (N) ,
1      RETARD (N)
5 CONTINUE
WRITE (8, 310) TIME / (60.0*1440.0)
DO 10 J=NY, 1, -1
WRITE (8, 320) (SQRT (P (I, J)) / 1.013E06, I=1, NX)
10 CONTINUE
WRITE (8, 330)
DO 11 J=NY, 1, -1
WRITE (8, 340) (1.0E+08*VISC*PERM (I, J) , I=1, NX)
11 CONTINUE
WRITE (8, 341)
DO 12 J=NY, 1, -1
WRITE (8, 342) (QX (I, J) , I=1, NX)
12 CONTINUE
WRITE (8, 343)
DO 13 J=NY, 1, -1
WRITE (8, 344) (QY (I, J) , I=1, NX)
13 CONTINUE
ENDIF
IF (MOD (NTSTEPS, IFLAGM) .EQ. 0) THEN
NGTIMES=NGTIMES+1
TOTALM=0.0
WRITE (8, 350) TIME / (60.0*1440.0)
GRAPH (NGTIMES, 1) =TIME / (60*1440.0)
DO 20 J=NY, 1, -1
DO 21 I=1, NX
TMASS (I) =0.0
DO 22 N=1, NCOMP
TMASS (I) =TMASS (I) + (MC (I, J, N) *MW (N) *1.0E06) /SDENS
22 CONTINUE
TOTALM=TOTALM+TMASS (I) *SDENS*DX*DY*THCK*1.0E-6
21 CONTINUE
WRITE (8, 360) (TMASS (I) , I=1, NX)
20 CONTINUE
WRITE (8, 365) TOTALM
IF (TOTALM.LT.1E-14) THEN
GRAPH (NGTIMES, 2) =1E-20
ELSE
GRAPH (NGTIMES, 2) =TOTALM
ENDIF
ENDIF
IF (MOD (NTSTEPS, IFLAGC) .EQ. 0) THEN
WRITE (8, 370) TIME / (60.0*1440.0)
DO 30 J=NY, 1, -1
DO 31 I=1, NX
GASCONC (I) =0.0
DO 32 N=1, NCOMP
GASCONC (I) =GASCONC (I) + (CI (I, J, N) *MW (N) *1.0E06)
32 CONTINUE
31 CONTINUE
WRITE (8, 380) (GASCONC (I) , I=1, NX)
30 CONTINUE
DO 33 I=2, NX-1
DO 33 J=2, NY-1
IF (W (I, J) .LT.0.0) THEN
TOTALGAS=0.0
WRITE (8, 372) I, J, TIME / (60.0*1440.0)
DO 34 N=1, NCOMP
TOTALGAS=TOTALGAS+CI (I, J, N) *MW (N) *1.0E06

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```

34          CONTINUE
          DO 35 N=1,NCOMP
            WRITE (8,373) LCNAME (N) , CI (I,J,N) *MW (N) *1.0E06,
1            1.0E08*MW (N) *CI (I,J,N) /TOTALGAS
35          CONTINUE
            WRITE (8,374) TOTALGAS
          ENDIF
33    CONTINUE
    ENDIF
    IF (MOD (NTSTEPS,IFLAGM) .EQ.0) THEN
      NCCOUNT=2
      DO 40 N=1,NCOMP+1
        IF (ICOMPFL (N) .GT.0) THEN
          NCCOUNT=NCCOUNT+1
          IF (N.EQ.NCOMP+1) THEN
            WRITE (8,391) LCNAME (N) , TIME/ (60.0*1440.0)
          ELSE
            WRITE (8,390) LCNAME (N) , TIME/ (60.0*1440.0)
          ENDIF
          TOTALM=0.0
          DO 41 J=NY,1,-1
            IF (N.EQ.NCOMP+1) THEN
              WRITE (8,360) ( (MC (I,J,N) *MW (N) *1.0E2) /SDENS , I=1,NX)
            ELSE
              WRITE (8,360) ( (MC (I,J,N) *MW (N) *1.0E06) /SDENS , I=1,NX)
            ENDIF
            DO 42 I=1,NX
              TOTALM=TOTALM+MC (I,J,N) *MW (N) *1.0E06/SDENS
42          CONTINUE
41          CONTINUE
          TOTALM=TOTALM*SDENS*DX*DY*THCK*1.0E-6
          WRITE (8,395) TOTALM
          WRITE (8,396) FLUXMASS (N)
          IF (TOTALM.LT.1E-19) THEN
            GRAPH (NGTIMES,NCCOUNT) =1E-20
          ELSE
            GRAPH (NGTIMES,NCCOUNT) =TOTALM
          ENDIF
        ENDIF
40    CONTINUE
    ENDIF
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C          MASS BALANCE CALCULATIONS
C
    IF (MOD (NTSTEPS,IFLAGM) .EQ.0) THEN
      RESMASS=0.0
      PUMPMASS=0.0
      DIFFMASS=0.0
      WRITE (8,400) TIME/ (60.0*1440.0)
      DO 50 N=1,NCOMP
        RESMOLE=0.0
        DO 51 I=1,NX
          DO 51 J=1,NY
            RESMOLE=RESMOLE+MC (I,J,N) *DX*DY*THCK
51          CONTINUE
          RESID=TOTMOLE (N) -RESMOLE
C          DIFFMOLE=DIFFLOSS (N) *DX*DY*THCK
          ERRMOLE=100.0* (-1.0* (PUMPMOLE (N) +DIFFLOSS (N) ) -RESID) /
1          (0.5* (-1.0* (PUMPMOLE (N) +DIFFLOSS (N) ) +RESID) )

```

```

WRITE (8, 405) LCNAME (N) , TOTMOLE (N) , PUMPMOLE (N) , DIFFLOSS (N) ,
1      RESMOLE , ERRMOLE
RESMASS=RESMASS+RESMOLE*MW (N)
PUMPMASS=PUMPMASS+PUMPMOLE (N) *MW (N)
DIFFMASS=DIFFMASS+DIFFLOSS (N) *MW (N)
50 CONTINUE
RESIDMAS=TOTMASS-RESMASS
OUTMASS=PUMPMASS+DIFFMASS
ERRMASS1=100.0*(-1.0*OUTMASS-RESIDMAS)/(TOTMASS-OUTMASS)
ERRMASS2=100.0*(-1.0*OUTMASS-RESIDMAS)/
1      (0.5*(RESIDMAS-OUTMASS))
WRITE (8, 420) TIME/(60.0*1440.0)
WRITE (8, 430) PUMPMASS, DIFFMASS, RESMASS, TOTMASS, ERRMASS1, ERRMASS2
ENDIF
IF (TIME.GE.RUNTIME) THEN
WRITE (8, 440)
DO 60 K=1,NGTIMES
WRITE (8, 450) (GRAPH (K, L) , L=1, NCCOUNT)
WRITE (10, 450) (GRAPH (K, L) , L=1, NCCOUNT)
60 CONTINUE
ENDIF
RETURN
300 FORMAT (1X, A80/I3, ' COLUMNS AT ', F7.1, ' CM EACH'/I3, ' ROWS AT'
1, 4X, F7.1, ' CM EACH'/' THICKNESS IN 3RD DIMENSION = ', F7.1, ' CM' /
2 ' TOTAL POROSITY = ', F7.2, '/' FRACTION ORGANIC C = ', F7.2, /
3 ' NUMBER OF COMPOUNDS = ', I7, '/' FREE AIR DIFFUSION = ', F7.3, /
4 ' CM2/SEC' )
304 FORMAT (/' INITIAL CONTAMINANT COMPOSITION AND PHYSICAL PROPERTIES' ,
1 //, 26X, ' MASS' , 6X, ' BOILING' , 7X, ' VAPOR' , 7X, ' SOLUB.' , 12X,
2 ' APPROX.' , /, ' COMPOUND' , 16X, ' FRACTION POINT (C) PRESS (ATM)' ,
3 ' (MG/L) Kd RETARDATION' , /, '-----' ,
4 '-----' ,
5 '-----' )
305 FORMAT (A25, F7.4, 1F10.2, 4F12.2)
310 FORMAT (/' PRESSURE ARRAY (ATMOSPHERES) AT TIME = ', F7.2, ' DAYS' /)
320 FORMAT (1X, 20F9.4)
330 FORMAT (///' RELATIVE PERMEABILITY ARRAY (DARCY) : ' /)
340 FORMAT (1X, 20G9.2)
341 FORMAT (///' X-DIRECTION DISCHARGES (CM/SEC) : ' /)
342 FORMAT (1X, 20G9.2)
343 FORMAT (///' Y-DIRECTION DISCHARGES (CM/SEC) : ' /)
344 FORMAT (1X, 20G9.2)
350 FORMAT (/' REMAINING TOTAL CONC. (MG/KG) AT TIME = ',
1 F7.2, ' DAYS' /)
360 FORMAT (1X, 20G9.2)
365 FORMAT (/, 1X, ' (TOTAL MASS = ', G11.4, ' GRAMS)' )
370 FORMAT (/' REMAINING TOTAL SOIL GAS CONC. (MG/L) AT TIME = ',
1 F7.2, ' DAYS' /)
372 FORMAT (/' CONCENTRATION OF VOLATILES IN SOIL GAS AT THE' , I3, ' , ' ,
1 I3, ' NODE, T = ', F7.2, ' DAYS : ' /' COMPOUND' , 19X, ' MG/L' , 12X,
2 ' PERCENT OF VOCS' , /)
373 FORMAT (1X, A25, F10.4, 5X, F10.4)
374 FORMAT (1X, ' TOTAL ', F10.4)
380 FORMAT (1X, 20G9.2)
390 FORMAT (/, 1X, ' REMAINING ', A25, ' IN SOIL (MG/KG) AT TIME = ',
1 F7.2, ' DAYS' /)
391 FORMAT (/, 1X, ' REMAINING ', A15, ' IN SOIL (WEIGHT PERCENT) AT ',
1 ' TIME = ', F7.2, ' DAYS' /)
395 FORMAT (/, 1X, ' (TOTAL MASS = ', G11.4, ' GRAMS)' )
396 FORMAT (/, 1X, ' (MASS FLUX = ', G11.4, ' GM/SEC INTO DIFF. ZERO' ,
1 ' CELLS)' )

```

```

400 FORMAT(// ' MOLE BALANCE CALCULATIONS AT TIME = ', F7.2, ' DAYS',
1      /, 29X, ' INITIAL', 5X, ' PUMPED   DIFF. LOSS  RESIDUAL  PERCENT',
2      /, 8X, ' COMPOUND', 14X, ' MOLES', 6X, ' MOLES', 6X, ' MOLES', 6X, ' MOLES',
3      6X, ' ERROR', /, ' -----',
4      ' -----')
405 FORMAT(1X, A24, 2X, 5G11.3)
410 FORMAT(1X, I5, 14X, F7.2)
420 FORMAT(// ' MASS BALANCE CALCULATIONS AT TIME = ', F7.2, ' DAYS'/
1      ' PUMPED MASS  DIFF. LOSS  MASS REMAINING  INITIAL MASS  ',
2      ' MASS ERROR (%)  ERROR (%)')
430 FORMAT(1X, G10.4, 4X, G10.4, 4X, G10.4, 7X, G10.4, 4X, G9.3, 4X, G9.3)
440 FORMAT(///, 1X, ' TOTAL MASSES OF SELECTED COMPOUNDS WITH TIME:',
1      /, '      TIME          TOTAL          ETC.-- (H2O LAST)-->')
450 FORMAT(1X, 8E11.3)
      END

```

APPENDIX B

DATA INPUT FORMAT

DATA INPUT FORMAT

All numbers are read by the program in free format, so position and decimal digits are unimportant for individual variables. An ASCII data file is constructed thus:

Line number	Variable name	Description
Line 1	TITLE	Simulation title
Line 2	NX	Number of columns (NX<21)
	DX	Column width (cm)
	NY	Number of rows (NY<21)
	DY	Row width (cm)
	THCK	Thickness in third dimension (cm)
	POR	Total Porosity (vol. fraction) (0<POR<1)
	MOIST	Soil moisture (vol. fraction) (0<MOIST<POR)
	NWELLS	Number of wells
	NZEROC	Number of constant conc. cells (for diffusion)
Line 3	SDENS	Soil density (gm/cm ³)
	TEMP	Simulation temperature (oC)
	OMEGA	Flow iteration acceleration parameter (1<OMEGA<2)
	CRIT	Flow iteration criteria (percent)
	RH	Relative humidity of incoming air (0<RH<1)
	RHINJ	Relative humidity of injected air (0<RHINJ<1)
	CINJ	Concentration of injected air (mole/cm ³)
Line 4	NCOMP	Number of compounds (NCOMP<50)

	DENSLIQ	Contaminant liquid density (gm/cm ³)
	AIRDIFF	Air diffusion coefficient (cm ² /s)
	FOC	Fraction organic carbon
Line 5	RUNTIME	Total simulation time (days)
	NSTEPS	Number of printout time steps
	TMULT	Multiplier for printout time step size
	CELLDIS	Fraction of cell dimension travelled per step allowed
	WELLCRIT	Fraction of total moles extracted by pumping per time step allowed
Line 6	IFLAGM	Number of time steps between soil concentration data printout
	IFLAGC	Number of time steps between vapor concentration data printout
	IFLAGIMP	Flag for implicit or explicit solution (at present, IFLAGIMP=1)
NWELLS Lines		
	I,J,W(I,J)	Nodal location and pumping rate of each well (l/m, extract = negative)
NZEROC Lines		
	I,J	Nodal location of zero concentration nodes (simulating ground surface, for example)

What follows are the arrays for permeability, surface leakage, and initial total contaminant concentration distribution. Each array starts with one line specifying whether the array is homogeneous and can be described by one value (FACTOR). If not, then an array follows and each value is multiplied by the number FACTOR. The arrays are as follows:

Intrinsic permeability:

Line 1	INFLAG	(if INFLAG=1, INTRK array follows, and is x FACTOR. If INFLAG=0, all INTRK(I,J)= FACTOR) (darcy).
	FACTOR	see above

Plus or minus Intrinsic permeability array

Vertical leakage permeability:

Line 1	INFLAG	(if INFLAG=1, VPERM array follows, and is x FACTOR. If INFLAG=0, all VPERM(I,J)= FACTOR) (darcy).
	FACTOR	see above
	OVERBRDN	thickness of leaky confining layer (feet)

Plus or minus confining bed vertical permeability

Initial concentration array:

Line 1	INFLAG	(if INFLAG=1, C array follows, and is x FACTOR. If INFLAG=0, all C(I,J)= FACTOR) (darcy).
	FACTOR	see above

Plus or minus Initial concentration array

NCOMP Lines of

MASSF(N)	mass fraction of compound n (dimensionless)
MW(N)	molecular weight of compound n (gm/mol)
BP(N)	boiling point of compound n (degrees C)
VP(N)	vapor pressure of compound n at 20°C (ATM)
SOL(N)	solubility of compound n (mg/l)
KD(N)	octanol/water partition coefficient of compound n
ICOMPFL(N)	flag specifying whether to print concentrations of compound n at every printout time step (0=do not print, 1=print)

NCOMP Lines of

LCNAME(N) the name of compound n

APPENDIX C

SAMPLE INPUT AND OUTPUT FILES

The following is a sample data input file, and the corresponding output is listed after the input file:

```

UNSPECIFIED PLASTICS MANUFACTURER - TRACK ETHYLBENZENE
6 304.8 6 304.8 609.6 0.4 0.1 1 0
1.5 15.56 1.5 0.0001 1.0 1.0 0.0
6 0.8 0.084 0.001
1095.0 3 1.2 1.9 0.001
1 1 1
4 3 -283.0
0 50.0
0 0.0 10.0
1 1.0
0 0 0 0 0 0
0 0.0601 0.0193 0.0302 0.1482 0
0 3.1603 5.1180 25.514 49.467 0
0 20.369 13112. 9819.2 70.202 0
0 61.07 8185.2 4422.3 12.226 0
0 0 0 0 0 0
0.000303 78.1 80 0.1 1780 135 0
0.003907 92.1 111 0.029 515 490 0
0.52425 106.2 138 0.0092 161 1413 1
0.02022 106.2 138 0.0086 198 1413 0
0.049306 104.1 145 0.0075 310 891 0
0.402011 120.2 159 0.003 60 4786 0
BENZENE
TOLUENE
ETHYLBENZENE
p-XYLENE
STYRENE
C9 ALKYL BENZENES

```

OUTPUT FILE:

```

UNSPECIFIED PLASTICS MANUFACTURER - TRACK ETHYLBENZENE
6 COLUMNS AT 304.8 CM EACH
6 ROWS AT 304.8 CM EACH
THICKNESS IN 3RD DIMENSION = 609.6 CM
TOTAL POROSITY = 0.40
FRACTION ORGANIC C = 0.00
NUMBER OF COMPOUNDS = 6
FREE AIR DIFFUSION = 0.084 CM2/SEC

```

INITIAL CONTAMINANT COMPOSITION AND PHYSICAL PROPERTIES

COMPOUND	MASS FRACTION	BOILING POINT (C)	VAPOR PRESS (ATM)	SOLUB. (MG/L)	Kd	APPROX. RETARDATION
BENZENE	0.0003	80.00	0.08	1780.00	0.09	8.39
TOLUENE	0.0039	111.00	0.02	515.00	0.31	15.10
ETHYLBENZENE	0.5242	138.00	0.01	161.00	0.89	30.82
p-XYLENE	0.0202	138.00	0.01	198.00	0.89	40.38
STYRENE	0.0493	145.00	0.01	310.00	0.56	49.02
C9 ALKYL BENZENES	0.4020	159.00	0.00	60.00	3.02	98.28

PRESSURE ARRAY (ATMOSPHERES) AT TIME = 0.00 DAYS

```

1.0000 1.0000 1.0000 1.0000 1.0000 1.0000
1.0000 0.9999 0.9997 0.9995 0.9998 1.0000

```

1.0000	0.9997	0.9991	0.9984	0.9993	1.0000
1.0000	0.9996	0.9984	0.9953	0.9988	1.0000
1.0000	0.9998	0.9994	0.9988	0.9996	1.0000
1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

RELATIVE PERMEABILITY ARRAY (DARCY) :

50.	50.	50.	50.	50.	50.
50.	12.	12.	12.	12.	50.
50.	12.	12.	12.	12.	50.
50.	12.	8.9	9.7	12.	50.
50.	12.	10.	11.	12.	50.
50.	50.	50.	50.	50.	50.

X-DIRECTION DISCHARGES (CM/SEC) :

0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-0.46E-03	-0.47E-03	-0.30E-03	0.57E-03	0.78E-03	0.00E+00
-0.12E-02	-0.14E-02	-0.15E-02	0.22E-02	0.24E-02	0.00E+00
-0.15E-02	-0.23E-02	-0.54E-02	0.71E-02	0.43E-02	0.00E+00
-0.71E-03	-0.89E-03	-0.11E-02	0.16E-02	0.16E-02	0.00E+00
-0.92E-07	-0.92E-07	-0.92E-07	-0.92E-07	-0.92E-07	0.00E+00

Y-DIRECTION DISCHARGES (CM/SEC) :

0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-0.92E-07	0.46E-03	0.12E-02	0.17E-02	0.78E-03	0.00E+00
-0.92E-07	0.45E-03	0.14E-02	0.26E-02	0.99E-03	0.00E+00
-0.92E-07	0.23E-03	0.13E-02	0.62E-02	0.12E-02	0.00E+00
-0.92E-07	-0.52E-03	-0.17E-02	-0.68E-02	-0.16E-02	0.00E+00
-0.92E-07	-0.71E-03	-0.20E-02	-0.40E-02	-0.16E-02	0.00E+00

REMAINING TOTAL CONC. (MG/KG) AT TIME = 0.00 DAYS

0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0.00E+00	0.60E-01	0.19E-01	0.30E-01	0.15	0.00E+00
0.00E+00	3.2	5.1	26.	49.	0.00E+00
0.00E+00	20.	0.13E+05	0.98E+04	70.	0.00E+00
0.00E+00	61.	0.82E+04	0.44E+04	12.	0.00E+00
0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

(TOTAL MASS = 0.3040E+07 GRAMS)

REMAINING TOTAL SOIL GAS CONC. (MG/L) AT TIME = 0.00 DAYS

0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0.00E+00	0.83E-02	0.27E-02	0.41E-02	0.20E-01	0.00E+00
0.00E+00	0.43	0.70	3.5	6.8	0.00E+00
0.00E+00	2.8	24.	24.	9.6	0.00E+00
0.00E+00	8.4	24.	24.	1.7	0.00E+00
0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

CONCENTRATION OF VOLATILES IN SOIL GAS AT THE 4, 3 NODE, T = 0.00 DAYS:

COMPOUND	MG/L	PERCENT OF VOCS
BENZENE	0.1115	0.4567
TOLUENE	0.4187	1.7149
ETHYLBENZENE	17.6205	72.1730
p-XYLENE	0.6306	2.5827
STYRENE	1.3433	5.5023
C9 ALKYL BENZENES	4.2897	17.5703
TOTAL	24.4142	

REMAINING ETHYLBENZENE IN SOIL (MG/KG) AT TIME = 0.00 DAYS

0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0.00E+00	0.32E-01	0.10E-01	0.16E-01	0.78E-01	0.00E+00
0.00E+00	1.7	2.7	13.	26.	0.00E+00

0.00E+00 11. 0.69E+04 0.51E+04 37. 0.00E+00
 0.00E+00 32. 0.43E+04 0.23E+04 6.4 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.1594E+07 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

REMAINING WATER IN SOIL (WEIGHT PERCENT) AT TIME = 0.00 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.1359E+09 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

MOLE BALANCE CALCULATIONS AT TIME = 0.00 DAYS

COMPOUND	INITIAL MOLES	PUMPED MOLES	DIFF. LOSS MOLES	RESIDUAL MOLES	PERCENT ERROR
BENZENE	11.8	0.000E+00	0.000E+00	11.8	???????????
TOLUENE	129.	0.000E+00	0.000E+00	129.	???????????
ETHYLBENZENE	0.150E+05	0.000E+00	0.000E+00	0.150E+05	-200.
p-XYLENE	579.	0.000E+00	0.000E+00	579.	???????????
STYRENE	0.144E+04	0.000E+00	0.000E+00	0.144E+04	???????????
C9 ALKYL BENZENES	0.102E+05	0.000E+00	0.000E+00	0.102E+05	???????????

MASS BALANCE CALCULATIONS AT TIME = 0.00 DAYS

PUMPED MASS	DIFF. LOSS	MASS REMAINING	INITIAL MASS	MASS ERROR (%)	ERROR (%)
0.0000E+00	0.0000E+00	0.3040E+07	0.3040E+07	0.000E+00	???????????

REMAINING TOTAL CONC. (MG/KG) AT TIME = 300.68 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.19E-02 0.13E-02 0.61E-03 0.68E-03 0.00E+00
 0.00E+00 0.89E-02 0.00E+00 0.78E-01 0.48E-03 0.00E+00
 0.00E+00 0.61 0.84E+04 45. 0.00E+00 0.00E+00
 0.00E+00 1.0 0.45E+04 29. 0.00E+00 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.1107E+07 GRAMS)

REMAINING TOTAL SOIL GAS CONC. (MG/L) AT TIME = 300.68 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.12E-03 0.82E-04 0.37E-04 0.41E-04 0.00E+00
 0.00E+00 0.64E-03 0.00E+00 0.97E-02 0.29E-04 0.00E+00
 0.00E+00 0.66E-01 22. 5.5 0.00E+00 0.00E+00
 0.00E+00 0.11 21. 3.4 0.00E+00 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

CONCENTRATION OF VOLATILES IN SOIL GAS AT THE 4, 3 NODE, T = 300.68 DAYS:

COMPOUND	MG/L	PERCENT OF VOCS
BENZENE	0.0000	0.0001
TOLUENE	0.0165	0.3024
ETHYLBENZENE	3.5872	65.7319
p-XYLENE	0.1350	2.4744
STYRENE	0.3125	5.7264
C9 ALKYL BENZENES	1.4061	25.7649
TOTAL	5.4573	

REMAINING ETHYLBENZENE IN SOIL (MG/KG) AT TIME = 300.68 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.14E-04 0.11E-04 0.00E+00 0.28E-07 0.00E+00
 0.00E+00 0.65E-03 0.00E+00 0.34E-01 0.00E+00 0.00E+00

0.00E+00 0.19 0.36E+04 18. 0.00E+00 0.00E+00
 0.00E+00 0.32 0.18E+04 11. 0.00E+00 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.4563E+06 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

REMAINING WATER IN SOIL (WEIGHT PERCENT) AT TIME = 300.68 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 10. 10. 10.0 10. 0.00E+00
 0.00E+00 10. 10.0 10. 10.0 0.00E+00
 0.00E+00 10. 10. 10.0 10. 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.1359E+09 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

MOLE BALANCE CALCULATIONS AT TIME = 300.68 DAYS

COMPOUND	INITIAL MOLES	PUMPED MOLES	DIFF. LOSS MOLES	RESIDUAL MOLES	PERCENT ERROR
BENZENE	11.8	-11.8	0.000E+00	0.109E-02	0.364E-01
TOLUENE	129.	-122.	0.000E+00	6.80	0.432E-01
ETHYLBENZENE	0.150E+05	-0.107E+05	0.000E+00	0.430E+04	0.435E-01
p-XYLENE	579.	-404.	0.000E+00	175.	0.396E-01
STYRENE	0.144E+04	-964.	0.000E+00	476.	0.368E-01
C9 ALKYL BENZENES	0.102E+05	-0.532E+04	0.000E+00	0.484E+04	0.316E-01

MASS BALANCE CALCULATIONS AT TIME = 300.68 DAYS

PUMPED MASS	DIFF. LOSS	MASS REMAINING	INITIAL MASS	MASS ERROR (%)	ERROR (%)
-.1933E+07	0.0000E+00	0.1107E+07	0.3040E+07	0.152E-01	0.391E-01

REMAINING TOTAL CONC. (MG/KG) AT TIME = 661.71 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.87E-04 0.76E-03 0.39E-03 0.26E-05 0.00E+00
 0.00E+00 0.48E-02 0.21 0.15 0.43E-04 0.00E+00
 0.00E+00 0.87 0.35E+04 47. 0.00E+00 0.00E+00
 0.00E+00 1.2 0.11E+04 30. 0.11E-01 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.3982E+06 GRAMS)

REMAINING TOTAL SOIL GAS CONC. (MG/L) AT TIME = 661.71 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.76E-05 0.81E-04 0.40E-04 0.25E-06 0.00E+00
 0.00E+00 0.45E-03 0.20E-01 0.14E-01 0.46E-05 0.00E+00
 0.00E+00 0.74E-01 16. 4.0 0.00E+00 0.00E+00
 0.00E+00 0.92E-01 14. 2.2 0.93E-03 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

CONCENTRATION OF VOLATILES IN SOIL GAS AT THE 4, 3 NODE, T = 661.71 DAYS:

COMPOUND	MG/L	PERCENT OF VOCS
BENZENE	0.0000	0.0000
TOLUENE	0.0001	0.0016
ETHYLBENZENE	1.4778	37.0501
p-XYLENE	0.0649	1.6268
STYRENE	0.1909	4.7873
C9 ALKYL BENZENES	2.2549	56.5343
TOTAL	3.9886	

REMAINING ETHYLBENZENE IN SOIL (MG/KG) AT TIME = 661.71 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.15E-04 0.23E-03 0.11E-03 0.64E-06 0.00E+00
 0.00E+00 0.11E-02 0.47E-01 0.32E-01 0.13E-04 0.00E+00

0.00E+00 0.14 0.64E+03 7.6 0.00E+00 0.00E+00
 0.00E+00 0.13 88. 2.6 0.15E-02 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.6289E+05 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

REMAINING WATER IN SOIL (WEIGHT PERCENT) AT TIME = 661.71 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 10. 10. 10.0 10. 0.00E+00
 0.00E+00 10. 10.0 10. 10.0 0.00E+00
 0.00E+00 10. 10. 10.0 10. 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.1359E+09 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

MOLE BALANCE CALCULATIONS AT TIME = 661.71 DAYS

COMPOUND	INITIAL MOLES	PUMPED MOLES	DIFF. LOSS MOLES	RESIDUAL MOLES	PERCENT ERROR
BENZENE	11.8	-11.8	0.000E+00	0.835E-13	0.362E-01
TOLUENE	129.	-129.	0.000E+00	0.891E-02	0.499E-01
ETHYLBENZENE	0.150E+05	-0.144E+05	0.000E+00	592.	0.674E-01
p-XYLENE	579.	-551.	0.000E+00	28.5	0.649E-01
STYRENE	0.144E+04	-0.134E+04	0.000E+00	99.0	0.630E-01
C9 ALKYL BENZENES	0.102E+05	-0.749E+04	0.000E+00	0.268E+04	0.552E-01

MASS BALANCE CALCULATIONS AT TIME = 661.71 DAYS

PUMPED MASS	DIFF. LOSS	MASS REMAINING	INITIAL MASS	MASS ERROR (%)	ERROR (%)
-.2643E+07	0.0000E+00	0.3982E+06	0.3040E+07	0.292E-01	0.628E-01

REMAINING TOTAL CONC. (MG/KG) AT TIME = 1094.99 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.28E-03 0.21E-02 0.75E-03 0.22E-04 0.00E+00
 0.00E+00 0.55E-02 0.33E-01 0.14E-01 0.20E-03 0.00E+00
 0.00E+00 0.74E-01 0.14 0.41E-01 0.29E-03 0.00E+00
 0.00E+00 0.29E-01 0.49E-01 0.13E-01 0.21E-03 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 33.79 GRAMS)

REMAINING TOTAL SOIL GAS CONC. (MG/L) AT TIME = 1094.99 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.17E-04 0.13E-03 0.46E-04 0.14E-05 0.00E+00
 0.00E+00 0.33E-03 0.20E-02 0.83E-03 0.12E-04 0.00E+00
 0.00E+00 0.45E-02 0.84E-02 0.25E-02 0.17E-04 0.00E+00
 0.00E+00 0.18E-02 0.30E-02 0.78E-03 0.13E-04 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

CONCENTRATION OF VOLATILES IN SOIL GAS AT THE 4, 3 NODE, T = 1094.99 DAYS:

COMPOUND	MG/L	PERCENT OF VOCS
BENZENE	0.0000	0.0000
TOLUENE	0.0000	0.0000
ETHYLBENZENE	0.0000	0.0004
p-XYLENE	0.0000	0.0002
STYRENE	0.0000	0.0057
C9 ALKYL BENZENES	0.0025	99.9937
TOTAL	0.0025	

REMAINING ETHYLBENZENE IN SOIL (MG/KG) AT TIME = 1094.99 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.69E-07 0.53E-07 0.12E-07 0.73E-09 0.00E+00
 0.00E+00 0.82E-07 0.12E-06 0.43E-07 0.68E-09 0.00E+00

0.00E+00 0.11E-06 0.14E-06 0.47E-07 0.30E-09 0.00E+00
 0.00E+00 0.12E-06 0.76E-07 0.16E-07 0.14E-09 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.7600E-04 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

REMAINING WATER IN SOIL (WEIGHT PERCENT) AT TIME = 1094.99 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 10. 10. 10. 10. 0.00E+00
 0.00E+00 10. 10. 10.0 10. 0.00E+00
 0.00E+00 10. 10.0 10. 10.0 0.00E+00
 0.00E+00 10. 10. 10.0 10. 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.1359E+09 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

MOLE BALANCE CALCULATIONS AT TIME = 1094.99 DAYS

COMPOUND	INITIAL MOLES	PUMPED MOLES	DIFF. LOSS MOLES	RESIDUAL MOLES	PERCENT ERROR
BENZENE	11.8	-11.8	0.000E+00	0.000E+00	0.362E-01
TOLUENE	129.	-129.	0.000E+00	0.000E+00	0.494E-01
ETHYLBENZENE	0.150E+05	-0.150E+05	0.000E+00	0.716E-06	0.651E-01
p-XYLENE	579.	-579.	0.000E+00	0.520E-06	0.616E-01
STYRENE	0.144E+04	-0.144E+04	0.000E+00	0.142E-04	0.587E-01
C9 ALKYL BENZENES	0.102E+05	-0.102E+05	0.000E+00	0.281	0.416E-01

MASS BALANCE CALCULATIONS AT TIME = 1094.99 DAYS

PUMPED MASS	DIFF. LOSS	MASS REMAINING	INITIAL MASS	MASS ERROR (%)	ERROR (%)
-.3042E+07	0.0000E+00	33.79	0.3040E+07	0.276E-01	0.552E-01

REMAINING TOTAL CONC. (MG/KG) AT TIME = 1095.00 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.28E-03 0.21E-02 0.75E-03 0.22E-04 0.00E+00
 0.00E+00 0.55E-02 0.33E-01 0.14E-01 0.20E-03 0.00E+00
 0.00E+00 0.74E-01 0.14 0.41E-01 0.29E-03 0.00E+00
 0.00E+00 0.29E-01 0.49E-01 0.13E-01 0.21E-03 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 33.78 GRAMS)

REMAINING TOTAL SOIL GAS CONC. (MG/L) AT TIME = 1095.00 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.17E-04 0.13E-03 0.46E-04 0.14E-05 0.00E+00
 0.00E+00 0.33E-03 0.20E-02 0.83E-03 0.12E-04 0.00E+00
 0.00E+00 0.45E-02 0.84E-02 0.25E-02 0.18E-04 0.00E+00
 0.00E+00 0.18E-02 0.30E-02 0.78E-03 0.13E-04 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

CONCENTRATION OF VOLATILES IN SOIL GAS AT THE 4, 3 NODE, T = 1095.00 DAYS:

COMPOUND	MG/L	PERCENT OF VOCS
BENZENE	0.0000	0.0000
TOLUENE	0.0000	0.0000
ETHYLBENZENE	0.0000	0.0004
p-XYLENE	0.0000	0.0002
STYRENE	0.0000	0.0057
C9 ALKYL BENZENES	0.0025	99.9937
TOTAL	0.0025	

REMAINING ETHYLBENZENE IN SOIL (MG/KG) AT TIME = 1095.00 DAYS

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
 0.00E+00 0.69E-07 0.53E-07 0.12E-07 0.73E-09 0.00E+00
 0.00E+00 0.82E-07 0.12E-06 0.43E-07 0.68E-09 0.00E+00

0.00E+00 0.11E-06 0.14E-06 0.47E-07 0.30E-09 0.00E+00
 0.00E+00 0.12E-06 0.76E-07 0.16E-07 0.14E-09 0.00E+00
 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00

(TOTAL MASS = 0.7597E-04 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

REMAINING WATER IN SOIL (WEIGHT PERCENT) AT TIME = 1095.00 DAYS

-0.35E-03 -0.35E-03 -0.35E-03 -0.35E-03 -0.35E-03 -0.35E-03
 -0.35E-03 10. 10. 10. 10. -0.35E-03
 -0.35E-03 10. 10. 10.0 10. -0.35E-03
 -0.35E-03 10. 10.0 10. 10.0 -0.35E-03
 -0.35E-03 10. 10. 10.0 10. -0.35E-03
 -0.35E-03 -0.35E-03 -0.35E-03 -0.35E-03 -0.35E-03 -0.35E-03

(TOTAL MASS = 0.1359E+09 GRAMS)

(MASS FLUX = 0.0000E+00 GM/SEC INTO DIFF. ZERO CELLS)

MOLE BALANCE CALCULATIONS AT TIME = 1095.00 DAYS

COMPOUND	INITIAL MOLES	PUMPED MOLES	DIFF. LOSS MOLES	RESIDUAL MOLES	PERCENT ERROR
BENZENE	11.8	-11.8	0.000E+00	0.000E+00	0.362E-01
TOLUENE	129.	-129.	0.000E+00	0.000E+00	0.494E-01
ETHYLBENZENE	0.150E+05	-0.150E+05	0.000E+00	0.715E-06	0.651E-01
p-XYLENE	579.	-579.	0.000E+00	0.520E-06	0.616E-01
STYRENE	0.144E+04	-0.144E+04	0.000E+00	0.142E-04	0.587E-01
C9 ALKYL BENZENES	0.102E+05	-0.102E+05	0.000E+00	0.281	0.416E-01

MASS BALANCE CALCULATIONS AT TIME = 1095.00 DAYS

PUMPED MASS	DIFF. LOSS	MASS REMAINING	INITIAL MASS	MASS ERROR (%)	ERROR (%)
-.3042E+07	0.0000E+00	33.78	0.3040E+07	0.276E-01	0.552E-01

TOTAL MASSES OF SELECTED COMPOUNDS WITH TIME:

TIME	TOTAL	ETC.-- (H2O LAST) -->
0.000E+00	0.304E+07	0.159E+07 0.136E+09
0.301E+03	0.111E+07	0.456E+06 0.136E+09
0.662E+03	0.398E+06	0.629E+05 0.136E+09
0.109E+04	0.338E+02	0.760E-04 0.136E+09
0.109E+04	0.338E+02	0.760E-04 0.136E+09

ABSTRACT

ABSTRACT

Prediction of the transport of volatile mixtures within unsaturated soils can be complicated by the interaction of chemical compounds with variable physical properties. The analysis and design of vapor-extraction remedial systems depends on models which can simulate the chemical and physical factors which affect the removal of vapor-phase chemical mixtures, such as gasoline. Present models fall into two categories: 1) non-dimensional (no transport), multi-compound phase distribution models or 2) multi-dimensional, single-compound transport models. In this paper, a numerical simulation is presented which couples the steady-state vapor flow equation, the parabolic advection-diffusion transport equation, and a multiple-compound, four-phase equilibrium model. The simulation allows spatially variable fields of permeability, surface leakage, and initial contaminant concentrations. The user can specify the location and discharge rates of any number of extraction or injection wells, including zero wells, in which case the simulation will solve transport by diffusion only. The utility of the model is shown by solving hypothetical gasoline spill remediation by vapor extraction when the natural conditions are non-ideal. The non-ideal conditions include inhomogeneous soil permeability, irregular surface leakage (from fill areas or surface seals), and irregular contaminant distribution. The model is also run in the pure diffusion mode to show the limitations of three-phase (no separate-phase), single-compound vapor flux models in predicting chemical fate and transport.