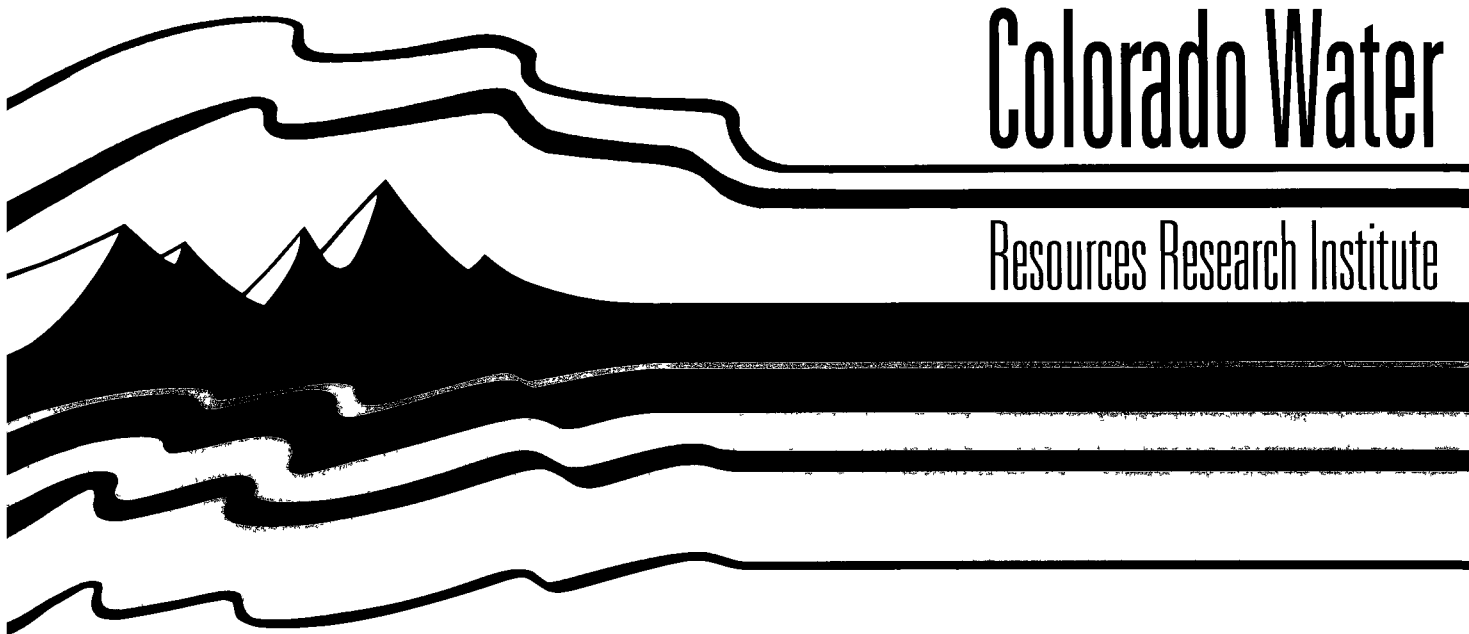


Technology Effectiveness Assessment of Soil Vapor Extraction

by
David Barnes
David McWhorter
Robert Ward

October 1994

Technical Report No. 62



Colorado Water

Resources Research Institute

The activities on which this report is based were financed in part by the Department of Energy and by the Department of the Interior, U.S. Geological Survey through the Colorado Water Resources Research Institute. The report is prepared as part of the requirements for Grant No. 14-08-0001-G2008. The contents of this publication do not necessarily reflect the views and policies of the Departments of Energy or Interior, nor does mention of trade names or commercial products constitute their endorsement by the United States Government.



The Water Resources Research Act at Work on America's Water Problems...

U. S. Department of Energy
National Institutes for Water Resources
Technology Integration Program Project

Technology Effectiveness Assessment of Soil Vapor Extraction

Prepared by

David Barnes, David McWhorter, Robert Ward
Colorado Water Resources Research Institute

Table of Contents

Preface	
1. Introduction	1
2. Basic Science Principles of Unsaturated Zone Contaminant Transport	1
2.1 Gas Flow Through Porous Media	1
2.1.1 Background	1
2.1.2 Properties of Porous Media	2
2.1.3 Fluid Flow Through Porous Media	5
2.2 Mass Transfer of VOCs to Gas Flow	8
2.2.1 Advection and Diffusion	8
2.2.2 Volatilization From a Compound in Equilibrium	9
2.2.3 Volatilization From an Aqueous State in Equilibrium	12
2.2.4 Sorption	14
2.2.5 Non-Equilibrium	15
2.2.6 Advection-Diffusion Equation	16
3. Description of Soil Vapor Extraction Design Variables	17
3.1 Description of SVE Systems	17
3.2 Design Variables	18
3.2.1 Site Geology/Hydrogeology	18
3.2.2 Soil Characteristics	23
3.2.3 Physical Characteristics of VOCs	30
4. Assessment of Soil Vapor Extraction	32
4.1 Optimum Conditions and Sensitivity to Non-Optimum Conditions	32
4.2 Performance Measures	34
4.3 Expected Costs of SVE Systems	34
5. Conclusion	35
6. References	36

List of Tables

1. Particle Size Limits of Soil Constituents, ASTM Classification	3
2. Vapor Pressures of Some Common Compounds Found in Ground Water	10
3. Solubility in Water of Some Common Compounds Found in Ground Water	12
4. Henry's Law Constant of Some Common Compounds Found in Ground Water	13
5. Intrinsic Permeabilities of Different Soil Types	32

List of Figures

1. Characteristic water retention curve	3
2. Effects of diffusion in a heterogeneous medium	19
3. Cross sectional schematic of the conditions used in the model to determine the effects water table depth has on the gas flux through the ground surface	20
4. Effects of water table depth on gas flux through the ground surface	21
5. Schematic of the conditions used in the model to compare the effect on the gas flux through the unsaturated zone of a capped surface versus an uncapped surface	22
6. Effect of capped surface on vapor flux at a constant horizontal distance from the extraction well	23
7. Relative air phase permeability as a function of capillary pressure	25
8. Vapor concentration as a function of temperature	27
9. Change in vapor concentration from dissolved state with temperature	28
10. Schematic of the conditions used in the model to compare the effect the value of permeability has on the gas flux through the ground surface	29
11. Effects of the value of permeability on gas flux through the ground surface	29
12. Effect of vapor pressure on equilibrium NAPL vapor phase concentration	30
13. Effect of Henry's Law Constant on equilibrium vapor phase concentration from an aqueous phase solution	31

Preface

A great deal of time, effort, and money have been expended in the United States toward the goal of remediating contaminated ground waters. Such effort was mandated by law, long before it was known whether restoration of ground water was technically feasible. The restoration mandate was also recognized as having important implications for the probable success or failure of remediation efforts.

The mandate to restore aquifers, essentially to their pre-contamination status, has motivated the appearance of many technologies intended for that purpose. It has also fostered a proliferation of vendors of those technologies, all too often with overly optimistic claims for their performance and effectiveness. The user community, under pressure to do something, has embraced these technologies without thorough understanding of the site-specific performance that could actually be achieved.

All of this has combined to result in a colossal expenditure with very little return. To this day, for example, there does not exist in the refereed literature a documented case of ground-water restoration to maximum contaminant level (MCL) in an aquifer originally contaminated with dense, nonaqueous-phase liquids. Instead of a gradual increase in the appearance of documented success stories, as might be anticipated, there are more documented failures.

The success or failure of a technology at a particular site is tied directly to the standard against which success will be judged. A typical standard is the drinking-water MCL. To achieve this level often requires that contaminants be reduced by several orders of magnitude in concentration, relative to the source concentrations. Furthermore, such low target concentrations in restored ground water translate to virtually 100 percent removal. Chlorinated hydrocarbons are among the most common contaminants of ground water, and they are particularly difficult to remove at the source. Even minute quantities left in the subsurface are sufficient to cause continuing ground-water contamination.

There exists a large gulf between restoration requirements and that which is technologically feasible. Few on either side have been willing to admit to this conflict. However, the empirical evidence is accumulating that makes denial an increasingly untenable position. There is now wording in regulations, position papers, and guidance documents that show recognition of the fact that technology is sometimes incapable of achieving that which we desire, no matter how much effort and money are spent. There is also an increased willingness on the part of scientists, engineers, and technology vendors to openly discuss the inherent limitations of technology.

This easing of tension is healthy and productive, and it will go a long way to eliminate the waste of resources by trying to achieve that which is not achievable. On the other hand, technology limitations should not become a crutch used to justify no action when there are sensible things that could be done. Reaching an appropriate balance in this regard depends primarily on knowledge of performance effectiveness and applicability of technologies under consideration. It is the goal of this project to contribute to attaining the right balance at contaminated sites by providing thorough assessments of technology effectiveness.

The following technology effectiveness assessment of soil vapor extraction is part of a larger project conducted by the National Institutes for Water Resources (NIWR) for the United States Department of Energy. This technology effectiveness assessment is the first of an intended series of assessments on ground water and soil remediation technologies.

Technology Effectiveness Assessment of Soil Vapor Extraction

1. Introduction

Aeration of soils by inducing an air flow through the medium is not a new technology. Blight (1971) describes the use of in-situ aeration for solution mining of low grade ore deposits. The first reported use of soil aeration for removal of volatile organic compounds from soil was in 1983 (Terra Vac Corp., 1990). Since then, soil aeration by vapor extraction techniques has become a popular method for removing volatile organic compounds (VOCs) from the soil.

Soil vapor extraction (SVE) is an in-situ treatment technology based on the principle that volatile compounds contained in the unsaturated zone will volatilize and establish an equilibrium with the air contained within the pore space between the soil particles. Once equilibrium between the air and the compound is established, the transport of the compound within the unsaturated zone is limited to diffusion, and advection by infiltrated water toward the saturated zone. The volatilization rate of the compound can be enhanced by replacing air within the pore space with relatively fresh air.

The air flow is established either by evacuating air, creating a negative pressure or by forcing air into the unsaturated zone, creating a positive pressure. The most common method is evacuating air because it allows control over the contaminated air flow. The vacuum is created by attaching a blower or vacuum pump to an extraction well, which on pulling the vapor toward the well, causes fresh air to be pulled into the soil column. The soil-gas that is extracted is then treated to remove any contaminants before its discharge to ambient air. The principles of this technology and the variables controlling the design are discussed in more detail within this text.

2. Basic Science Principles of Unsaturated Zone Contaminant Transport

The validity of soil vapor extraction (SVE) as a treatment technology will be established by first investigating the basic science underlying the principles of the technology. The basic science will then be applied to the engineering aspects associated with the application of SVE to the subsurface.

2.1 Gas Flow Through Porous Media

2.1.1 Background

The subsurface can be divided into two major sections, the saturated zone and the unsaturated zone (often referred to as the vadose zone). Each of these sections can be further divided into subsections. The main area with which SVE is concerned is the unsaturated zone, but in order to establish a basis for examining the unsaturated zone, the zone of saturation will be examined as well.

The unsaturated zone is divided into three subsections: the soil water zone, the intermediate zone, and the capillary fringe. The uppermost zone is termed the soil water zone. This zone extends from the surface down through the vegetation root zone. The moisture contained within the soil water zone is directly affected by conditions on the ground surface. The fluctuation in water content within this zone is influenced by humidity, seasonal and diurnal patterns of precipitation, infiltration through irrigation practices, evapotranspiration, evaporation and the presence of shallow water tables. This zone usually extends from 3 to 30 feet below the ground surface.

Below the soil water zone is the intermediate zone. This zone extends from the soil water zone to the capillary fringe. In comparison to the other zones within the subsurface, this zone contains

a relatively small volume of water.

The capillary fringe contains water that has been drawn up from the ground water table by capillary action. The height of the zone is determined by the soil type within the zone. Fine well-graded sediment can draw water to greater heights than coarse grained sediment. Below the capillary fringe lies the ground water table, which is the surface on which the water pressure is atmospheric.

The saturated zone can be visualized as a huge natural reservoir or system of reservoirs in the sediment whose capacity for holding water is determined by the total volume of space between the sediment particles (called the total pore space). The ground water in the saturated zone is contained in an aquifer, which is a saturated geologic formation that is able to produce water through wells. Other geologic formations within the saturated zone that cannot produce sufficient quantities of water are called aquitards. Formations within the saturated zone that are impermeable to water are called aquicludes.

Zones of saturation can also be contained in areas of the unsaturated zone. These saturated zones, called perched water, are a result of low permeability layers located in the unsaturated zone that are capable of restricting the downward flow of infiltrated water.

In porous media, the rate of gas flow depends on the moisture content of the soil in which flow is occurring. The unsaturated zone retains moisture predominantly due to interfacial forces. When water and air are in contact in a porous medium, a curved surface develops at the interface. Capillary pressure is the difference between the air pressure and the water pressure at this interface. Capillary pressure is zero at the water table and increases with distance above the water table.

The amount of soil moisture in the unsaturated zone can be illustrated by a characteristic curve called a water retention curve. Figure 1 shows a representative water retention curve. On this graph, the abscissa is the saturation (the volume fraction of the total pore volume that is occupied by the water). Capillary pressure is on the ordinate. The capillary fringe on this graph extends from the point of zero capillary pressure up through where the saturation remains practically unity. In this figure, the displacement pressure P_d represents the capillary pressure necessary for the coexistence of two continuous fluids. In the region of low moisture content a point is reached where the capillary pressure increases rapidly with negligible decrease in the volumetric water content. The saturation where this occurs is termed the specific retention, S_r .

2.1.2 Properties of Porous Media

It is difficult to provide an exact definition of porous media. Bear (1972), used the following:

- (a) [Porous media is] a portion of space occupied by heterogeneous or multiphase matter. At least one of the phases comprising this matter is not solid. They may be gaseous and/or liquid phases. The solid phase is called the solid matrix. That space within the porous medium domain that is not part of the solid matrix is referred to as void space (or pore space).
- (b) The solid phase should be distributed throughout the porous medium within the domain occupied by a porous medium; solids must be present inside each

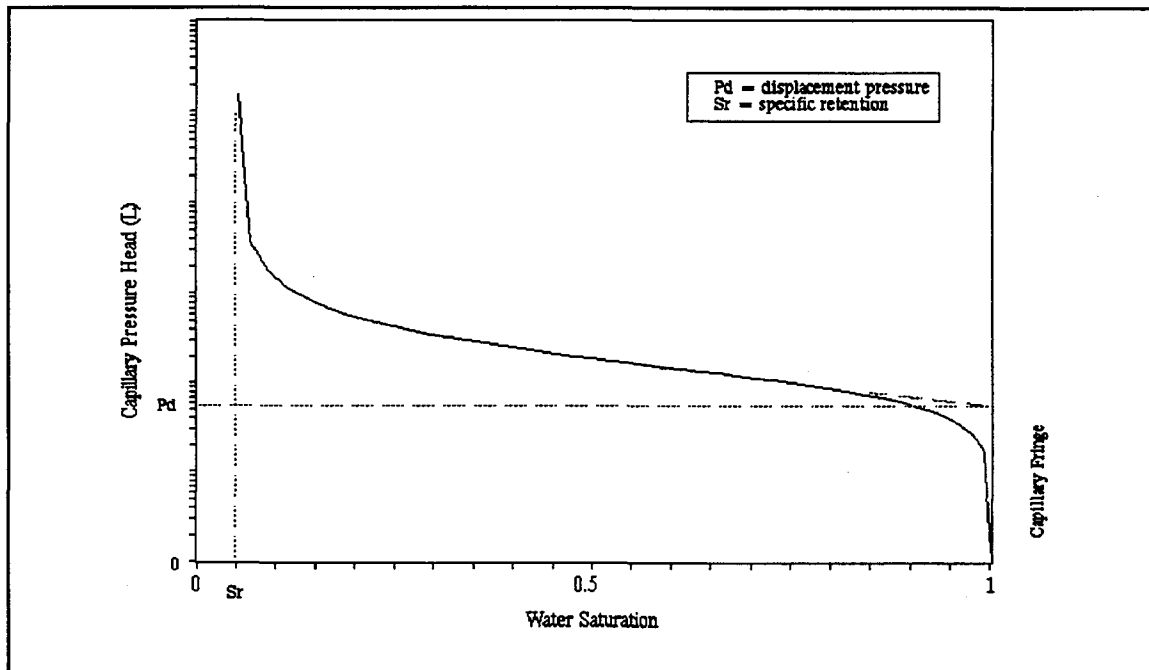


Figure 1. Characteristic water retention curve.

representative elementary volume. An essential characteristic of a porous medium is that the specific surface of the solid matrix is relatively high. In many respects, this characteristic dictates the behavior of fluids in porous media. Another basic feature of a porous medium is that the various openings comprising the void space are relatively narrow.

(c) At least some of the pores comprising the void space should be interconnected.

The principal types of materials that constitute porous media are clay, silt, sand, gravel, and rock. The sediment in the porous medium will generally be a mixture of these constituents. In some cases porous media contain fractured rock only. Fluid flow through fractured rock can be difficult to describe due to the heterogenous connections of the fractures. For engineering purposes, the most commonly used sediment size limits are those developed by the American Society of Testing Materials (ASTM). This classification is shown in Table 1 (Peck, 1974).

Table 1. Particle Size Limits of Soil Constituents, ASTM Classification (Peck, 1974)

Soil Type	Size Limit (mm)
Gravel	Larger than 4.75
Coarse sand	4.75 - 2.00
Medium sand	2.00 - 0.425
Fine sand	0.425 - 0.075
Fines (combined silt and clay)	Smaller than 0.075

The particle size distribution of a sample is determined by an analysis technique described in Driscoll (1986) and Peck (1974). Results of the particle-size analysis are expressed as percentages of the sample fraction on a dry-weight basis. These results can be plotted on a graph and used to describe the uniformity properties of the soil. The uniformity of the soil can be inferred by the slope of the middle portion of the curve. If the soil is well graded, that is, the soil has particles of many different sizes, the slope of the middle portion of the curve is gradual. If the soil is uniform, that is, the soil is made up of predominantly one particle size, the slope of the middle section of the curve is steep. A more analytical method of determining the uniformity of a soil can be described using the uniformity coefficient. This coefficient is defined as the 40% retained size of the sediment divided by the 90% retained size. A low value represents a more uniform grading or well graded soil. Uniformity coefficients above five have no meaning.

Four additional properties of subsurface materials that are important to vapor transport through the unsaturated zone are the specific surface of the soil matrix, the porosity of the soil, the permeability of the soil, and the water content. Porosity of soil is determined by the portion of the soils that are openings or pores and the portion of the soils that are solid material. This value is mathematically represented as the volume of voids divided by the total volume. The porosity of soils is related to its uniformity. Uniform soils have higher porosities due to the lack of smaller material that tends to fill in the void spaces in well-graded materials. The shape of soil particles also relates to porosity. Soil matrices composed of well-rounded particles will have relatively higher porosities. Fine textured soils have higher porosities than coarse textured materials.

The intrinsic permeability (hereafter referred to as permeability) of the soil is a measure of the ability of a soil to transmit fluid and is a function of the properties of the porous medium only. Conductivity is a coefficient of proportionality that describes the rate at which a fluid can move through the porous medium. Conductivity takes into account the density and dynamic viscosity of the fluid and the physical properties of the soil. When water is the fluid, this term is referred to as hydraulic conductivity. (In this report some of the units used will be expressed as: mass (M), length (L), time (t), and temperature (T).) The relationship between permeability and conductivity is defined as the following:

$$k = \frac{K\mu}{\rho g} \quad (1)$$

where: k = permeability (L²)
 K = conductivity (L/t)
 μ = viscosity (M/Lt)
 ρ = density (M/L³)
 g = acceleration due to gravity (L/t²)

As described above the porosity is a measure of the void space in the soil matrix. More important to permeability are the size and interconnection of these pores and the amount of dead end pores. Effective porosity can be defined as the ratio of the interconnected pore volume to the total pore volume of the medium.

The vertical permeability and the horizontal permeability of a soil profile will most likely be different because of how the layers of soil in the formation were deposited. During underwater deposition, soil particles, which are not normally spherical, generally will be deposited with the flat sides down. In flowing water the particle may be tilted slightly upward in the direction of flow. Thus, vertical permeability will be less than horizontal permeability. This difference is called anisotropy. Anisotropic permeability means that resistance to flow through the media depends on the direction of flow.

Ions contained in the infiltrated water may also have an effect on the permeability of soil. Clayey soils are composed of layers of negatively charged colloidal particles. Cations in soil-pore water will be attracted to the surface of the particles to normalize the negative charge, creating an electrostatic double layer. The size of the electrostatic double layer depends on the moisture content, the charge of the cation in solution (monovalent or divalent), and the concentration of the cations. The electrostatic double layer will tend to swell clay layers and possibly break off particles of the clay layer. The swelling of the clay layer and presence of the loose clay particles clog the pores in the soil, decreasing the permeability.

The specific surface of the soil matrix is defined as the total interstitial surface area of the pores per unit bulk volume of the porous medium. Fine-grained materials, such as clays, will have a higher specific surface than coarse-grained materials such as sands. The specific surface has an effect on two major aspects of gas flow through porous media, the frictional resistance to flow and the amount of surface area available for sorption of the contaminant to the soil particles. In high specific surface soils such as clay, the resistance to flow will increase, having a direct effect on the amount of soil gas that can be transported through the soil matrix. The effect on the sorption of contaminants will be addressed in Section 2.2.4.

The homogeneity of the soil media has a marked effect on the gas flow over large areas. Fluids will tend to take the path of least resistance in a porous medium. If the soil matrix is homogeneous, the flow through the soil column will be somewhat uniform. The flow of fluids through the non-homogeneous soil matrix will tend to be greater through the more permeable areas within the soil.

As shown in Figure 1, soil water content varies with the capillary pressure. The amount of fluid in the pore spaces has a large effect on the permeability of the soil to liquid and gas flow. This effect will be explored further in Section 3.2.2.

2.1.3 Fluid Flow Through Porous Media

Fluid flow through porous media depends on the composition of the porous media and on the properties of the fluid. The driving forces of fluid flow are pressure gradients and gravitational forces. Fluid flow through porous media also experiences resistant forces. These forces are predominantly surface forces due to shear resulting from the drag of the solid particles on the viscous fluid.

Fluid flow in a porous media follows a tortuous path as it flows about the soil particles that make up the porous matrix. As the fluid moves through the soil matrix it changes direction when it encounters the soil particles. Thus, the flow rate is dependent on the permeability of the soil matrix. The more permeable a soil matrix is the more fluid it can transmit. The dynamics of the flow through the permeable soil matrix depend upon whether the flow is laminar or turbulent. For a fluid flow to

be considered laminar, its velocity must be relatively slow with the fluid particles traveling in smooth paths relatively parallel to the pore space in the soil matrix. Turbulent flow, on the other hand, is a flow in which the water molecules travel in irregular paths, forming eddies. The velocity of both ground water and soil gas in porous media is normally slow so that the flow is considered laminar.

Flow rate through porous soil depends on the viscosity of the fluid. Viscosity can be defined as a fluid's resistance to shear forces. An ideal viscous fluid under laminar flow conditions will tend to adhere to the soil matrix particles forming a layer around their surface. This fluid can be considered to have a velocity of zero at points of contact with the solid. Adhesion is caused by interfacial tension, which is the amount of work required to separate a unit area of one substance from another. The adhesion of the flowing fluid to the particles will tend to move them, if they are not secure. If the particles are secure, a shear force will be created between the boundary layer and the passing fluid, which causes energy losses in the flow due to friction.

In the case where there is more than one fluid in the soil matrix the interfacial tension also distinguishes between a wetting fluid and a non-wetting fluid. In a two-fluid system, the wetting fluid is the one most strongly adsorbed to the soil surface while the non-wetting fluid is displaced. In the unsaturated zone where there is both water and air in the porous media, the water will tend to be the wetting fluid and the air will tend to be the non-wetting fluid.

The flow of fluid through a porous media changes direction and velocity frequently. A simple mathematical description of the flow in this situation is nearly impossible. A simplified description can be obtained by using an averaging process. The change in direction of fluid flow can be considered to follow a uniform distribution. The change in velocity can also be considered uniformly distributed and can be averaged out to zero on a macroscopic level.

The mathematical description of fluid flow in the subsurface can be generated by balancing the external forces acting on the fluid. This equation can be represented by the following one dimensional equation, which is the mathematical representation of Darcy's Law:

$$q = -\frac{k}{\mu} \left(\frac{dp}{dx} + \rho g \frac{dz}{dx} \right) \quad (2)$$

where:

- q = volume flux of fluid (L/t)
- k = intrinsic permeability (L²)
- p = pressure (ML/t²)
- x = length (L)
- g = acceleration due to gravity (L/t²)
- z = depth (L)
- μ = viscosity (M/Lt)
- ρ = density (M/L³)

The flux term q is defined as the volume of discharge per unit of bulk area of the soil matrix per unit of time. Bulk area is considered the area of both the pore space and solids.

The density of a gas found in the subsurface is considered negligible. Under this assumption the gravitational force per unit volume is considered zero, reducing the equation to the following:

$$q = -\frac{k}{\mu} \frac{dp}{dx} \quad (3)$$

For water, if the density is assumed constant, the equation is reduced to the following:

$$q = -K \frac{dh}{dx} \quad (4)$$

where: h = piezometric head (L)

In Equation 4 the piezometric head is a combination of the pressure head and the elevation head.

During gas flow through a porous medium, a situation sometimes occurs called slip flow, or the Klinkenberg effect. Viscous flow, from which Darcy's Law is derived, assumes that the velocity of fluid in contact with the solids is zero. Zero velocity does not occur during slip flow, resulting in higher apparent permeabilities and thus larger flows. Slip flow occurs in porous media when the pressures are low and the radii of the pore sizes are small, i.e., clay soils. In most SVE applications slip flow is not a factor due to the relatively large pore space radii.

Using Darcy's Law and an elemental volume, a three dimensional equation can be derived for the flow of water in saturated porous media, as follows:

$$K_x \frac{\partial^2 h}{\partial x^2} + K_y \frac{\partial^2 h}{\partial y^2} + K_z \frac{\partial^2 h}{\partial z^2} = S_s \frac{\partial h}{\partial t} \quad (5)$$

where: x, y, z = rectangular coordinate system (L)
 K_i = hydraulic conductivity in the i direction (L/t)
 S_s = specific storage coefficient (dimensionless)
 t = time

Specific storage is the volume of water that a permeable soil column will release from storage per unit volume of aquifer per unit decline in total head. This has no impact on vapor transport through the unsaturated zone. This partial-differential equation represents the piezometric head as a function of time and space in a confined aquifer. The solution to this equation is mathematically complex so simplifying assumptions have been made for the solution. Solutions to this equation for different conditions are presented in (Bear, 1979; McWhorter and Sunada, 1977). The purpose of presenting this equation is to show the similarity between the mathematical description of fluid flow through saturated porous media and the mathematical description of gas flow through unsaturated porous media.

Again, using Darcy's Law and an elemental volume, the equation for gas flow through unsaturated porous media can be derived. The derivation of this equation assumes the vapor behaves as an ideal gas and that there is a uniform water content. This equation is as follows:

$$\frac{k_x}{\mu} \frac{\partial (P \frac{\partial P}{\partial x})}{\partial x} + \frac{k_y}{\mu} \frac{\partial (P \frac{\partial P}{\partial y})}{\partial y} + \frac{k_z}{\mu} \frac{\partial (P \frac{\partial P}{\partial z})}{\partial z} = \frac{\partial (P\phi)}{\partial t} \quad (6)$$

where: k = intrinsic permeability (L^2)
 P = pressure (F/L^2)
 ϕ = porosity
 μ = viscosity (M/Lt)

Simplifying assumption can be made to solve the above equation for different boundary conditions. Comparing equation (5) and equation (6), the main difference between these two equations is the density of water that is assumed constant in equation (5). The use of equation (6) will be shown in subsequent sections.

2.2 Mass Transfer of VOCs to Gas Flow

Contaminants can exist in the soil pores in the unsaturated zone in different phases: non-aqueous phase liquid (NAPL) held in the soil pores, dissolved in the soil pore-water, sorbed onto the soil particles, and as a gas. The transport of these compounds through the subsurface is governed by two processes, advection and diffusion. This section is a presentation of the process of contaminant transport in the vapor phase through porous media.

2.2.1 Advection and Diffusion

The physical/chemical processes that transport contaminants through porous media are molecular diffusion and advection. Molecular diffusion is a mass transport process that has as its driving force the concentration gradient of the contaminants. The contaminants move from areas of relatively high concentrations to areas of relatively low concentrations. In multiphase systems not in equilibrium the true driving force is the chemical potential. In most multiphase processes the diffusion in each phase is considered separately, thus the concentration can be used to express the driving force.

Fick's First Law mathematically describes this process and is represented by the following equation in one dimension.

$$F_D = -D\rho \frac{\partial \omega_i}{\partial x} \quad (7)$$

where: F_D = diffusive mass flux (M/L^2t)
 D = diffusivity (L^2/t)
 ρ = mass density of soil gas (M/L^3)
 ω_i = mass fraction of compound i
 x = distance in x direction (L)

Diffusive mass flux, which is represented by F_D in the above equation, is a term used to describe the mass per unit time of contaminants flowing across an area perpendicular to the direction of flow. Fick's Law can also be expressed in terms of moles.

The second mass transport operation in porous media is advection. This is the process of mass transport by the bulk soil-gas movement. The contaminant is transported along with the flow of the soil-gas, which is driven by a pressure gradient. This process is usually faster than molecular diffusion. The one-dimensional advection equation for fluids can be mathematically represented by the following equation:

$$F_A = q\rho_i\omega_i \quad (8)$$

where: F_A = advective mass flux (M/L^2t)
 q = volume flux (L/t)
 ρ_i = concentration of compound i (M/L^3)

2.2.2 Volatilization From a Concentrated Compound In Equilibrium

As described above, contaminant compounds can exist in the subsurface in a concentrated solution. Compounds that exist in this state are called non-aqueous phase liquids (NAPLs). Within the unsaturated zone, NAPLs will volatilize into the soil-pore space. Before the volatilization of these contaminants can be further examined, it will be helpful to review the concepts of ideal and real gases, and ideal fluid.

The ideal gas law is a combination of Boyle's Law, the Law of Charles and Gay-Lussac, and Avogadro's Law. Boyle's Law describes the dependence of the volume of a gas on the pressure. The Law of Charles and Gay-Lussac describes the dependence of the volume of a gas on the temperature. Avogadro's Law describes the dependence of the volume of the gas on the number of molecules of the gas. These laws combine to make the ideal gas law, which is as follows:

$$PV = nRT \quad (9)$$

where: P = pressure (M/Lt^2)
 V = volume (L^3)
 n = number of moles
 R = gas constant ($ML^2/t^2 \text{ mole } T$)
 T = temperature (T)

Most gases will obey the ideal gas law under certain conditions. The ideal gas law assumes that there are no attractive forces between the molecules of the gas and that the sizes of the molecules are inconsequential. Thus, the conditions in which a gas will approximate the ideal gas law, are for the gas to have a low density and a low pressure. From this equation it can be shown that all gases will behave nearly the same under these conditions.

The deviation from ideal behavior for gases can be expressed by a compressibility factor, where a value of unity describes the behavior of an ideal gas. The compressibility factor can be added into the above equation to give the following equation:

$$PV = ZnRT \quad (10)$$

where: Z = compressibility factor

The ideal gas law (equation 9) is valid under subsurface environmental conditions.

Treybal (1980) states that in order for a fluid to be considered ideal, the following conditions must be met:

- The average intermolecular forces of attraction and repulsion in the solution are unchanged on mixing the constituents.
- The volume of the solution varies linearly with composition.
- There is neither absorption nor evolution of heat in mixing the constituents.
- The total vapor pressure of the solution varies linearly with composition expressed as mole fractions.

There are no fluids that can actually be considered ideal, but many fluids approximate the condition sufficiently for engineering purposes.

The tendency for a compound to volatilize depends on the compound's vapor pressure. When a liquid is in equilibrium with its vapor, the pressure of the vapor is the compound's vapor pressure. Table 2 shows the vapor pressures for some common compounds found in ground water.

Table 2. Vapor Pressures of Some Common Compounds Found in Ground Water (Verschueren, 1983)

Compound	Vapor Pressure at 205C (mm Hg)
Benzene	76
1,1,2,2-Tetrachloroethylene (PCE)	14
Toluene	22
Carbontetrachloride	90
Trichloroethylene (TCE)	60

Intuitively it can be seen that a higher vapor pressure indicates a more volatile compound. The vapor pressure of the compound is temperature dependent. Using the assumption of an ideal gas this can be described with the Clausius-Clapeyron Equation:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap} (T_2 - T_1)}{RT_1 T_2} \quad (11)$$

where: P_2 = pressure at T_2 (M/Lt²)
 P_1 = pressure at T_1 (M/Lt²)
 ΔH_{vap} = heat of vaporization (ML²/t²mole)
 T_1 = reference temperature (T)
 T_2 = actual temperature (T)

The heat of vaporization is the amount of heat that is adsorbed at the boiling point at different pressures. The assumptions used in the derivation of the above equation are that the gas behaves as an ideal gas and the molar volume of the liquid is small in comparison to the molar volume of the gas and can thus be neglected.

Within the subsurface a NAPL may consist of more than one compound. If the gas phase of the contaminating compounds can be considered ideal, and the mole fractions of each compound are known, the partial vapor pressures of the mixture of compounds can be determined using Dalton's Law. This law states that the total pressure of the vapor mixture is the sum of the partial pressures of each of the compounds within the mixture.

The partial pressure that the vapor phase of a compound within a mixture of compounds exerts can be determined by Raoult's Law. Raoult's Law assumes that the vapor phase acts as an ideal gas and the liquid phase acts as an ideal liquid. With these assumptions, Raoult's Law states that under equilibrium conditions, the pressure of the compound can be described by the following equation:

$$P_i = X_i P_{vi} \quad (12)$$

where: P_i = partial pressure of compound i (M/Lt²)
 X_i = mole fraction of compound i
 P_{vi} = vapor pressure of compound i (M/Lt²)

Using the above equation and the Ideal Gas Law, the concentration of the gas in the confined space can be determined from the following equation:

$$\frac{\rho_i}{X_i} = \frac{P_{vi} W_i}{RT} \quad (13)$$

where: ρ_i = mass concentration of compound i (M/L³)
 W_i = molecular weight of compound i (M/mole)

2.2.3 Volatilization From an Aqueous State in Equilibrium

In the unsaturated zone, contaminating compounds will dissolve into the soil-pore water to a certain extent. Substances that are more soluble in water tend to be less likely to volatilize. The solubilities of some of the compounds that are most likely to be removed by SVE and are found most commonly in a contaminated subsurface are shown in Table 3.

Table 3. Solubility in Water of Some Common Compounds Found in Ground Water (Verschueren, 1983)

Compound	Solubility (mg/L)
Benzene	1780 (20°C)
1,1,2,2-Tetrachloroethylene (PCE)	150 (25°C)
Toluene	515 (20°C)
Carbontetrachloride	800 (20°C)
Trichloroethylene (TCE)	1,100 (25°C)

A volatile contaminant that is dissolved in water will volatilize to a certain extent into the head space of a closed container. The extent depends on the temperature of the solution and the concentration of the contaminant within the aqueous solution. Volatilization of the contaminant will continue until equilibrium is reached between the concentration of the contaminant in the aqueous solution and the vapor phase in the head space. This equilibrium condition is mathematically represented by Henry's Law, which states that the partial pressure of the compound in the head space is proportional to the concentration of the compound in the aqueous solution. The equation is the following:

$$P_i = H_i X_i \quad (14)$$

where: H_i = Henry's Law constant of compound i (ML^2/t^2)

Using concentrations, equation (14) can be written in the following form:

$$C_{ig} = H_d C_{iw} \quad (15)$$

where: C_{ig} = concentration of compound i in the gas phase (moles/ L^3)
 C_{iw} = concentration of compound i in the water phase (moles/ L^3)
 H_d = Henry's Law constant (dimensionless)

Henry's Law holds for mixtures in which the molar concentration of the solute is small in comparison to the molar concentration of the solvent. In the case of contaminants dissolved in the

soil-pore water in the unsaturated zone, the molar concentration of the contaminant will most often be small in comparison to the molar concentration of the water. Henry's Law also makes the assumption that the solute is an ideal gas.

Units of Henry's Law constant are dependent on whether concentration or mole fraction units are used. The units of H include the following:

- If equation (14) is used, H will be expressed in pressure units.
- If in equation (14) the concentration of the compound is substituted for the mole fraction, H will be expressed as a pressure term over a concentration term such as atmospheres/mole/liter.
- If equation (15) is used, H is dimensionless.

The temperature dependence of the Henry's Law constant in equations (14) and (15) can be mathematically described using a van't Hoff type relation (Kavanaugh and Trussell, 1980):

$$\log H_d = \frac{-\Delta H^\circ}{RT} + C \tag{16}$$

where: C = constant (dimensionless)
 ΔH° = enthalpy of dissolution (ML²/t²mole)

Equation (16) assumes ΔH° is constant over small temperature changes. Kavanaugh and Trussell (1980) reported values of ΔH° and C that were developed from water treatment studies of air stripping. These values along with equation (16) can be used to determine the temperature dependence of Henry's Law constant for several different VOCs that are of interest in the SVE technology.

Table 4 presents the Henry's Law constants for selected contaminants of interest. The

Table 4. Henry's Constant of Some Common Compounds Found in Ground Water (Montgomery, 1990)

Compound	Henry's Law Constant (atm m ³ /mole)
Benzene	0.00548 (25°C)
1,1,2,2-Tetrachloroethylene (PCE)	0.0592 (37°C)
Toluene	0.00674 (25°C)
Carbon tetrachloride	0.024 (20°C)
Trichloroethylene (TCE)	0.0099 (20°C)

reported values of Henry's Law constant for a given compound vary widely within the literature, thus care should be taken in choosing a value.

2.2.4 Sorption

As contaminants move through the unsaturated zone, a certain portion of the contaminant will be adsorbed and/or absorbed to the soil particles. The attraction of contaminants to the surface of the soil particle is called adsorption. The penetration of the contaminant into the soil particle is called absorption. Since it is nearly impossible to distinguish between them, the term sorption is used to describe the combination of both processes.

Volatile contaminants that can be removed by SVE must be non-ionic, non-polar, organic compounds. With this in mind, the properties of the contaminating compound and the subsurface that determine the extent of sorption are as follows: the soil water content, the natural organic matter content, the soil type, the water solubility, and the octanol/water partition coefficient.

Sorption processes for VOCs are different at different soil-water contents. Qualitatively these effects can be divided into three categories, dry, damp, and wet. On the surface of soil particles that are dry or damp, there is competition between water molecules and VOCs for sorption sites. In dry soil conditions the competition is at a minimum due to the lack of water molecules. In this case the VOCs tend to be strongly sorbed to the mineral surfaces of the soil particles.

As the soil-water content increases, the competition for sorption sites on the mineral surfaces and on the natural organic matter (NOM) increases, causing less VOCs to be sorbed. When the soils are wet the mineral surfaces and NOM are covered by water, restricting the sorption of the VOCs onto the soil particles. Under these conditions, since the VOCs are hydrophobic and non-polar, the VOCs will have a stronger affinity for the NOM and will partition between the NOM and the water.

The most important property for the sorption of VOCs onto dry and damp soil is the soil type. Sorption onto mineral surfaces of soil particles is strongly dependent upon the available surface area of the particles. Valsaraj and Thibodeaux (1988) pointed out that even though the mineral matter of the soil particles predominates, the NOM content will influence the sorption by blocking sorption sites.

On wet soils the solubility of the VOCs and the NOM content of the soils becomes increasingly important due to the non-polar hydrophobic nature of the VOCs. The water solubility of VOCs was described in Section 2.2.3. For the purposes of sorption, the water solubility of a contaminant influences the attraction of the compound for the surface of the soil particle. This attraction for non-polar, non-ionic organic compounds is a measure of its hydrophobicity.

Hydrophobic compounds tend to be attracted to organic compounds as opposed to existing in an aqueous solution. The hydrophobicity of a compound can thus be measured by its distribution between an organic compound (octanol) and water. This partition coefficient is called the octanol/water partition coefficient. The equation for the octanol/water coefficient is the following:

$$K_{ow} = \frac{C_{oct}}{C_{water}} \quad (17)$$

where: K_{ow} = octanol water partition coefficient
 C_{oct} = concentration of compound in octanol (moles/L³)
 C_{water} = concentration of compound in water (moles/L³)

Within classes of chemicals, K_{ow} varies in a predictable way. By knowing the structure of the compound in question and the K_{ow} for a compound that is in the same class, the K_{ow} of the compound in question can be estimated.

Sorption is mathematically described by isotherms which describe the equilibrium sorption capacity of solids at constant temperatures. The two main classifications of equilibrium isotherms are Langmuir and Brunauer, Emmett, and Teller (BET). Langmuir isotherms describe sorption onto solid particles at a capacity that corresponds to the sorption of a single layer of molecules around the solid particle (referred to as a monomolecular layer). BET isotherms correspond to multimolecular layer sorption.

Sorption of vapor onto soils in dry and damp conditions have been shown to be described most accurately by the BET equation (Poe, et. al., 1988; Jurinak, 1957). The sorption of VOCs onto soil particles in wet conditions has been described by experimentally determined partitioning coefficients (Fetter, 1993), which are as follows:

$$K_d = K_{oc} f_{oc} \quad (18)$$

where: K_d = ratio of concentration in solid phase to concentration in solution
 f_{oc} = fraction of organic carbon
 K_{oc} = organic carbon partitioning coefficient

The organic carbon partition coefficient can be correlated with the octanol-water partition coefficient. However, K_{oc} is now available for many chemicals of environmental concern.

2.2.5 Non-Equilibrium

In the subsurface, non-equilibrium conditions will exist between the air flow created by the extraction wells and the VOCs. For NAPLs contained in the soil pores, Johnson, et. al. (1990a) shows that local equilibrium can be assumed. Using a theoretical model for mass transfer, a rigorous analysis of the mass transfer of aqueous phase VOCs to the soil-gas flow can be performed.

If soil-gas is flowing past an aqueous solution, assuming equilibrium over the whole system may not be completely valid. In this situation the contaminating compound will diffuse through the liquid to the liquid-vapor interface. At this interface, if no reaction is taking place, equilibrium can be assumed and Henry's Law or Raoult's Law can be utilized. Once in the vapor phase the contaminating compound will diffuse through the vapor. This theoretical model is called the Two

Film Resistance Theory. The rate of the mass transfer depends on the mass-transfer rate coefficient. The driving force for the mass transfer is the concentration difference between the liquid phase and the gas phase. The mathematical description for the mass transfer at the macroscopic scale can be represented by the following mathematical equation:

$$N = K(C_{a1} - C_{A\infty}) \quad (19)$$

where: N = mole flux (mole/L²t)
 K = mass transfer coefficient (mole/L² t mole/L³)
 C_{A1} = molar concentration of A in liquid at gas liquid interface (mole/L³)
 $C_{A\infty}$ = molar concentration of A in free stream (mole/L³)

In most applications of soil vapor extraction the less rigorous approach of assuming equilibrium is used.

2.2.6 Advection-Diffusion Equation

Using equations (7) and (8), a mathematical relationship can be derived to describe the transport of contaminants in the soil gas by advection and diffusion. To obtain this equation it is necessary to assume that there are no residual NAPLs present and the soil is homogeneous. This equation is shown below.

$$v \nabla \rho_i^g - D_e \nabla^2 \rho_i^g = R^g \frac{\partial \rho_i^g}{\partial t} \quad (20)$$

where: v = seepage velocity (L/t)
 ρ_i^g = mass of species A per unit volume of soil gas (M/L³)
 D_e = effective diffusion coefficient (L²/t)
 R^g = storage coefficient (dimensionless)
 ∇ = gradient operator

Seepage velocity is defined as the average velocity of fluid elements through the voids. In equation (20), R^g , the storage coefficient, takes into account the mass of contaminant i that is in the aqueous phase, solid phase and in the soil gas. R^g is defined as follows:

$$R^g = 1 + \frac{S_w}{(1 - S_w) H_d} + \frac{\rho_b K_d}{\phi (1 - S_w) H_d} \quad (21)$$

where: S_w = the ratio of the volume of water in the pore space to the volume of the pore space
 H_d = dimensionless Henry's Constant
 ρ_b = bulk density (M/L³)
 ϕ = porosity
 K_d = ratio of concentration in solid phase to concentration in solution

The effective diffusion coefficient, D_e , in equation (20) is the tortuosity multiplied by the molecular diffusion constant in free space. This molecular diffusion constant is a value that can be obtained from a handbook. The tortuosity can be estimated with the following equation (Shearer, et al., 1973):

$$\tau = \phi^{1/3} (1 - S_w)^{7/3} \quad (22)$$

where: τ = tortuosity

In the advection-diffusion process, molecular diffusion is often the less dominant process. It can thus be considered the rate-limiting process in situations where there is a high percentage of low permeability soil. In a soil in which the majority of the soil is highly permeable, molecular diffusion may not be a factor. Solutions to the advection-diffusion equation for different conditions are presented in van Genuchten (1982).

3. Description of Soil Vapor Extraction Design Variables

In Section 2 the basic science of vapor behavior in porous media and mass transfer of volatile organic compounds to the gas flow was presented. This section will relate those concepts to the current design variables for soil vapor extraction systems.

Currently there are two approaches to the design of SVE systems, a rigorous mathematical modeling approach and a less rigorous "iterative" approach. The rigorous approach uses some of the equations presented in the last section with various simplifying assumptions. The resulting mass balance is usually solved with a mathematical model (Sabadell, 1989; Sepehr and Samani, 1993). The iterative approach uses a combination of field testing and much less rigorous mathematical models with many simplifying assumptions (Johnson, 1990a, 1990b). Each of these design methods uses common design variables. Before the design variables are examined, a brief description of common SVE systems is required.

3.1 Description of SVE Systems

Other references have described typical SVE systems in detail (Pederson, 1991; Curtis, 1992; Hutzler, 1989). A brief description here will aid in the development of the ideas to follow. Extraction wells are placed in the area of contamination in such a manner as to create negative pressure gradient zones that will cover the area of contamination. A manifold piping system connects each extraction well to a vacuum blower which can be a positive displacement (PD) blower, a centrifugal blower or a vacuum pump. Variations on the simple design can include an impervious cap on the ground surface above the area of contamination to force a larger radius of influence, horizontal wells for areas with shallow water tables, and heating of the influent air to enhance VOC removal. The off gas from the blower can also be treated by several different methods to remove the VOCs before the gas is released to the atmosphere. Methods of vapor treatment include adsorption onto granular activated carbon (GAC), destruction by catalytic oxidation, destruction by thermal processes, and biodegradation. Vapor condensation is often used to reduce the water content of the off gas before vapor treatment.

3.2 Design Variables

The variables for the design of an SVE system can be divided into different categories:

- site geology/hydrogeology,
- soil characteristics, and
- physical/chemical characteristics of VOCs.

Each of these categories has parameters that influence the design and use of SVE.

3.2.1 Site Geology/Hydrogeology

Summarizing the background presented in Section 2, the following geological and hydrogeological variables are of concern in the design of an SVE system:

- degree of homogeneity and anisotropy in the area of contamination,
- depth to the water table,
- site layout and location of contamination, and
- water content.

Soil vapor extraction is most efficient in a homogeneous porous medium. The existence of a completely homogeneous soil column is rare, so the degree of homogeneity is an important factor in the determination of feasibility and in the design of an SVE system. As was shown in the previous section, gas flow will follow the path of least resistance.

On a macroscopic level, if there are areas within the contaminated zone that are of lower permeability than other areas, the vapor will tend to flow around these areas. This effect influences optimum placement of extraction wells within the contaminated area. The areas of low permeability will also control the removal of VOCs as was seen in Section 2.2.1. This factor determines the feasibility and time required to remove the contamination. The locations of soil horizons separated by aquicludes and aquitards will control the depth of extraction wells.

A simplified example can be used to illustrate the effect that very low permeability areas have on the performance of an SVE system. For this example, consider a silty clay layer sandwiched between two layers of highly permeable sand (Figure 2). If cross-cutting trenches are used for both an air inlet and an air outlet, the flow through the soil column can be considered one-dimensional. An initial sample of the soil gas in the upper layer shows a trichloroethylene (TCE) concentration of 200 milligrams per liter (mg/l). If equilibrium is assumed, this soil gas concentration will be initially uniform throughout the soil column. The air flow through the middle layer is considered to be negligible owing to the low intrinsic permeability of the soil and the high water content. With these assumptions, the dominant transport mechanism in the middle layer can be considered to be diffusion.

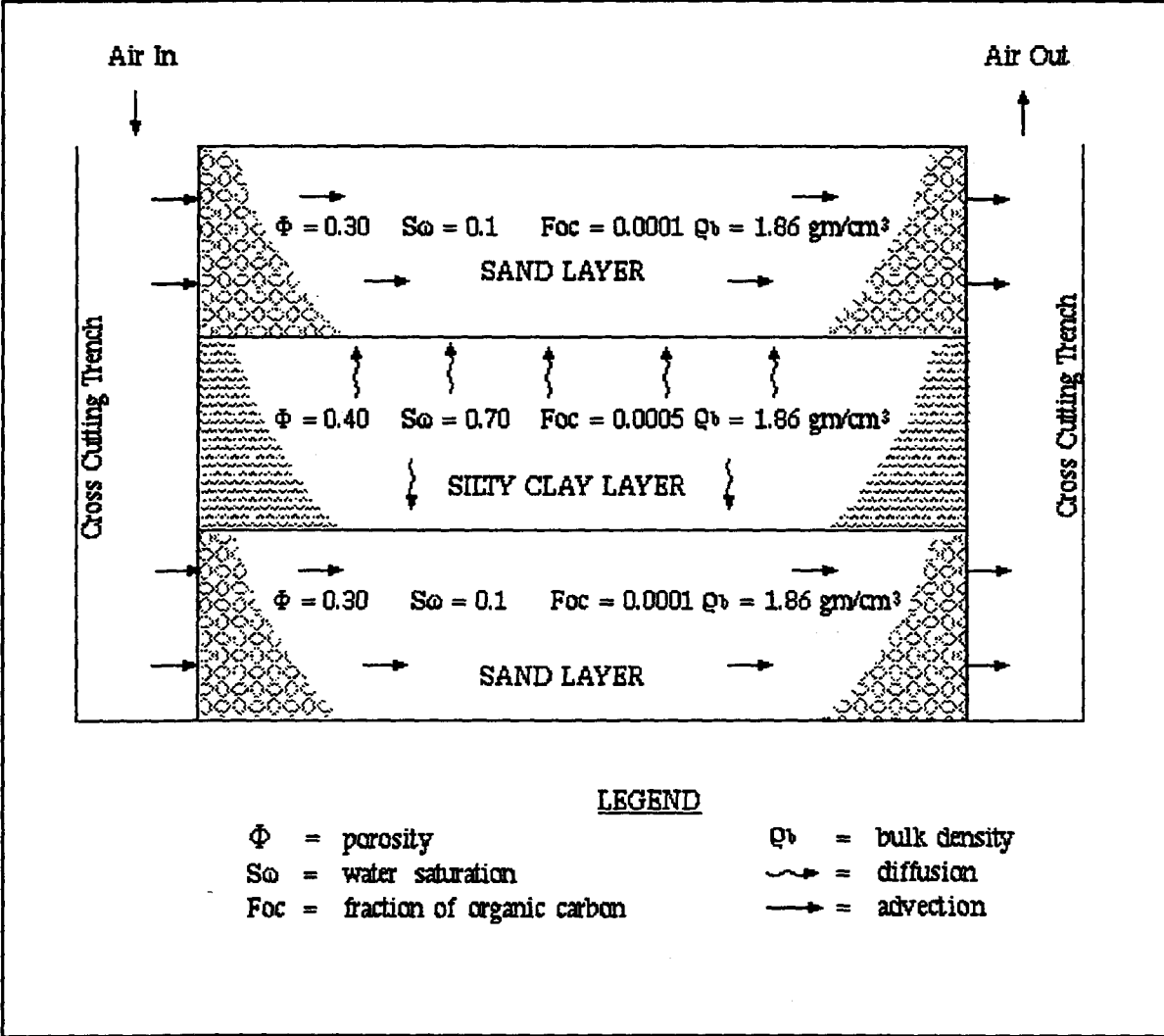


Figure 2. Effects of diffusion in a heterogeneous medium.

In the upper and lower layers the assumption is that one pore volume of fresh air through the layers will be sufficient to remove the contamination from these layers. Admittedly this is an over simplification, but is sufficient for the purposes of this example. With this assumption the time for the SVE system to remove the contamination in the upper and lower layers is 0.16 days. In the middle layer, using equations (20), (21), and (22), the time to achieve a 99% reduction in the concentration of TCE by diffusion is 445 days. This simplified example illustrates the effect very low permeable layers, such as clay lenses, have on the time required for removal of VOCs from the subsurface with SVE.

The depth to the ground water will influence the feasibility and design of an SVE system. If the ground water is shallow an SVE system may not be feasible due to water table upwelling caused by the negative pressure created in the well. Shallow ground water will also effect the vapor volume flux through the unsaturated zone. Using equation (6), this effect can be illustrated with a simplified

analytical model of volume flux through the ground surface to a horizontal vacuum well. This model makes the following assumptions:

- the air is incompressible,
- the soil is homogeneous and isotropic,
- the temperature is constant,
- the source for the negative pressure is a horizontal well,
- the radius of the well is negligible in comparison to the radius in which the gas flux is being determined, and
- water table upwelling due to the decreased pressure is ignored.

The cross sectional schematic of the conditions in the subsurface used for this model is shown in Figure 3.

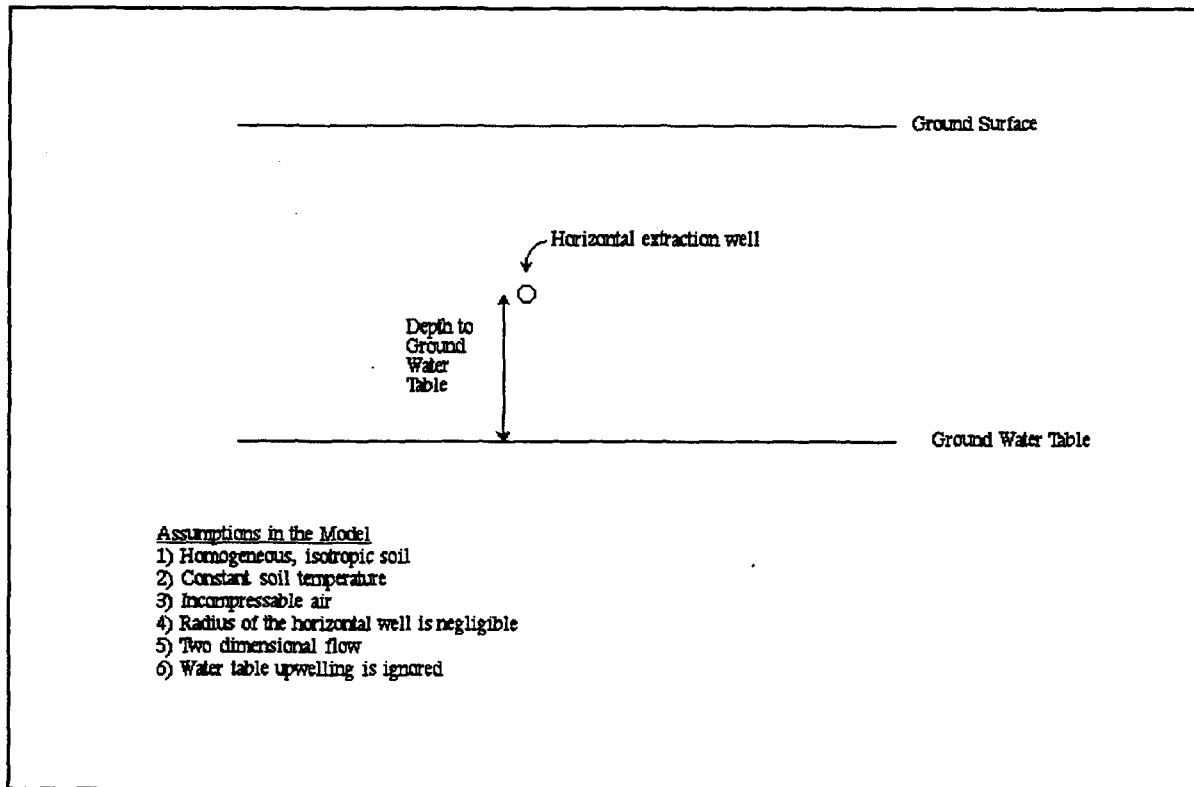


Figure 3. Cross sectional schematic of the conditions used in the model to determine the effects water table depth has on the gas flux through the ground surface.

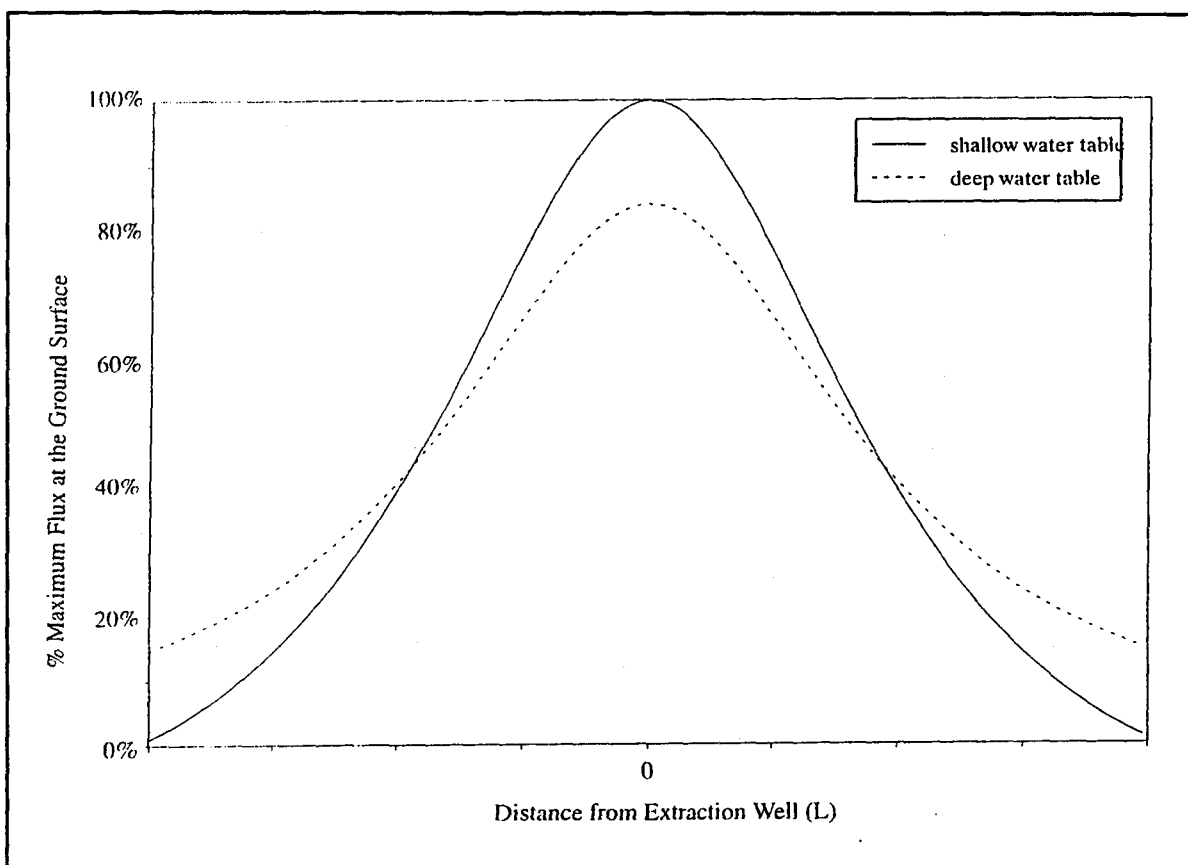


Figure 4. Effects of water table depth on gas flux through the ground surface.

The results of this simplified model are shown in Figure 4. The volume flux through the ground surface is shown as a percentage of the maximum volume flux for the two scenarios. This example illustrates that shallow ground water tables tend to increase the maximum volume flux through the ground surface and decrease the radius of influence.

Seasonal fluctuations of the water table may have an effect on the placement of extraction wells. In some cases a seasonal high water table may cover the well screens. Perched water zones also may influence the placement of extraction wells.

The site layout can influence the location for the placement of extraction wells and can also affect the gas flow created. In some contaminated locations, structures and paved surfaces may be located in the spill area. The effect that these areas have on the ability to place the extraction wells in optimum locations is evident. These structures and paved surfaces may act as an impervious cap, which will have an effect on the distribution of the gas flux and thus on the radius of influence of the flux within the unsaturated zone. If the gas flux is induced underneath an impermeable surface, the vertical gas flux directly underneath the surface is zero. Since the air is not being supplied from the atmosphere directly above the extraction well, the air will be pulled in from areas that are further away from the extraction well. This causes a larger radius of influence. This positive effect can be created in areas that do not already have a cap by installing an impervious layer. Using equation (6), a

comparison of the effects of a capped versus an uncapped surface on the gas flux can be illustrated with a simple example. This model makes the following assumptions:

- the air is incompressible,
- the soil is homogeneous and isotropic,
- the temperature is constant,
- the source for the negative pressure is a vertical well with a screen section that approximates a sphere,
- the cap in the capped case is infinitely long, and
- the radius of the well is negligible in comparison to the radius in which the gas flux is being determined.

The cross sectional schematic of the conditions used for this model is shown in Figure 5.

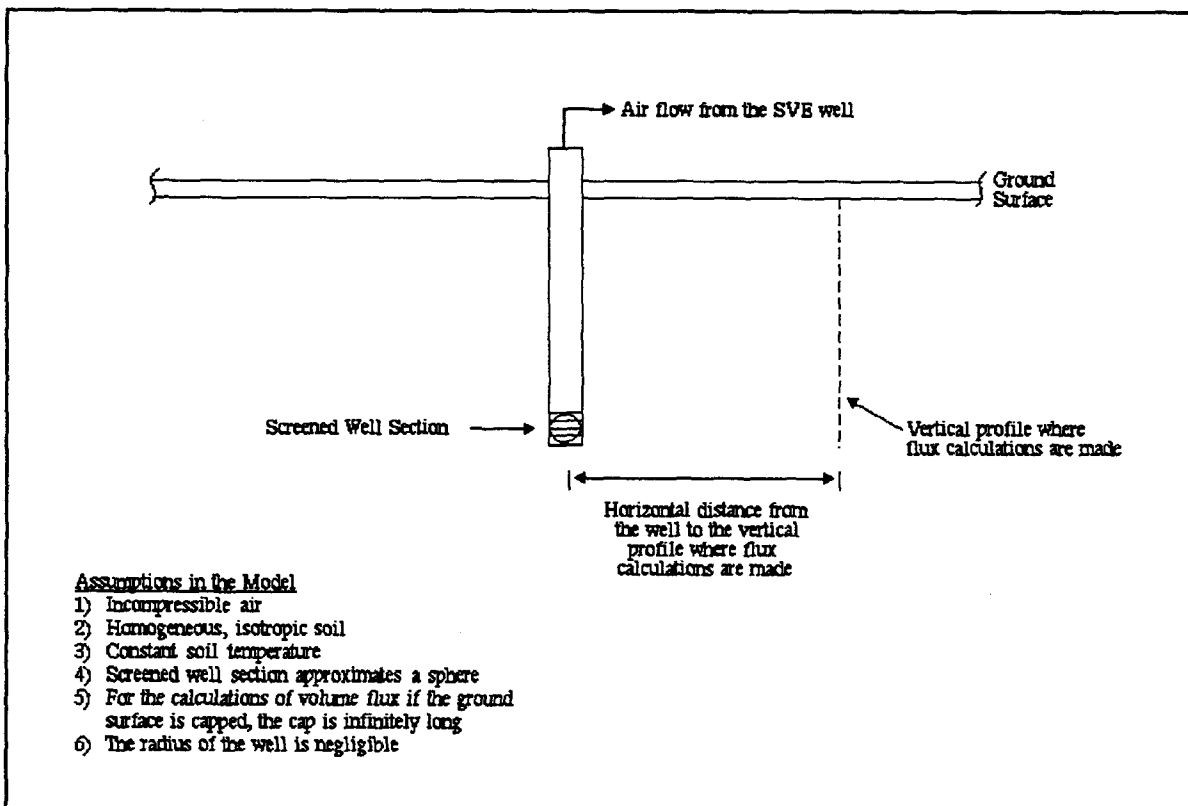


Figure 5. Schematic of the conditions used in the model to compare the effect on the gas flux through the unsaturated zone of a capped surface versus an uncapped surface.

The results of this model are shown in Figure 6. To display the results in two dimensional form, the gas flux is calculated on a line at a certain horizontal distance from the extraction well. The resulting gas fluxes from this model are shown as a percentage of the maximum gas flux obtained from the two cases. It is evident that the capped surface provides a larger radius of influence than the uncapped surface.

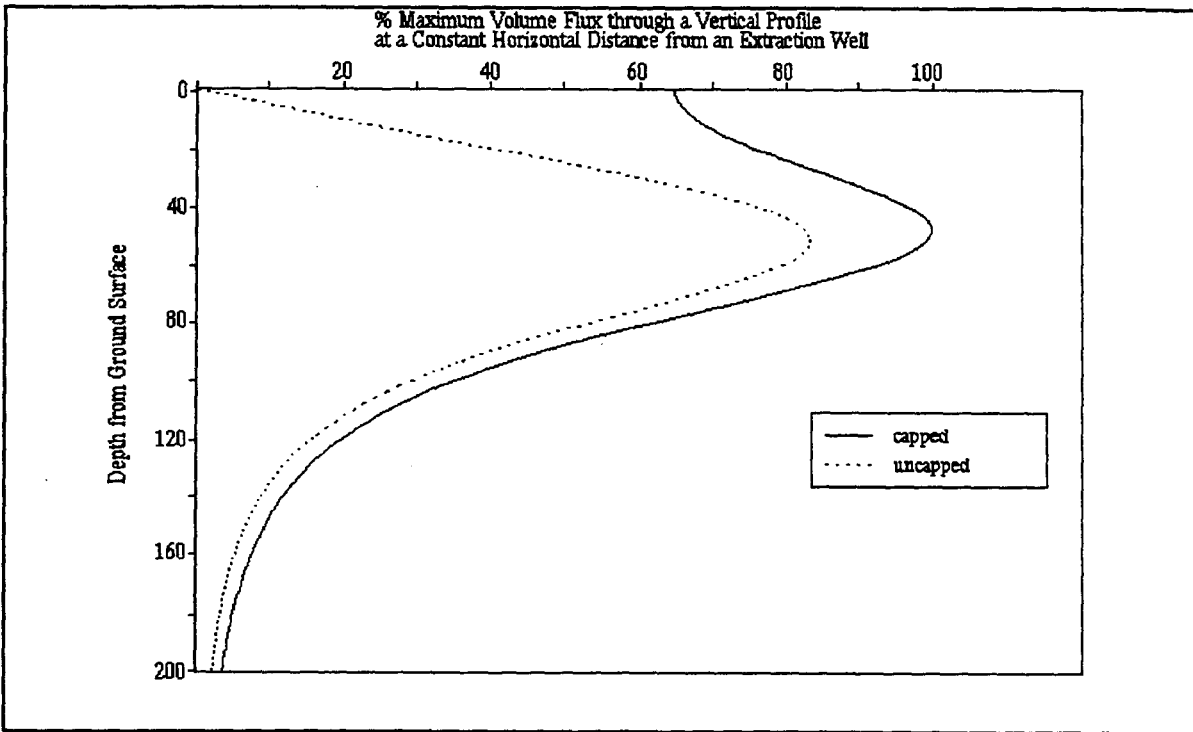


Figure 6. Effect of capped surface on vapor flux at a constant horizontal distance from the extraction well.

3.2.2 Soil Characteristics

The soil characteristics of concern for an SVE system are the following:

- soil moisture content,
- air permeability,
- organic carbon content, and
- temperature.

Soil Moisture Content

The amount of water contained in the soil affects several properties which influence SVE design. These include the sorption of VOCs to the soil particle and the diffusion of VOCs through the soil pore space. The permeability of the soil is affected as well, due to a decrease in pore space.

Burdine (1952) mathematically described the effect that soil water has on the relative permeabilities of two components, a non-wetting fluid (air) and a wetting fluid (water) in a porous medium. Burdine defines relative permeability as the ratio of the effective permeability to the permeability of the wetting phase or the non-wetting phase when only one phase occupies the soil column. The effective permeability is the permeability of a porous medium to a particular fluid phase when the medium is occupied by more than one fluid phase. Burdine derives the following equations for relative permeabilities.

$$K_{rw} = \left(\frac{S - S_r}{1 - S_r} \right)^2 \frac{\int_0^{S_e} \frac{dS_e}{P_c^2}}{\int_0^1 \frac{dS_e}{P_c^2}} \quad (23)$$

$$K_{rnw} = (1 - S_e)^2 \frac{\int_{S_e}^1 \frac{dS_e}{P_c^2}}{\int_0^1 \frac{dS_e}{P_c^2}} \quad (24)$$

where:

- S = saturation, the ratio of the volume of wetting fluid to the volume of interconnected pore space in a bulk element of the medium
- S_r = residual saturation
- P_c = capillary pressure (F/L^2)
- K_{rw} = relative wetting phase permeability
- K_{rnw} = relative non-wetting phase permeability
- S_e = effective saturation = $(S - S_r)/(1 - S_r)$

In order for these equations to be used, a functional relationship between the saturation and the capillary pressure is required. The Brooks-Corey (Brooks and Corey, 1964) relationship will be used in this text. The Brooks-Corey equation, which was experimentally determined, is as follows:

$$S_e = \left(\frac{P_d}{P_c} \right)^\lambda \quad (25)$$

for $P_c \geq P_d$

where:

- P_b = displacement pressure (F/L^2)
- λ = characteristic constant of the medium

The results of combining the Brooks-Corey equation with the Burdine equation and integrating, are equations (26) and (27).

$$K_{rw} = S_e^{\frac{2+3\lambda}{\lambda}} \tag{26}$$

$$K_{rnw} = (1 - S_e)^2 \left(1 - S_e^{\frac{2+\lambda}{\lambda}}\right) \tag{27}$$

The equation for the relative permeability for the non-wetting phase is of most interest to us for gas flow through porous media. Examining this equation at the extremes indicates that when the saturation is equal to the residual saturation, K_{rnw} will equal unity, and when S_e is equal to unity, K_{rnw} will equal zero. This follows the theory of the derivation of the Burdine equations. In conceptual terms, the extremes of the equation indicate that when the water content in the soil approaches the minimum, the permeability of the soil to gas will approach the maximum value. On the other end of the spectrum, when the water content approaches the maximum the permeability of the soil to air flow will approach zero. An illustration of relative permeability with depth is shown in Figure 7. This relation illustrates that in most cases SVE will be less effective near the capillary fringe due to the increased water content.

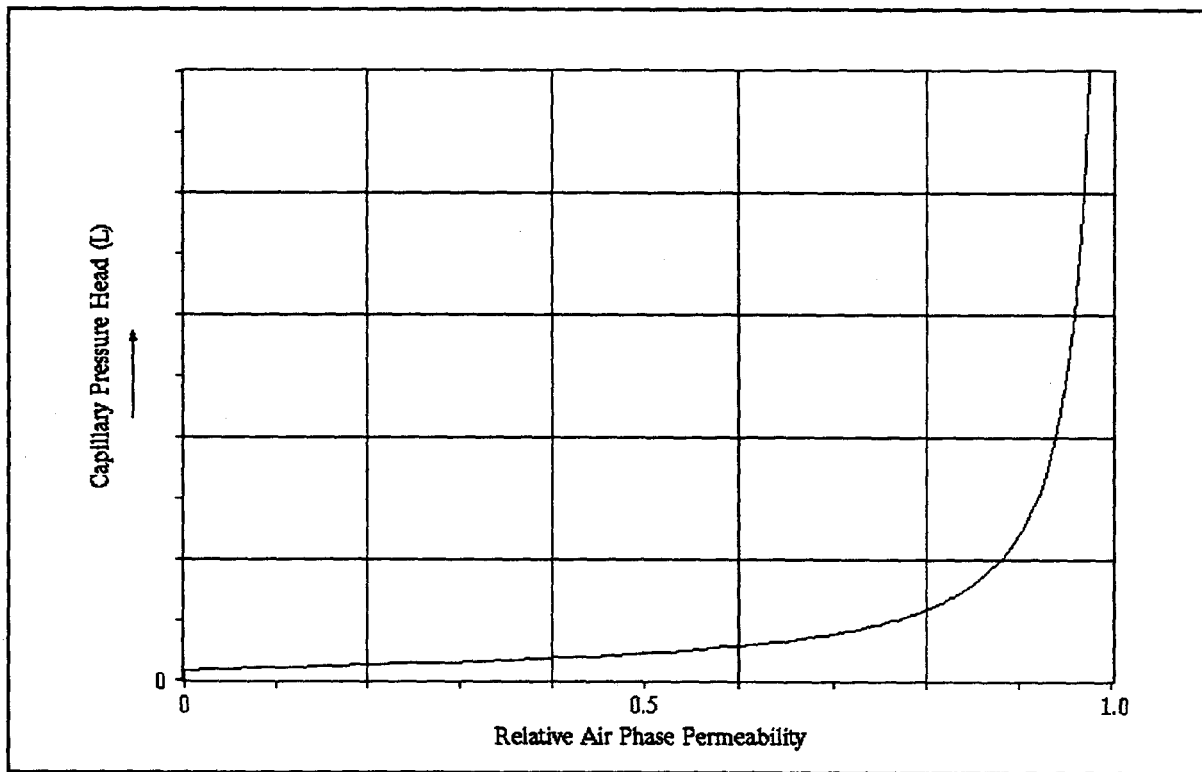


Figure 7. Relative air phase permeability as a function of capillary pressure.

Sorption

As was described previously, sorption processes are different for the three categories of soil water contents; dry, damp, and wet. The distinction between these three categories is in the area of coverage by a monomolecular layer of water molecules. In most cases in which SVE is used, the soil can be considered to be covered by a complete monomolecular layer of water. Sorption onto soils that are considered wet is controlled by the natural organic matter in the soil. Equation (18) illustrates that the ratio of the amount of contaminant sorbed to the solid phase to the amount remaining in the aqueous phase is directly proportional to the fraction of organic carbon. Soils with high organic carbon content, such as clays, will sorb more contaminant than soils with low organic carbon contents, such as sands.

Soil Temperature

In the absence of any heat sources or sinks, the temperature of the soil in the unsaturated zone varies both on a diurnal and annual basis. The diurnal and annual variations approximate a sinusoidal oscillation, the amplitude of which dampens with depth. At a certain depth in the unsaturated zone, the oscillation in temperature can be considered to be negligible and the temperature is considered to remain uniform. This uniform temperature, in most cases, is the annual climatic temperature of the area. The depth at which this occurs varies with latitude. Miller et. al. (1958) report that at latitudes around the equator the uniform temperature is reached at a depth of 3 to 4 feet and at latitudes that correspond to the New York area the depth is approximately 50 feet.

Fluctuating temperatures in the unsaturated zone can result in a change in the rate of removal of VOCs. The main cause of this change is the temperature dependence of vapor pressure and Henry's Law constant. Most often, temperature changes in the deep reaches of the unsaturated zone are not extreme. Soils that are closer to the surface will experience a wider variation in temperature with the changes of the season. Temperature can also affect the flow rate, but these changes are so small they are usually ignored.

In Section 2.2.2, the Clausius-Clapeyron Equation (equation 11) was presented. This equation indicates that when the temperature in the unsaturated zone is increased (or decreased), the result is a corresponding increase (or decrease) in the vapor pressure. As the vapor pressure changes with temperature, the concentration of the VOC in the gas flow will change as well. If the contamination exists as a mixture of different VOCs, Raoult's Law (equation 12) can be used to determine the concentrations in the gas flow.

The effect temperature has on the concentration of VOCs in soil gas results from NAPLs can be illustrated with an example. This example uses three VOCs that are commonly found in contaminated subsurfaces, trichloroethylene (TCE), tetrachloroethylene (PCE), and benzene. It is assumed in this example that each of the VOCs exists separately and as NAPLs. The Clausius-Clapeyron equation was used to determine the change in vapor pressure as the temperature increased or decreased from 20°C. The vapor pressures for each compound at the different temperatures were used to determine the equilibrium vapor concentration of each separate VOC that would be found in the soil pores. These results are shown in Figure 8.

Of the three VOCs shown in Figure 8, temperature fluctuations affect TCE the most. If the temperature ranges between 15°C and 25°C the vapor concentration of TCE found in the soil pores will fluctuate between 0.35 gm/L and 0.55 gm/L.

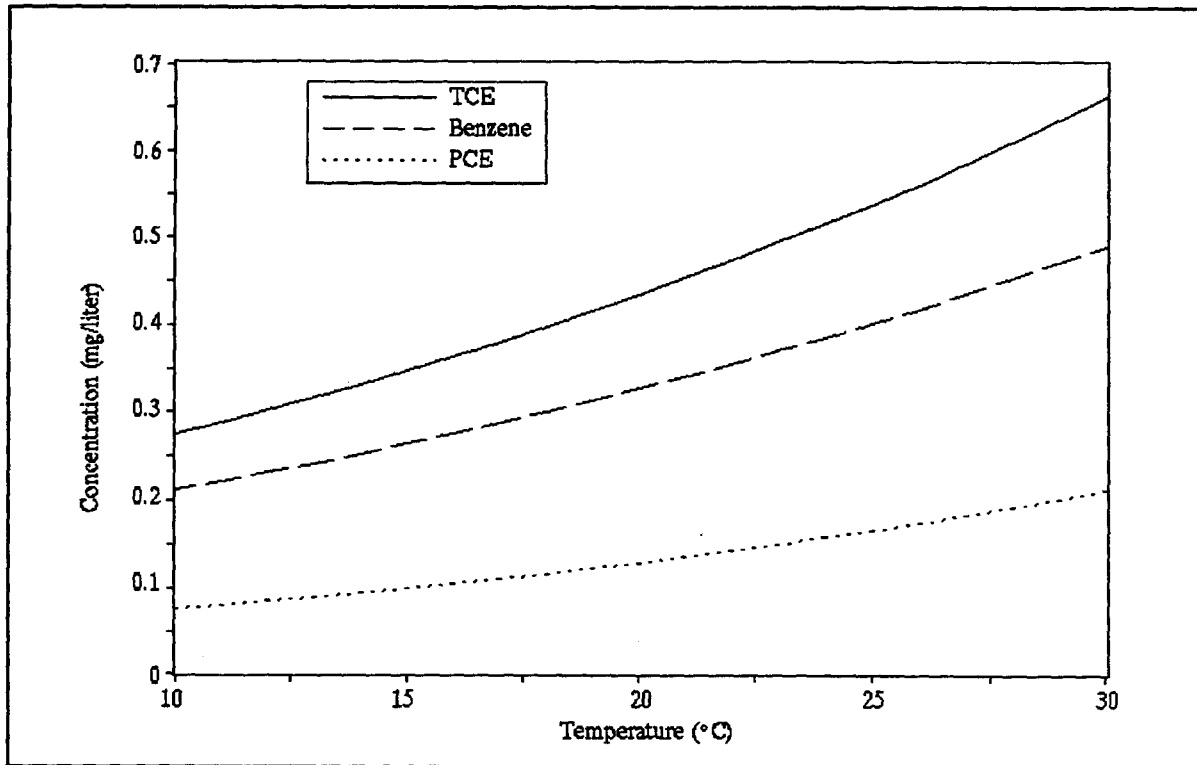


Figure 8. Vapor concentration as a function of temperature.

The volatilization of VOCs, from an aqueous state was shown to be mathematically described by Henry's Law. As discussed previously, the Henry's Law constant is susceptible to temperature changes. Again this can be shown with an example using TCE, PCE, and benzene. This example assumes that each of the VOCs exist separately and each VOC exists in the soil pore water at a concentration of 1.0 mg/l. Using equation (16) and the appropriate constants (Kavanaugh, 1980), the effect of temperature on the Henry's Law constant can be determined. Using the temperature-dependent Henry's Law constants, the equilibrium vapor concentrations of the VOCs at different temperatures can be determined. These values are shown graphically in Figure 9.

In this example PCE is affected the most by temperature changes. As the temperature ranges from 10°C to 30°C the equilibrium vapor concentrations in the soil pores ranges from approximately 0.42 mg/l to 1.3 mg/l.

In both of the examples above, temperature changes are shown to affect the concentrations of VOCs found in the soil gas. These fluctuations in vapor concentration will affect the time required for removal of the contaminant from the subsurface by SVE, which will in turn affect the cost of removal.

Air Permeability

Variations in the permeability of the soil to be treated with SVE will have varying effects on the area that is covered by gas flow. A descriptive illustration of permeabilities was provided in Section 2.1.3. In this section a simplified example will be provided to demonstrate the effect of different permeabilities on the gas flow through the system.

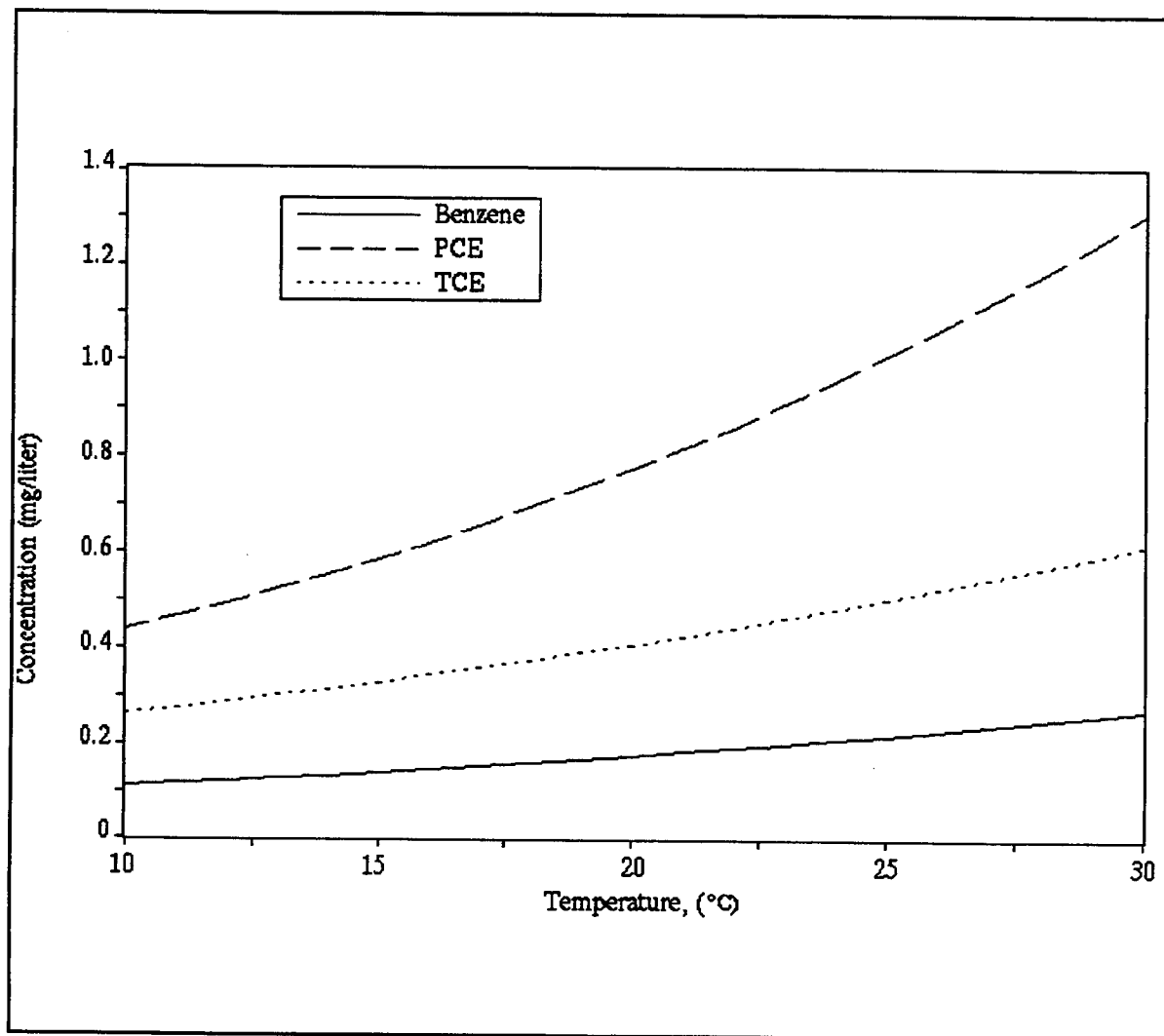


Figure 9. Change in vapor concentration from dissolved state with temperature.

The simplified scenario chosen for the example is a horizontal well in a homogeneous isotropic soil. The cross sectional schematic of the subsurface for this example is shown in Figure 10. The volume flux is evaluated across the ground surface using equation (6) to obtain the pressure distribution and Darcy's Law (equation 3) to obtain the volume flux. Further simplifying assumptions are that the gas is incompressible and the temperature is constant. Holding the pressure at the well constant, intrinsic permeabilities of k and $k/2$ are compared. Figure 11 shows the percent of the maximum volume flux distribution at the ground surface for both of the permeabilities. The abscissa in this figure is the horizontal distance measured away from the suction well with the suction well being located at the origin. As expected from equation (3), the volume flux distributions in these plots show that the volume flux is directly proportional to the value of k . In these ideal conditions, this simplified model shows the effect that small variations in the intrinsic permeabilities of soils can have on the vapor volume flux through the subsurface.

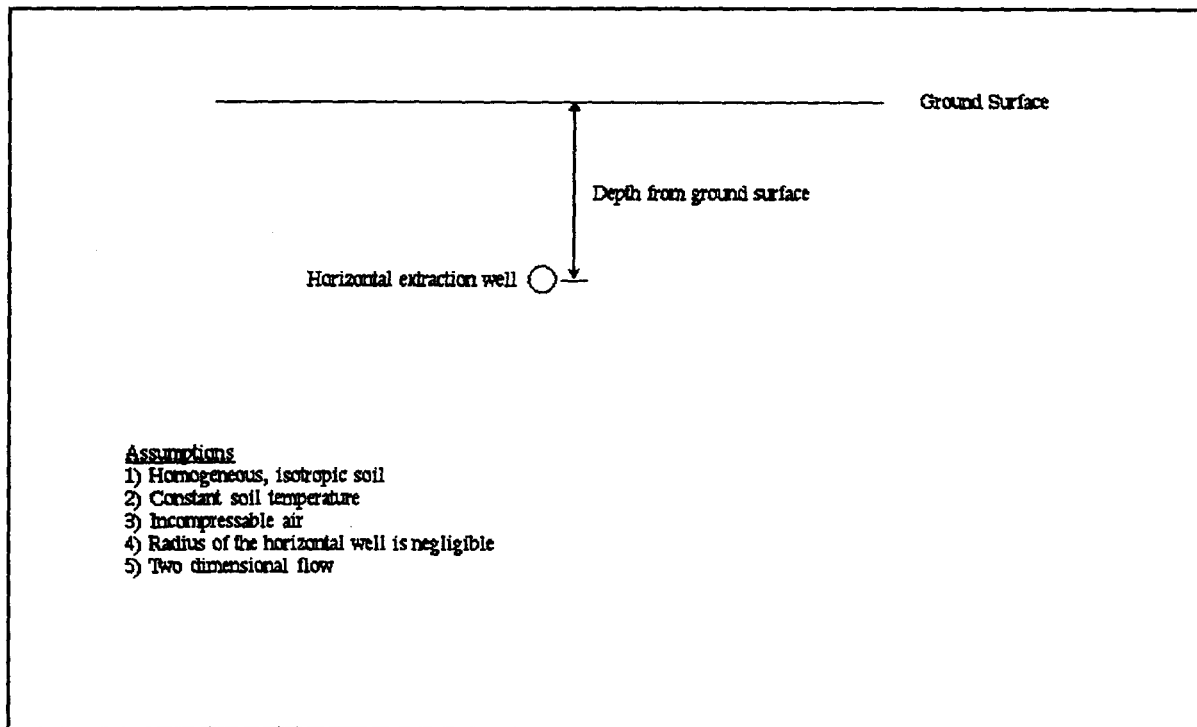


Figure 10. Schematic of the conditions used in the model to compare the effect the value of permeability has on the gas flux through the ground surface.

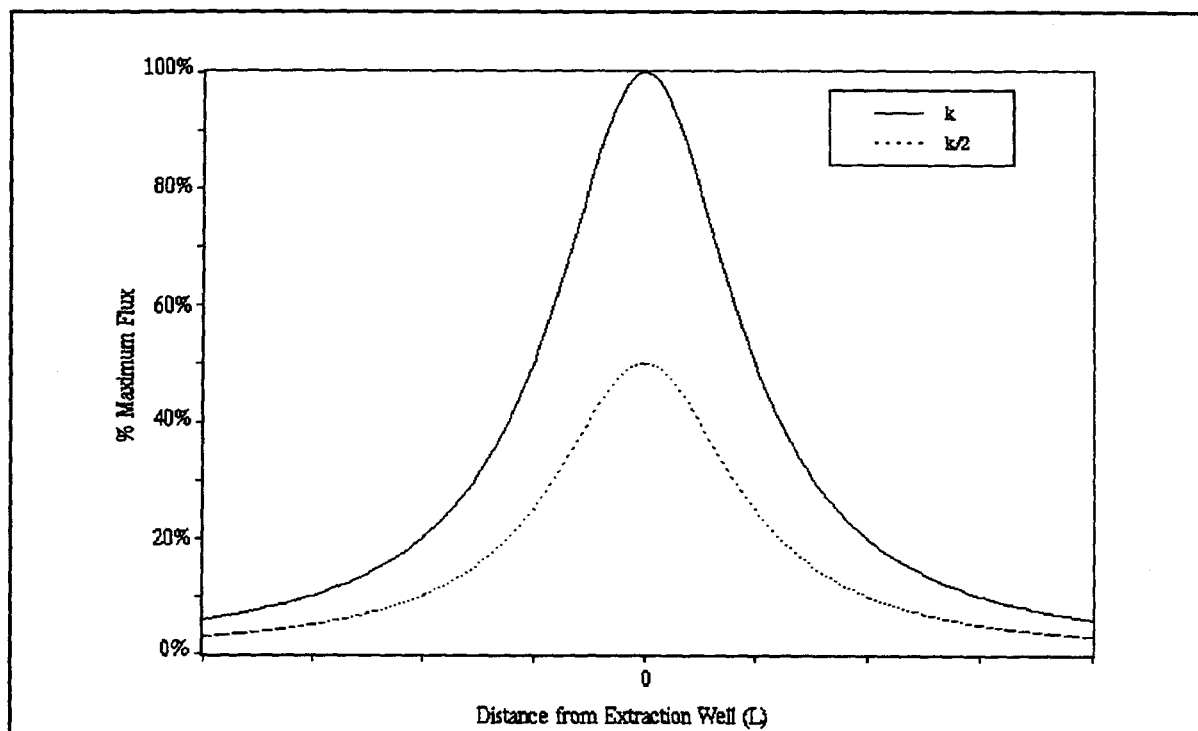


Figure 11. Effects of the value of permeability on gas flux through the ground surface.

3.2.3 Physical Characteristics of VOCs

Vapor Pressure

The effect vapor pressure has on the volatilization of VOCs from NAPLs was illustrated in the above discussion on temperature effects and will be discussed further here. If the VOC exists as a single compound, the concentration of contaminant in the vapor phase can be calculated from the vapor pressure of the compound. Compounds with low vapor pressures will be more difficult to remove by SVE. Depending on the conditions of the subsurface it will become impracticable to remove certain organic compounds that have low vapor pressure. To illustrate the effect of vapor pressure on the vapor concentration at equilibrium the vapor pressure of some common contaminants and their equilibrium vapor concentrations at 25°C are shown in Figure 12.

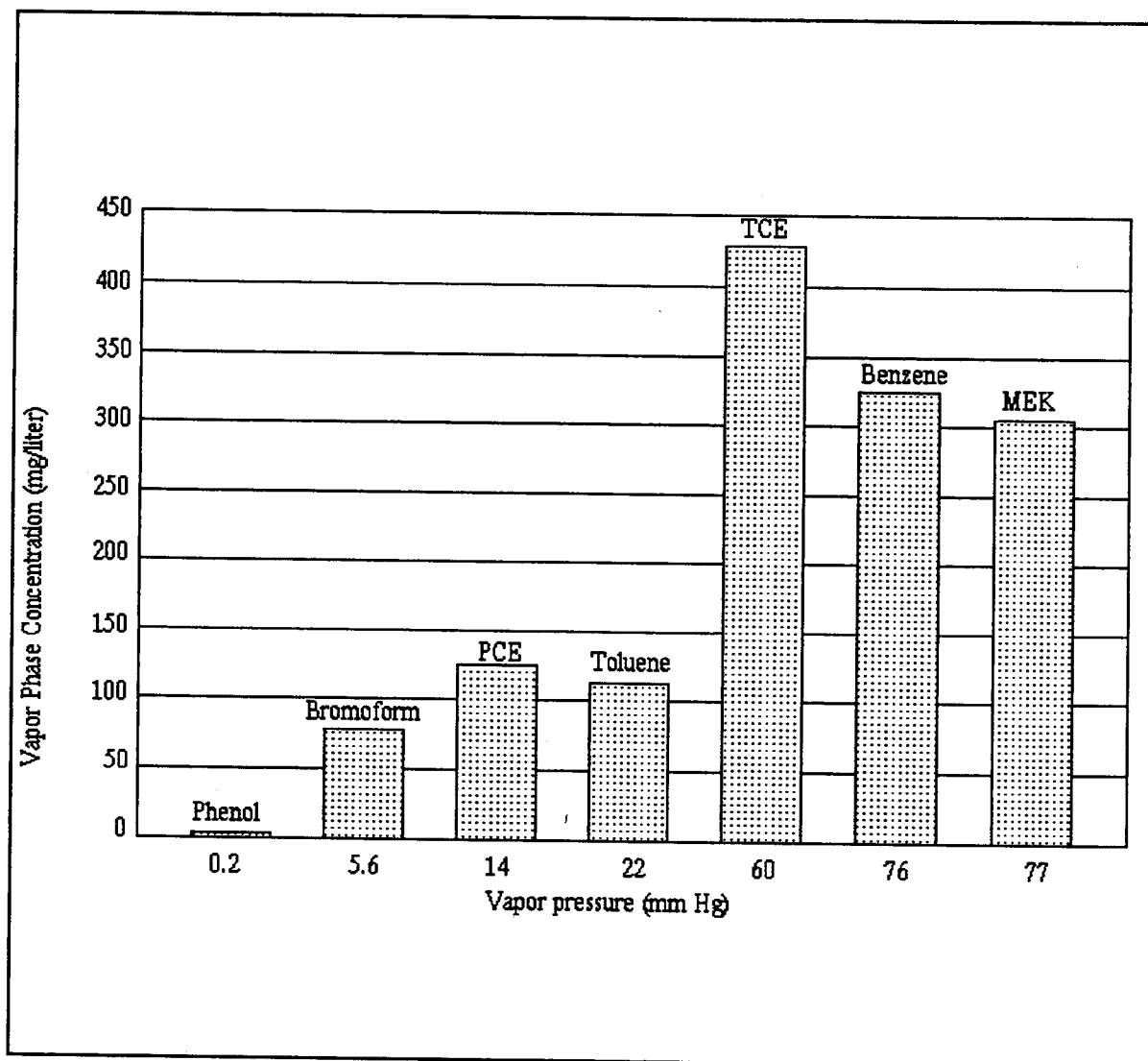


Figure 12. Effect of vapor pressure on equilibrium NAPL vapor phase concentration.

Henry's Law Constant

As described above, the Henry's Law constant of a VOC influences how readily that compound will be removed from an aqueous state. Assuming equilibrium, the vapor phase concentration of VOCs can be determined with the use of Henry's Law (equation 14). Just as in volatilization of organic compounds existing as NAPLs, the removal of organic compounds in an aqueous phase will become impracticable at a certain Henry's Law constant. At a constant temperature of 20°C and an initial water phase concentration of 10 mg/l, the expected equilibrium vapor phase concentrations for some common contaminants are shown in Figure 13.

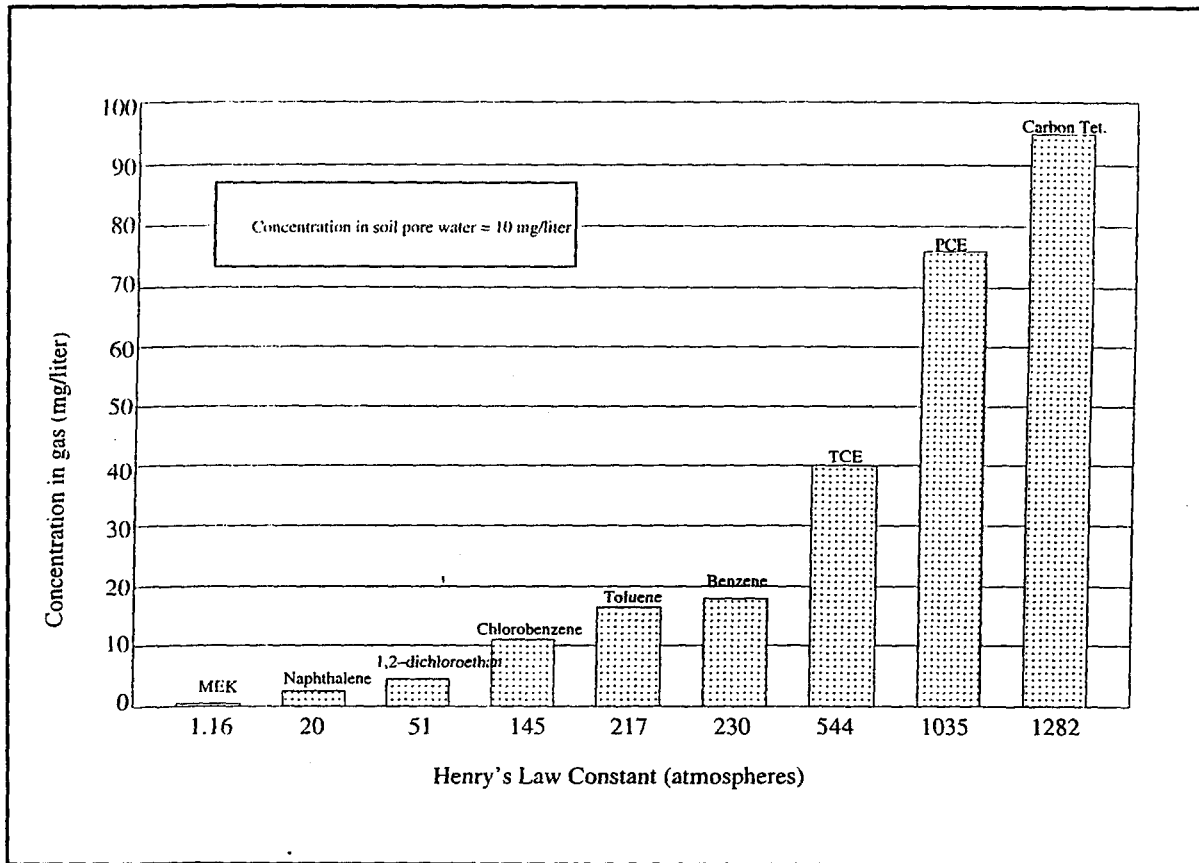


Figure 13. Effect of Henry's Law Constant on equilibrium vapor phase concentration from an aqueous solution.

4. Assessment of Soil Vapor Extraction

The basic science of SVE and how this science relates to the design variables was presented in Sections 2 and 3. Optimum conditions for operation of an SVE system and how the design variables are affected by deviations from these optimum conditions can be illustrated with the concepts from the previous sections. This section also provides a rough estimate of the general costs of SVE.

4.1 Optimum Conditions and Sensitivity to Non-Optimum Conditions

Other researchers provide quantitative values for the optimum SVE conditions (Hutzler, 1989; Metcalf & Eddy, 1991). With the aid of the examples in Section 3, this section will provide a qualitative description of the optimum conditions. This description gives the reader information for making site-specific judgments as to the effectiveness of an SVE system. The conditions that will be examined are the following:

- permeability and homogeneity,
- vapor pressure and Henry's Law constant,
- soil temperature,
- soil moisture content,
- natural organic matter content, and
- water table depth.

Permeability of the soil was shown to have a large effect on the magnitude of the volume gas flux through the soil and on the overall extent of coverage provided by the vacuum (Section 3.2.2). The results from the simplified model showed that order of magnitude differences in the permeability of soils to air will have an order of magnitude difference in the volume flux of gas through the ground surface (other factors held constant). Johnson (1990a) provides values for the air permeability of soils for different types of soils (Table 5).

Table 5. Intrinsic Permeabilities of Different Soil Types
(Johnson, 1990a)

Soil Type	Intrinsic Permeability (cm ²)
Coarse Sands	100 < k ≤ 1000
Medium Sands	10 < k ≤ 100
Fine Sands	1 < k ≤ 10
Clayey Sands	0.1 < k ≤ 1

These values illustrate that in ideal conditions, and holding other factors constant, the difference in permeability between a fine-grained sandy soil and a medium-grained sandy soil will have an order of magnitude difference on the value of the volume flux through the soil.

Homogeneity of the soil to be treated by SVE has a large effect on the performance of an SVE system. Heterogeneous soils will develop preferred flow channels through the areas of higher permeabilities, causing the areas with low permeabilities to be cleaned up by the slower process of diffusion as opposed to the faster process of advection (Section 3.2.1). Due to the slow diffusion process, soils with low permeabilities that are contained in heterogeneous soil profiles will tend to be the rate-limiting factor in an SVE operation. Optimum soil conditions would thus be soils that tend towards homogeneous with a relatively high intrinsic permeability.

The effect of the VOC's vapor pressure and Henry's Law constant on the extent of volatilization was discussed in Section 3.2.3. The example in this section determined the equilibrium concentrations of VOC that would be expected in the head space of a closed system at 20°C. In the unsaturated zone these concentration values will be affected by mass transfer limitations, sorption and temperature. Usually, for simplification, the mass transfer limitations are considered small and are ignored.

In the unsaturated zone, the removal of compounds that are present as NAPLs by SVE may no longer be feasible below a certain vapor-pressure. This threshold vapor pressure is dependent upon the temperature of the unsaturated zone and the gas flow rate obtainable. For contaminants that are in the aqueous phase, a threshold Henry's Law constant can be determined for site specific conditions.

Section 3.2.2 provided an example of how the equilibrium concentration of VOCs in the soil gas is temperature dependent. The variations in soil temperature will have less of an influence on contaminants in deep soils due to the damping effect the soils have on temperature fluctuations as the depth from the ground surface is increased. The temperature changes in shallow soils have both diurnal and seasonal effects. In these areas the performance of an SVE system can be expected to decrease in the colder months and in some cases in the colder times of the day. This result can increase the time for remediation and in turn increase the costs. Usually, the uniform temperature in soil at depth is the annual climatic temperature of the area. Optimum conditions for SVE will be areas with mild climates. Estimates of the effectiveness of SVE at a site can be made by determining the annual climatic temperature and using the Clausius-Clapeyron equation (equation 11) to determine the vapor pressure.

Soil moisture content of the soil has been shown to influence the magnitude of the sorption of the VOC to the soil surfaces (Section 3.2.2). In areas of very low moisture content the VOC will tend to sorb to the mineral surfaces. As the moisture content increases sorption of the VOC onto the soil will decrease due to competition with the water molecules. When the soil moisture content obtains a level where the soil particles are completely wetted by the water, the natural organic matter content controls the sorption. From equation (18) it is noted that the fraction of natural organic material in the soil is directly proportional to the amount of contaminant sorbed to the soil particles. Sorption will decrease the effectiveness of SVE systems in areas that are dry such as the desert southwest and in areas that have wet organic soils.

Soil moisture content also has an influence on the air permeability of the soils (Section 3.2.2). Areas with high moisture content will decrease the effective permeability of the soil to air. Decreases in the air permeability of the soil will be most noticeable near the capillary fringe and in any fine grained strata that may exist. An example of this effect was shown in Section 3.2.2.

Depth to ground water will influence the operation of SVE systems in several ways. Holding permeability constant, a shallow water table, in comparison to a deep water table, will cause the volume flux through the ground surface to increase and the extent of effective coverage to decrease. This result was illustrated with a simplified model using a horizontal well in Section 3.2.2. This model does not account for the expected decrease in permeability due to the elevated moisture content of the soil near the ground water table (Section 3.2.2). Optimum water table depth will thus depend on the gradation of the soil. By decreasing the extent of coverage by the vacuum wells, more wells are necessary to provide for complete coverage of the contaminated area. Shallow ground water may also increase the chance of upwelling water into the extraction wells from the ground water table.

4.2 Performance Measures

The expected results from applying a vacuum to the soil will be an immediate high concentration of VOC in the effluent, which will taper off with time becoming asymptotic to a low concentration that is controlled by diffusion. At the point that the removal of VOCs becomes diffusion limited, the operation of the SVE system may become more economical if the extraction process is intermittently stopped and started, a process known as surging. When the extraction process is stopped contaminants will continue to diffuse into the more permeable zones. Upon re-starting extraction, high removal rates will be obtained, which will once again taper off to an asymptotic level. This surge process does not speed up the removal process, but it may make the removal process less energy consumptive. The reason surging does not decrease the remediation time can be shown by referring to Section 2.2.1. In this section, contaminant transport by diffusion is shown to be controlled by the concentration gradient. Stopping the extraction process, will decrease the concentration gradient with time and thus the diffusion rate from these areas. Allowing the extraction process to run continuously maintains the concentration gradients at the maximum, providing a high mass removal rate.

The effectiveness of SVE can be determined by measuring the concentration of VOC in the off gas (before gas treatment). With these measurements the mass of VOC removed over time can be determined. Methods of assessing the success of the system include soil borings and soil gas monitoring. Soil borings will indicate the level of contamination remaining in the soil after the operation of an SVE system for a certain time interval. Depending on the heterogeneity of the treatment area and the location of the sample points, the accuracy of this type of assessment may be questionable. With the use of soil gas monitoring, samples can be obtained over larger areas. Soil gas sampling has some of the same limitations as SVE. Sampling in this manner may not indicate sorbed contamination and may be mass transfer limited.

4.3 Expected Costs of SVE Systems

The costs in SVE systems are from the following items: installation of extraction wells, installation of observation wells, piping, blowers, monitoring, vapor treatment, and operation and maintenance. The costs for this section were obtained from U.S. Environmental Protection Agency (1991). The costs were adjusted to reflect inflation.

The cost of installing extraction and observation wells is highly dependent on depth, geology of the area being drilled, type of well being installed (horizontal or vertical), and the diameter of the well bore. Typical costs will be \$2,000 to \$5,000 per well.

Polyvinyl chloride (PVC) piping is normally used for SVE systems. Typical costs will be \$1 to \$3 per foot for 2-inch diameter, \$3 to \$5 per foot for 4-inch diameter, \$7 to \$13 per foot for 6-inch diameter and \$15 to \$20 per foot for 8-inch diameter. Typical costs for PVC ball valves are \$75 for 2-inch valves, \$190 for 4-inch valves, \$880 for 6-inch valves and \$1,600 for 8-inch valves. PVC joints could cost \$14 for 2-inch diameter, \$60 for 4-inch diameter, \$125 for 6-inch diameter, and \$580 for 8-inch diameter.

The number of wells, the required head and the flow rate will dictate the size of blower(s) required for an SVE system. PD blowers, centrifugal blowers and vacuum pumps are most commonly used. Typical costs for these blowers are \$6,000 to \$40,000.

A topic that was briefly mentioned in Section 3.1 is the treatment of the off gas vapors including water removal and contaminant removal. The expected cost of a vapor liquid separator is \$4,500 to \$25,000. The most popular off gas treatment method is GAC. The expected capital costs of GAC are \$850 for a 200 pound container to \$25,000 for a 5,700 pound container.

Operation and maintenance of an SVE system includes GAC replacement as the removal capacity of the GAC becomes exhausted, power costs for the blowers, and sampling costs.

5. Conclusion

The main objective of this report is to present the basic science of soil vapor extraction, how this science applies to the design variables, and the optimum conditions for its use. By presenting the basic principles of SVE, it is hoped that the reader will gain an overall understanding of the conditions in which SVE is applicable and be able to make site-specific judgments as to the use of SVE.

From the development presented previously, the following general conclusions on soil vapor extraction can be stated:

- SVE is applicable in a porous medium and is dependent upon the intrinsic permeability and the degree of homogeneity of the medium.
- Areas of low permeability such as clay layers will most often greatly extend remediation time due to the diffusion-dominated transport of VOCs through these layers.
- Applicability of SVE is dependent upon the physical characteristics of the contaminants to be removed, more specifically the vapor pressure, Henry's Law constant, and solubility.
- Feasibility of SVE is dependent upon the soil water content which affects the effective permeability, sorption, and the amount of contaminant in the dissolved phase.
- Capped surfaces will, in most cases, increase the flux through the subsurface.
- Shallow SVE systems may be affected by diurnal and seasonal variations in temperature.
- Shallow water table depths may decrease the effective area of coverage by an SVE well.

6. References

- Alberty, R.A. and R.J. Silbey, Physical Chemistry, 1st ed., John Wiley and Sons, New York, 1992.
- Bear, J., Dynamics of Fluids in Porous Media, American Elsevier Publishing Company, Inc., New York, 1972.
- Blight, G.E., "Flow of Air Through Soils," Journal of the Soil Mechanics and Foundations Division, Proceedings of the American Society of Civil Engineers, SM4, 607-624, 1971.
- Bouwer, H., Groundwater Hydrology, McGraw-Hill Book Company, New York, 1978.
- Brooks, R.H. and A.T. Corey, "Hydraulic Properties of Porous Media" Hydrology Paper No. 3, Civil Engineering Department, Colorado State University, Fort Collins, Colorado, March, 1964.
- Brooks, R.H. and A.T. Corey, "Properties of Porous Media Affecting Fluid Flow," Journal of the Irrigation and Drainage Division Proceedings of the American Society of Civil Engineers, IR2, 1966.
- Burdine, N.T., "Relative Permeability Calculations from Pore-Size Distribution Data," Petroleum Transactions American Institute of Mining Engineers, 198, 71-77, 1952.
- Corey, A.T., Mechanics of Immiscible Fluids in Porous Media, Water Resources Publications, Littleton, Colorado, 1986.
- Curtis, J.T., "Soil Vapor Extraction Removes Subsurface VOCs," Pollution Engineering, 24, 56-59, 1992.
- Driscoll, F. G., Groundwater and Wells, 2d ed., Johnson Division, Saint Paul, Minnesota, 1986.
- Fetter, C.W., Contaminant Hydrogeology, Macmillan Publishing Company, New York, 1993.
- Fetter, C.W., Applied Hydrogeology, 2d ed., Merrill Publishing Company, Columbus, Ohio, 1988.
- Hutzler, N.J., B.E. Murphy and J.S. Gierke, State of Technology Review: Soil Vapor Extraction Systems, EPA/600/2-89/024, 27, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, 1989.
- Johnson P.C., M.W. Kemblowski and J.D. Colthart, "Quantitative Analysis for the Cleanup of Hydrocarbon-Contaminated Soils by In-Situ Soil Venting," Ground Water, 28(3), 413-429, 1990a.
- Johnson, P.C., C.C. Stanley, M.W. Kemblowski, D.C. Byers and J.D. Colthart, "A Practical Approach to the Design, Operation, and Monitoring of In-Situ Soil-Venting Systems," Ground Water Monitoring Review, 10(2), 159-178, 1990b.

- Jurinak, J.J. and D.H. Volman, "Applications of the Brunauer, Emmett, and Teller Equation to Ethylene Dibromide Adsorption by Soils," *Soil Science*, 83, 487-496, 1957.
- Kavanaugh, M.C. and R.R. Trussell, "Design of Aeration Towers to Strip Volatile Contaminants for Drinking Water," *American Water Works Association Air Stripping for Volatile Organic Contaminant Removal*, Denver, Colorado, 43-51, 1980.
- McWhorter, D.B. and D.K. Sunada, Ground-Water Hydrology and Hydraulics, Water Resources Publications, Littleton, Colorado, 1977.
- Metcalf & Eddy, *Handbook Stabilization Technologies for RCRA Corrective Actions*, EPA/625/6-91/026, U.S. Environmental Protection Agency, Office of Research and Development Center for Environmental Research Information, Cincinnati, Ohio, 1991.
- Miller, C.E., L.M. Trok and H.D. Foth, Fundamentals of Soil Science, 3d ed., John Wiley and Sons Inc., New York, 1958.
- Montgomery, J.H. and L.M. Welkom, Groundwater Chemicals Desk Reference, Lewis Publishers, Inc., Chelsea, Michigan, 1990.
- Ong, S.K. and L.W. Lion, "Effects of Soil Properties and Moisture on The Sorption of Trichloroethylene Vapor," *Water Research* (25)1, 29-36, 1991.
- Peck, R.B., W.E. Hanson and T.H. Thornburn, Foundation Engineering, 2d ed., John Wiley & Sons, New York, 1974.
- Pederson, T.A. and J.T. Curtis, Soil Vapor Extraction Technology, Noyes Data Corp, Park Ridge, New Jersey, 1991.
- Poe, S.H., K.T. Valsaraj, L.J. Thibodeaux and C. Springer, "Equilibrium Vapor Phase Adsorption of Volatile Organic Chemicals on Dry Soils," *Journal of Hazardous Materials*, 19, 17-32, 1988.
- Sabadell, G.P., Modeling of Volatile Organic Contaminant Transport in Soils, Ph.D. Dissertation, Colorado State University, Fall 1989.
- Shearer, R.C., J. Latey, W.J. Farmer and A. Klute, "Lindane Diffusion in Soil," *Soil Science Society of America Proceedings*, 37, 189-193, 1973.
- Sepehr, M., and Z.A. Samani, "In Situ Soil Remediation Using Vapor Extraction Wells, Development and Testing of a Three-Dimensional Finite Difference Model," *Ground Water*, 31(3), 425-436, 1993.
- Terra Vac Corporation, Statement of Qualifications, San Leandro, California, 1990.
- Treybal, R.E., Mass-Transfer Operations, 3d ed., McGraw-Hill Book Company, New York, 1980.

- U.S. Environmental Protection Agency, Guide for Conducting Treatability Studies Under CERCLA: Soil Vapor Extraction Interim Guidance, EPA/540/2-91/019A, U.S. Environmental Protection Agency Risk Reduction Engineering Laboratory Office of Research and Development, Cincinnati, Ohio, 1991.
- Valasarj, K.T. and L.J. Thibodeaux, "Equilibrium Adsorption of Chemical Vapors on Surface Soils, Landfills and Landfarms - A Review," *Journal of Hazardous Materials* 19, 79-99, 1988.
- van Genuchten, M. Th. "Analytical Solutions of the One-Dimensional Convective Dispersive Solute Transport Equation," USDA, Agricultural Research Station, Technology Bulletin #1161, June 1982.
- Van Wylen, G.J. and R.E. Sonntag, Fundamentals of Classical Thermodynamics, 2d ed., John Wiley & Sons, New York, 1978.
- Verschueren, K., Handbook of Environmental Data on Organic Chemicals, 2d ed., Van Nostrand Reinhold Co., New York, 1983.