

Abstract

In recent years there has been increased concern regarding the subsurface contamination by volatile organic chemicals (VOC's). Many different subsurface remediation techniques have been used in order to remove these contaminants from the groundwater and from the unsaturated zone. Subsurface vapor extraction (SVE), also known as soil vapor extraction or soil venting, is one remediation technique which is being used with increased frequency to remove VOC's from the subsurface. The purpose of this research was to investigate the processes affecting the performance and applicability of this remediation technique.

Laboratory experiments were conducted in two different columns packed with glass beads. VOC's at residual saturation were removed from the columns using nitrogen gas. Two different contaminants, pure toluene and a toluene-xylene mixture, were used to residually saturate the columns in order to observe the affect of contaminant volatility on removal rate. Several different pore velocities were used in order to determine if the assumption of local equilibrium between phases was valid.

The results of this research indicate that the local equilibrium assumption is valid for the pore velocities to be encountered in the subsurface during the operation of a SVE system. Mass transfer rates between pure organic liquids and the vapor phase are sufficiently high for equilibrium to occur. Deviations from equilibrium were observed in several of the experiments as a result of diffusion and/or mass transfer limitations.

Acknowledgments

I would like to thank my advisor, Dr. Cass T. Miller, for both his technical and moral support during the course of this research. I would also like to thank Randall Goodman and Cliff Burgess for their help in developing the columns and instrumentation needed for this research. A special thanks to Dr. Donald Wilhoit and his assistants in the Department of Health and Safety for their often needed assistance. Finally, to my wife June, thanks for your support. Without your help this task would have been impossible.

This project was funded solely by funds provided through the Health and Safety Office at the University of North Carolina-Chapel Hill.

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1 Introduction

1.1 Background

In recent years there has been increasing concern regarding subsurface contamination by volatile organic compounds (VOC's) and other hazardous substances. The number of contamination problems discovered has increased substantially due to advances in detection methods, rapid growth in the production and disposal of organic chemicals, and the slow transport of VOC's in the subsurface (Barbash and Roberts, 1986). As a result of the increased number of contaminated sites needing clean-up, an extensive subsurface remediation industry has developed.

There are several reasons why the concern for subsurface contamination is justifiable. Groundwater serves as the primary source of drinking water for about half the US population (Saner and Roberts, 1991). In rural areas of the country, 95% of the people depend on groundwater as their sole source of drinking water. Many of the VOC's that have been discovered in groundwater are known carcinogens (e.g., benzene) or mutagens. Once introduced into the subsurface, VOC's are quite persistent since most are not readily degraded. They can be transported long distances by groundwater flow. Finally, groundwater remediation is usually a very slow and expensive process. The use of pump-and-treat remediation, the most commonly used decontamination method, can improve the quality of the groundwater and help control the further spreading of contamination. However, this remediation technique may require very long periods of time to return an aquifer back to its original condition (Mackay and Cherry, 1989).

In response to the growing concerns and discoveries of groundwater pollution problems, several pieces of federal legislation have addressed the issue of groundwater quality. The Resource Conservation and Recovery Act (RCRA) of 1976 was

1.1 Background

enacted to help regulate the safe disposal and treatment of hazardous wastes generated in the United States (RCRA Orientation Manual,1990), thereby attempting to eliminate contamination problems in the future. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly called Superfund, was enacted to address contamination problems caused by inactive or abandoned disposal sites or spills that require emergency response. CERCLA created a National Priorities List (NPL) of the most dangerous sites needing remediation. Currently there are about 1200 sites on the NPL (OTA,1989). Finally, the Safe Drinking Water Act (SDWA) established maximum contaminant levels (MCL's) for inorganic compounds, organic compounds, and pesticides in drinking water supplies. So far, MCL's have been set for only a few synthetic organic chemicals and VOC's. The MCL's set by the SDWA are often used as clean-up goals for groundwater remediation efforts (Goodrich et al., 1991).

As a result of increased governmental regulation and public concern, there are many sites being remediated at the current time. Because of the limited success of pump-and-treat remediation, many new remediation techniques are being used. All remediation technologies probably will not be able to remove all of the contaminants present because of the complex subsurface geology and the heterogeneous distribution of contaminants occurring at most sites (Mackay and Cherry, 1989).

1.2 Remedial Technologies for Subsurface Restoration

In most instances, once VOC's or other liquid hazardous chemicals are introduced into the subsurface they are transported through the unsaturated (vadose) zone first, before reaching the saturated zone or water table. Once bulk advective transport ceases, an immobile mass of contaminant remains trapped in the unsaturated zone by capillary forces. The residual saturation, percentage of pore space occupied by a liquid, can be quite substantial (Hoag and Marley, 1986). The

1.2 Remedial Technologies for Subsurface Restoration

amount of contaminant retained in the unsaturated pore space decreases with increasing particle diameter and soil moisture content. The degree of saturation for gasoline applied to initially dry sands in the laboratory ranged from 14-55%.

As infiltrating water moves past this immobile phase, some of the contaminant mass is dissolved into the aqueous phase and transported down to the aquifer. This immobile mass or residual saturation can continue to serve as a source of groundwater contamination for a long period of time since many VOC's are only slightly soluble in water (Corapcioglu and Baehr, 1987). Because complete remediation of groundwater is very difficult, it is important that all possible sources of contamination be removed from the soil in the unsaturated zone. Remediation of the contaminated soil above the water table is often done in conjunction with groundwater pump-and-treat decontamination (Malot and Wood, 1988).

The remedial technologies that are used to clean-up contaminated soils can be classified as either in situ or non-in situ. The non-in situ technologies include thermal treatment (incineration), landfilling, and solidification (Preslo and Miller, 1989). Because non-in situ technologies usually involve the physical removal of the contaminated soils, they can be very expensive to implement. Landfilling, a frequently used method for disposal of contaminated soils, is being used with less frequency due to increased cost and more stringent EPA regulations (Lowrance, 1990).

In situ remediation techniques can be further divided into physical, chemical, and biological methods (Vreeken and Sman, 1988). The three major physical methods of in situ treatment are water flushing, steam stripping, and subsurface vapor extraction (SVE). Steam stripping is the best method for removing the less volatile components in highly permeable soils. Water flushing can be used effectively when the contaminants are highly soluble in water.

1.2 Remedial Technologies for Subsurface Restoration

SVE, also known as forced venting, vacuum extraction, or air stripping, is a relatively new technique that is used to remove a wide range of VOC's from the subsurface (Hutzler et al., 1989). SVE systems are being used with increased frequency as part of remediation efforts. Because this remediation technology has only been used for the last decade or so, limited research has been conducted to investigate the processes affecting SVE performance and applicability.

1.3 Research Objectives

The main objective of this research was to gain a better understanding of the fundamental parameters that affect the removal of volatile organic chemicals from porous media by SVE. The parameters investigated were vapor flowrate, chemical properties, and temperature. The assumption of local equilibrium existing between the vapor phase and NAPL phase was studied. An attempt was made to model the SVE process in the laboratory using the local equilibrium assumption.

2 Vapor Extraction Systems

2.1 Introduction

This chapter presents a brief description of the design and field application of SVE. The factors that affect the performance and applicability of SVE systems in a general sense are discussed. A review of the limited, but rapidly growing, amount of literature published on SVE is also included.

SVE is an in situ remediation technique used to remove VOC's from the subsurface thereby eliminating the source of further groundwater contamination (Thorton and Wooden, 1982; Marley and Hoag, 1984; Hutzler et al., 1990). The method involves simply removing air from the unsaturated zone that contains VOC vapors. Air flow is created by introducing a vacuum in the soil through a series of recovery wells. The flow of clean unsaturated air through the contaminated soil increases the volatilization of the compounds present and provides a controlled pathway for their removal. SVE can also be used to help remove VOC's present as a floating product on top of groundwater (Crow et al., 1987).

SVE has several advantages over other soil remediation techniques (Hutzler et al., 1989). Unlike non-in situ technologies, SVE systems create minimal disturbance of the contaminated soil and can be installed in areas where space is limited. For example, SVE systems have been used to remediate soils contaminated with gasoline leaking from underground storage tanks below service stations (Hoag and Cliff, 1988). SVE systems can be constructed from standard equipment that is easy to obtain and operate. It can sometimes be more practical to treat large volumes of contaminated soil with SVE than with other methods that require soil excavation. SVE systems can help enhance the natural biodegradation of VOC's by increasing the oxygen supply in the soil air (Miller et al., 1990a). Finally, with SVE it is

2.1 Introduction

possible to recover the chemical product from the exhaust air and dispose of it properly.

2.2 Components of SVE Systems

The main components common to most SVE systems are shown in Figure 1. Extraction wells, air blowers or vacuum pumps, flow meters, vacuum gauges, and air sampling ports are usually included in a SVE installation (Hutzler et al., 1989). In addition, air inlet or injection wells, air-water separators, impermeable caps, and exhaust vapor treatment equipment are often used.

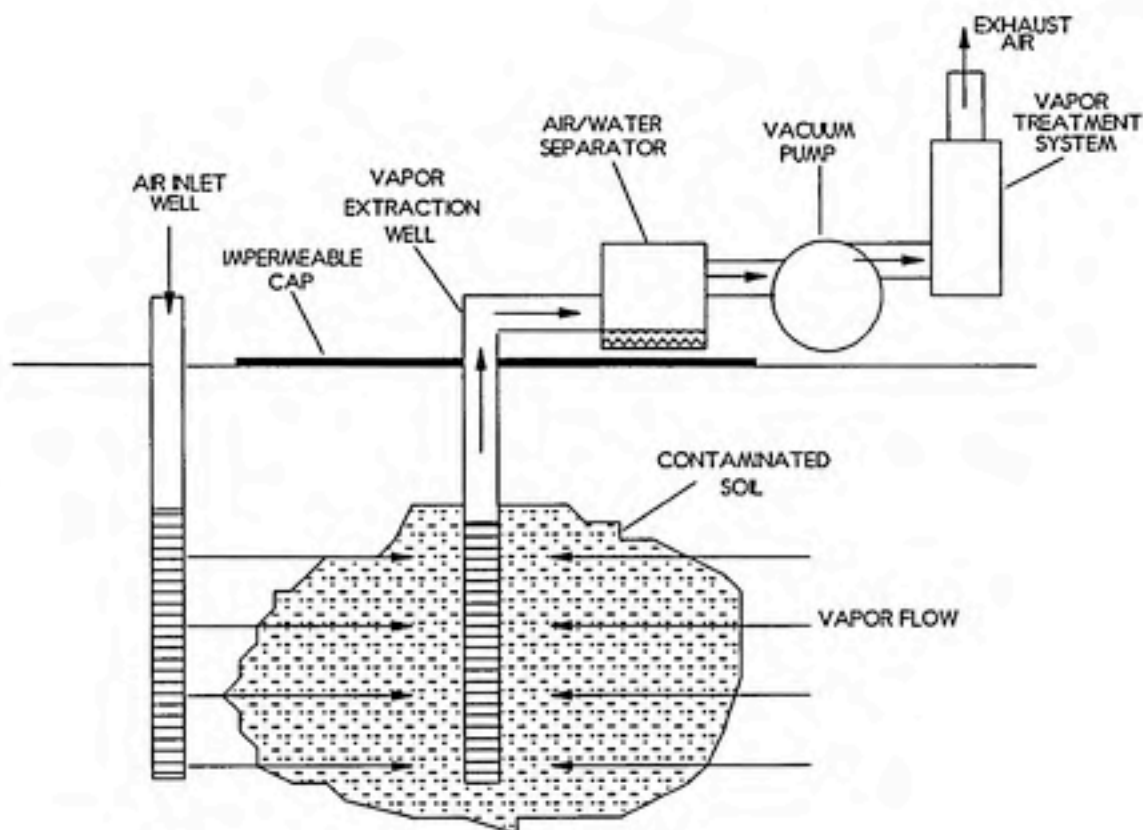


Figure 1. Schematic of a typical SVE system.

2.2 Components of SVE Systems

The extraction wells are usually installed in the areas of highest soil contamination. The screened section of an extraction well may extend all the way down to the capillary fringe zone just above the water table. Air inlet wells are used to help direct the path of air flow through the regions of highest contamination and to maintain vapor control in localized areas (Crow et al., 1987). In some instances, pressurized air is injected into air inlet wells in order to increase the vapor flow rate.

Air blowers or vacuum pumps are used to create the pressure drop that causes the air to flow towards the extraction wells. Typical extraction well pressures created by air blowers are in the range of 0.90–0.95 atmospheres (Johnson et al., 1990). Air flowrates usually range from 100 to 1,000 scfm.

Gas flow meters, vacuum gauges, and air sampling ports are used in order to determine the operational efficiency of the SVE system. Exhaust air samples are taken periodically along with flow rate measurements in order to calculate the contaminant mass removal rate. Vacuum gauges are used to determine if there are any pressure leaks in the system. They are also used to provide some estimate of the radius of influence of an extraction well along with the media permeability.

Air-water separators are installed to remove any condensation that may form in the exhaust air. Air in the subsurface is often near saturation with respect to water. As the air expands due to the vacuum applied, condensation may occur (Bennedsen, 1987). The air-water separator is used to protect the air blower as well as the exhaust vapor treatment equipment from moisture.

An impermeable cap is often placed over the contaminated site in order to enhance the horizontal flow of air towards the extraction well (Hutzler et al., 1990). Without an impermeable cap, air flow may short circuit from the ground surface near the extraction well thereby by-passing the zone of contamination. The radius of influence of the extraction well may be increased by installing an impermeable cap. An impermeable cap can also prevent the infiltration of precipitation through

2.2 Components of SVE Systems

the contaminated region. This may help improve the SVE process by inhibiting any further chemical migration to the groundwater table and by reducing the moisture content of the soil. By keeping the moisture content of the soil low, air-water separators may not be required.

The need for exhaust vapor treatment equipment depends upon the types of compounds being vented, health-based air quality standards, and government air quality standards (Hydro Geo Chem, 1990). Since the treatment of exhaust air can comprise up to 50% of the total installation and operational costs of a SVE system (Koltuniak, 1986), the decision to use exhaust vapor treatment is studied carefully. It may be possible to avoid using vapor treatment equipment by extending the period of SVE operation and lowering the emission rates. Types of air treatment systems that have been used in SVE installations include liquid-vapor condensers, gas incinerators, catalytic oxidation, and granular activated carbon canisters. Granular activated carbon (GAC) systems are used most frequently. For GAC systems it is very important to keep the moisture content of the exhaust air as low as possible in order to optimize the carbon usage rate.

2.3 Main Factors Affecting SVE Performance

Even though the operation of SVE systems is conceptually simple, the performance and applicability of this remediation technique depends on many factors. The three main factors that control the performance and removal efficiency of SVE systems are (Johnson et al., 1990):

- (1) chemical composition of the contaminant;
- (2) vapor flowrates through the contaminated soil; and
- (3) flow path of air relative to the location of contaminants.

For a contaminant to be removed by SVE, it must be sufficiently volatile in order to partition into the vapor phase from the other phases it is associated with.

2.3 Main Factors Affecting SVE Performance

If a substantial portion of the total contaminant mass is in a pure liquid phase, then volatility is determined by the vapor pressure of the liquid (Hydro Geo Chem, 1990). If most of the mass is associated with the aqueous phase, volatility will be controlled by the Henry's constant. Compounds with vapor pressures above 0.5 mm of mercury and dimensionless Henry's constants above 0.01 are good candidates for removal with SVE (Bennedsen et al., 1985).

Adequate vapor flowrates must be achieved through the zone of contamination in order to decrease the remediation time. The removal rate increases with increased flowrate as long as there is chemical equilibrium between all phases present. Because there is a limit to the amount of pressure drop that can be induced in an extraction well, the air permeability of the soil is the most important factor governing the air flowrates. The air permeability of a soil is a function of media type and volumetric air content (DiGiulio and Cho, 1990). In general, higher vapor flowrates can be achieved in sandy media as compared to clayey media.

Finally, the location of the air flow paths relative to the contaminants is very important to the overall removal rates of contaminants. In homogeneous media with uniform distribution of contaminants, the maximum removal rates will occur. If the soil contains zones of low permeability (i.e. clay), then the air flow paths may not be uniformly distributed causing contaminants to diffuse from a relatively stagnant areas to the air flow paths. Removal rates are much lower when diffusion limitations occur.

2.4 Case Studies of SVE Application

Because the SVE remediation technique has been used only recently, there are few case studies reported in the literature. A recent report conducted on behalf of the USEPA (Hutzler et al., 1989) attempted to summarize some of the field applications of SVE systems. The report showed that SVE has been applied with very good

2.4 Case Studies of SVE Application

success to a wide variety of remediation problems. Some of the compounds removed successfully with this method include trichloroethylene, benzene, carbon tetrachloride, and gasoline components. Most of the SVE systems were used in conjunction with other remediation techniques such as groundwater pump-and-treat.

Many SVE systems have been installed to remediate media contaminated by leaking underground storage tanks containing gasoline (Hoag and Cliff, 1988; Malot and Wood, 1988; Crow et al., 1987). In these applications, large amounts of gasoline were recovered from the unsaturated zone. Removal of large quantities of gasoline product floating on top of the water table was also observed.

Hutton (1990) reported on the successful remediation of an aquifer contaminated with chlorinated VOC's such as 1,1,1-trichloroethane (TCA). For one year previous to SVE installation, groundwater extraction had failed to reduce the contamination significantly. By using SVE along with groundwater extraction for 18 months, the total predicted remediation time was reduced by 5 years. Groundwater concentrations of TCA were reduced from 3,700 ppb to 160 ppb within a period of 118 days.

Towbridge and Malot (1990) presented a case study of SVE used to remove industrial solvents floating as a separate layer on top of the groundwater table. The thickness of the layer decreased substantially during the first 60 days of operation. Both chlorinated and aromatic hydrocarbons were removed.

In a majority of the cases reported, the initial mass removal rate was high and decreased in an exponential fashion with time. The reduction in removal rate has been associated with the preferential volatilization and biodegradation of lower molecular weight compounds and mass transfer limitations which become more important as the amount of contaminant mass in the soil is lowered (DiGiulio and Cho, 1990). Hoag and Cliff reported that 90% of all gasoline product recovered by

SVE was removed in the first month of a three month operational period. Other researchers report similar results.

2.5 Previous Laboratory Research

The limited amount of research conducted so far to investigate the SVE process has varied widely in scale and approach. Several models have been developed to predict the performance of SVE systems. None of the models have been validated under a wide range of field conditions.

Thorton and Wootan (1982) conducted a large scale experiment to study the effectiveness of SVE for removing gasoline from fine sand. A concrete and steel tank, which was 3-m wide, 6-m long, and 1.2-m deep, was used to conduct the SVE experiment. They observed a reduction in the gasoline removal rate with time as the more volatile components were removed. An increase in the CO₂ concentration in the effluent air was also observed, indicating some biological degradation of the contaminants. A 30% reduction in the vapor flowrate after 6 days of venting reduced the gasoline removal rate by about 50% indicating that equilibrium conditions existed. The more volatile paraffin components of gasoline (i.e., pentane and hexane) were removed more easily than the aromatics during the 11-day extraction period.

Marley and Hoag (1984) used a bench scale plexiglass column to examine the effects of media density, moisture content, solid particle size, and air flow rate on the removal of gasoline. They observed local equilibrium between the vapor phase and the residual phase regardless of the air flow rate or other column conditions. The mass loss rate declined very rapidly and leveled off. No mass transfer or diffusion limitations were observed. The equilibrium model developed by the authors agreed well with the experimental data.

2.5 Previous Laboratory Research

Large circular columns, 0.91-m diameter by 3.05-m high, were used by Rainwater et al. (1989) to remove a four-component hydrocarbon mixture by SVE. Equilibrium between the vapor phase and the liquid phase was not observed in their experiments during the 15-month operational period. An equilibrium model did not satisfactorily predict the removal of the components in the columns. A diffusion-controlled model was able to describe the data with good agreement by using curve-fitting methods. The authors noted that short-circuiting of air flow in the columns may have caused the low removal rates observed as well as the non-equilibrium conditions.

Lingineni and Dhir (1990) developed a one-dimensional non-isothermal model to predict temperature variations and contaminant removal in a rectangular 60-cm long plexiglass column. They observed significant temperature reductions in the column as ethyl alcohol was evaporated from glass beads. Equilibrium between phases was apparent. The specific discharges used during the experiments were much higher than that which could be expected in an actual SVE application (15 cm/s). They concluded that considerable decreases in soil temperature could cause condensation of water in incoming air during the SVE process, thereby lowering the removal rates.

Gierke et al. (1990) performed a set of laboratory experiments in order to validate a mathematical model, which predicted the removal of contaminants dissolved in the aqueous phase by SVE. The model was used to examine the impact of air advection, gas diffusion, sorption, and air-water mass transfer on SVE performance. In dry soils, gas advection and diffusion had the greatest impact on contaminant removal. In wet aggregated soils, the presence of moisture decreased the removal rate because of intraaggregate diffusion limitations.

In summary, the small number of experiments conducted to study the SVE process are somewhat inconclusive. Local equilibrium between phases was observed

2.5 Previous Laboratory Research

by some of the investigators, while others observed mass transfer and/or diffusion limitations. The mathematical models developed to predict experimental data have not been used on a field scale. There is some general understanding of the processes that seem to have the most effect on SVE performance, but more experimental research is needed.

3 Fate and Transport of VOC's in the Unsaturated Zone

3.1 Introduction

Since the major impetus of SVE is to remove volatile organic chemicals (VOC's) present in the unsaturated (vadose) zone, it is important to have some understanding of how the various natural processes affect the fate and transport of organic contaminants in this region. SVE systems remove contaminants present in the vapor phase, so it is important to understand how the various processes affect the partitioning of VOC's to this phase. If the VOC concentrations in the vapor phase are too low, it may not be economically or technically feasible to use SVE for subsurface restoration.

Mathematical modeling of the transport of contaminants in the vadose zone during the SVE process can aid in the design and operation of SVE systems. Several researchers have developed models to describe multiphase flow and transport of organic chemicals in the subsurface (Pinder and Abriola, 1986; Parker et al., 1986; Corapcioglu and Baehr, 1987; Abriola, 1988; Sleep and Sykes, 1989; Mayer and Miller, 1990a, 1990b). Sleep and Sykes included advective gas transport (SVE) in their model, but the NAPL (non-aqueous phase liquid) phase was assumed to be immobile. Volatilization and gas-aqueous phase partitioning were incorporated in the model using a simple mass transfer expression. Mayer and Miller (1990a, 1990b) presented a general multiphase model that included three mobile fluid phases, species transport, and rate-dependent interphase mass transfer among all phases.

Very few models have been developed specifically to simulate the SVE process. Most of the models described in the literature assume that local equilibrium exists between the phases present (Baehr and Hoag, 1988; Johnson et al., 1990; Marley

and Hoag, 1984; Stephanatos, 1990). Lingineni and Dhir (1990) presented a non-isothermal model to predict the performance of SVE systems. Rainwater et al (1989) developed a diffusion-controlled model to describe the removal of contaminants when there are diffusion limitations in the subsurface.

In this chapter, equations describing the transport of contaminants in the unsaturated zone during SVE are presented to better understand the fundamental processes involved. This formulation includes development of the compressible gas flow equation based on Darcy's Law. A simple equilibrium model, which was used to model the experimental data obtained during this research, is also formulated.

3.2 Contaminant Transport in the Subsurface

Contaminants (VOC's) are usually introduced into the subsurface as a separate non-aqueous phase liquid (NAPL) or in an aqueous solution (Corapcioglu and Baehr, 1987; Sleep and Sykes, 1989). The contaminant may comprise one single constituent (e.g., benzene or TCE) or a mixture of many constituents (e.g., gasoline). For instance, leaded gasoline contains over 180 different compounds (Sanders and Maynard, 1968).

If the contaminants are released in large enough quantities, they will be transported mostly by bulk advective flow. The general direction of flow will be downward in response to gravity, but the porous media will cause lateral spreading of the contaminants due to mechanical (kinematic) dispersion (Marsily, 1986). As the contaminant moves through the unsaturated zone, a significant amount of the total mass may be retained by capillary forces. If the contaminant is in the form of a NAPL, then interfacial forces acting between the air phase or aqueous phase and NAPL will cause residual "blobs" to be formed in the soil (Powers et al., 1991). The size and shape of these "blobs" will depend to large extent on the solid phase particle size distribution.

3.2 Contaminant Transport in the Subsurface

If all of the contaminant mass is not transformed into residual saturation or no impermeable strata are encountered, then VOC's will reach the saturated zone (water table). If the contaminant is in the form of a NAPL, its further movement will be governed largely by its density relative to water (Pinder and Abriola, 1986). If the NAPL is less dense than water (e.g., gasoline) it will tend to form a separate layer on top of the groundwater surface and will be further transported in the same general direction as the groundwater flow. NAPL's denser than water (e.g., trichloroethylene) will continue to move down through the aquifer until an impermeable zone is reached.

The VOC's remaining in the unsaturated zone after bulk flow ceases can occur in one of four phases:

- (a) a separate NAPL phase,
- (b) a sorbed phase on soil particles,
- (c) a dissolved (aqueous) phase, or
- (d) a vapor phase.

The various constituents of the contaminant will partition among the different phases present in attempts to reach equilibrium. The degree of partitioning of a specific VOC among these four phases will depend to a large extent on the volatility and water solubility of the VOC, the solid phase moisture content, and the type of solid phase present (Silka, 1988). The partitioning into the vapor phase is of utmost importance to the effectiveness of the SVE process.

3.3 Processes Affecting VOC Fate and Transport

3.3.1 Overview

Once introduced into the subsurface, the fate and transport of VOC's is affected by many processes, including dissolution, volatilization, and gas-water partitioning

3.3 Processes Affecting VOC Fate and Transport

(Sleep and Sykes, 1989). In addition biodegradation, vapor phase diffusion, and sorption can also be important. The extent and persistence of VOC's in the unsaturated zone will be highly influenced by the rate of volatilization to the vapor phase and dissolution to the aqueous phase.

As previously mentioned, since SVE removes contaminants present in the vapor phase, it is important to understand how the various processes affect the presence of compounds in this phase. The processes that are most important in regards to SVE are volatilization, gas-aqueous phase partitioning, and vapor phase diffusion.

3.3.2 Gas-Aqueous Phase Partitioning

Partitioning between the VOC's in the vapor phase and VOC's dissolved in the aqueous phase can be an important process in the unsaturated zone. Gas-aqueous phase partitioning, volatilization of VOC's from the aqueous phase to the vapor phase, is important to the SVE process only when a pure NAPL phase is not present in sufficient quantity (Hydro Geo Chem, 1990). If a NAPL phase exists, then most of the contaminant mass in the vapor phase will be a result of volatilization from this phase.

Henry's Law is used to describe the equilibrium partitioning of VOC's between the air and water phases (Corapcioglu and Baehr, 1987). This law states that the partial pressure of a constituent above the aqueous phase is proportional to the concentration in the aqueous phase. In terms of the concentrations in both phases at equilibrium, Henry's Law is

$$C_i^{v*} = H_c C_i^{w*} \quad (1)$$

where C_i^{v*} is the equilibrium concentration of component i in the vapor phase, C_i^{w*} is the equilibrium concentration in the water (aqueous) phase, and H_c is the

3.3 Processes Affecting VOC Fate and Transport

dimensionless Henry's constant. The Henry's constant can be estimated to a first approximation using the vapor pressure and the solubility of the VOC in water (Thibodeaux, 1979).

3.3.3 Volatilization from NAPL Phase

Volatilization, the mass transfer of a compound from a pure phase to the vapor phase, can be the dominant process affecting the fate and transport of immobile VOC's in the unsaturated zone (Sleep and Sykes, 1989). In situations where a pure NAPL phase exists, the volatilization process controls the overall partitioning of the VOC's among the phases present.

The volatilization rate is highly dependent upon the vapor pressures and mole fractions of the compounds present. Assuming that the NAPL is in equilibrium with the vapor phase and behaves as an ideal solution, the vapor pressure of each component can be expressed by Raoult's Law as

$$P_i^v = X_i P_i^{v*} \quad (2)$$

where P_i^v is the vapor pressure of component i [F/L^2], X_i is the mole fraction of i in the liquid phase [mol/mol], and P_i^{v*} is the vapor pressure above pure liquid i [F/L^2] (Barrow, 1973). By applying the ideal gas law, the estimated total contaminant vapor phase concentration in equilibrium with a pure NAPL mixture is given by

$$C_i^{v*} = \sum_{i=1}^{n_c} \frac{X_i P_i^{v*} M_i}{RT} \quad (3)$$

where C_i^{v*} is the total vapor phase concentration [M/L^3], M_i is the molecular weight of component i [M/mol], R is the gas constant [$FL/mol \text{ } ^\circ K$], and T is the system

3.3 Processes Affecting VOC Fate and Transport

temperature [$^{\circ}\text{K}$] (Johnson et al., 1990). For example, the total vapor phase concentration above pure gasoline is approximately 1300 mg/ ℓ .

The mass transfer rate from a pure liquid phase to the vapor phase is a function of the concentration gradient (driving force) and the interfacial area between the two phases (Sherwood et al., 1975). Raoult's Law predicts the maximum vapor phase concentration that may exist just above the NAPL at equilibrium, which is the upper limit to the concentration difference in the driving force expression. One of the fundamental principles behind the SVE process is to lower the vapor phase concentration in the bulk air phase in order to provide the maximum concentration gradient and thereby maximize the volatilization rate. Mass transfer will be discussed in more detail in Section 3-5 during the development of the contaminant transport equations.

3.3.4 Vapor Phase Diffusion

The diffusion of VOC vapors in the subsurface air can be an important mechanism for contaminant transport if moisture content is low and the media is permeable (Baehr, 1987). The diffusion process can cause the spreading of contamination in the subsurface, thereby increasing the potential for further groundwater quality problems. Since the vapor phase diffusion coefficients of VOC's are orders of magnitude higher than the aqueous phase diffusion coefficients, vapor diffusion will dominate over liquid diffusion and will serve as the primary transport mechanism within the vadose zone and from the vadose zone to the atmosphere as long as bulk advective flow is not occurring (Bruell and Hoag, 1984).

The steady-state diffusive flux in the unsaturated zone can be expressed by Fick's First Law:

$$J = -D_e \frac{dC}{dz} \quad (4)$$

3.3 Processes Affecting VOC Fate and Transport

where J is the contaminant vapor flux through the media [M/L^2T], D_e is the effective diffusion coefficient in the media [L^2/T], and dC/dx is the concentration gradient in the air phase [M/L^4] (Peterson et al., 1988; Roy and Griffin, 1990). The effective diffusion coefficient D_e is a function of chemical diffusivity in the bulk air phase, moisture content, and media porosity. The diffusion coefficient in porous media (D_e) is less than the diffusion coefficient in bulk air (D_a) [L^2/T] due to the obstructed movement caused by the tortuous nature of the air-filled pores. Millington and Quirk (1961) developed an empirical relationship between the two diffusion coefficients

$$D_e = D_a \frac{\epsilon_a^{10/3}}{n^2} \quad (5)$$

where ϵ_a is the volume fraction of the soil occupied by the air phase [L^3/L^3] and n is the porosity or void fraction of the porous media [L^3/L^3]. As the moisture content of the media increases, the effective diffusion coefficient decreases along with the vapor flux through the soil.

Experiments conducted by Wickramanayake et al. (1989) showed that the diffusive transport of hydrocarbon vapors was indeed reduced by the presence of moisture in the soil. They observed that the diffusion of the more water soluble compounds was retarded more than the less soluble ones. In addition, they concluded that as the vapor phase concentration increased, vapor transport was controlled by both diffusion and density-driven flow.

In regards to SVE, the diffusion of VOC vapors out of the contaminated zone into the regions of advective air flow can limit the removal rate of contaminants (Hutton, 1990; Rainwater et al., 1989). Concentration gradients can form between the preferential air flow paths and the stagnant zones containing NAPL thereby causing diffusive transport to occur.

3.4 Compressible Flow Equations

Flow models can aid in the design of SVE systems and in determining the vapor flowrates and directions in the subsurface. The advective flow of air in the soil during the SVE process can best be modeled using equations for compressible fluid flow. The differential equations governing compressible flow are nonlinear due to gas density dependence on pressure. It has been suggested that due to the small pressure drops encountered in most SVE installations, groundwater flow models may be used to approximate vapor flow (Massmann, 1989).

The basic equation describing the flow of water was developed by Henri Darcy in 1856. Darcy determined empirically that the flow of water through a sand filter was proportional to the hydraulic gradient (head loss) across the filter, and the total cross sectional area. Darcy's law for saturated flow can be expressed as

$$Q = -KA \frac{dh}{dl} \quad (6)$$

where Q is the volumetric flux through the porous medium [L^3/T], A is the cross sectional area [L^2], dh/dl is the hydraulic gradient [L/L], and K is the constant of proportionality known as the hydraulic conductivity of the porous media [L/T] (Marsily, 1986). Darcy's law is sometimes written in the form

$$q_i = -K \frac{dh}{di} \quad (7)$$

where q_i is the specific discharge or filtration velocity [L/T] in the direction i . The intrinsic permeability k [L^2], which is independent of the fluid characteristics, is often used in place of the hydraulic conductivity K . The hydraulic conductivity is determined from the equation

3.4 Compressible Flow Equations

$$K = \frac{k\rho g}{\mu} \quad (8)$$

where ρ is the density of the fluid [M/L³], g is the acceleration due to gravity [L/T²], and μ is the dynamic viscosity [LT/M]. A more generalized form of Darcy's law that is valid for both steady and unsteady flow of compressible fluids is

$$q_i = -\frac{k_{ij}}{\mu} \left(\frac{\partial p}{\partial x_j} + \rho g \frac{\partial z}{\partial x_j} \right) \quad (9)$$

where k_{ij} are the components of the intrinsic permeability tensor, p is the fluid pressure, and z is the elevation above a reference datum [L] (Huyakorn and Pinder, 1983). For the condition where the coordinate system is aligned to match the principal directions of the intrinsic permeability tensor, equation (9) can be expressed as

$$q_i = -\frac{k_i}{\mu} \left(\frac{\partial p}{\partial x_i} + \rho g \frac{\partial z}{\partial x_i} \right) \quad (10)$$

where i corresponds to the x , y , and z directions.

In order to obtain the governing equation for the flow of compressible fluids in porous media, equation (10) must be combined with the mass continuity equation of the form

$$-\frac{\partial(q_i\rho)}{\partial i} = \frac{\partial(n\rho)}{\partial t} \quad (11)$$

If the compressibility of the porous medium can be neglected the continuity equation becomes

$$-\frac{\partial(q_i\rho)}{\partial i} = n \frac{\partial\rho}{\partial t} \quad (12)$$

Substituting equation (10) into the continuity equation (12) yields

$$\frac{\partial}{\partial i} \left[\frac{k_i \rho}{\mu} \left(\frac{\partial p}{\partial i} + \rho g \frac{\partial z}{\partial i} \right) \right] = n \frac{\partial \rho}{\partial t} \quad (13)$$

which is the general form of the equation for compressible flow in porous media.

If the compressible fluid can be considered to obey the ideal gas law, then

$$\rho = \frac{MP}{RT} \quad (14)$$

For isothermal conditions, the relationship between gas density and pressure can be expressed as

$$\frac{\partial \rho}{\partial t} = \frac{M}{RT} \frac{\partial P}{\partial t} \quad (15)$$

Substituting equations (14) and (15) into equation (13) and neglecting the effect of gravity, the equation for compressible flow becomes

$$\frac{\partial}{\partial i} \left(\frac{k_i}{\mu} P \frac{\partial P}{\partial i} \right) = n \frac{\partial P}{\partial t} \quad (16)$$

Equation (16) can also be written in the form

$$\frac{\partial}{\partial i} \left(\frac{k_i}{\mu} \frac{\partial u}{\partial i} \right) = \frac{n}{P} \frac{\partial u}{\partial t} \quad (17)$$

where $u = P^2$.

For isotropic porous media and constant μ , equation (17) simplifies to (Johnson et al., 1990)

3.4 Compressible Flow Equations

$$\frac{\partial}{\partial i} \left(\frac{\partial u}{\partial i} \right) = \left(\frac{n\mu}{kP} \right) \frac{\partial u}{\partial t} \quad (18)$$

which can also be expressed as

$$\nabla^2 P^2 = \frac{2n\mu}{k} \frac{\partial P}{\partial t} \quad (19)$$

For the case where the void space contains more than one phase (i.e. aqueous, NAPL, or air), n in equation (19) is replaced with ϵ_a , the volume fraction of the porous media occupied by the air phase ($\epsilon_a < n$). Assuming that ϵ_a remains constant and only the air phase is mobile, equation (19) can be used to model the advective flow of air as in SVE systems. If the saturations of the NAPL and aqueous phases are relatively high and these phases flow along with the air phase, then k must be multiplied by the relative permeability. The relative permeability is the ratio of the effective permeability of a particular fluid phase to the absolute permeability k . The relative permeability k_r is dependent on the fluid saturations of the phases present (Craft and Hawkins, 1959).

3.5 Contaminant Transport Equations

The transport of contaminants in the unsaturated zone is a multiphase process. The transport of each constituent can occur as a solute in the aqueous phase, vapor in the gas (air) phase, and as part of the immiscible (NAPL) phase (Corapcioglu and Baehr, 1987). The chemical compositions of each of the phases present will depend on the susceptibilities of the constituents to the various mass transfer and chemical processes occurring in the subsurface.

The equations describing multiphase flow and transport are derived from the mass balance and momentum balance equations. The mass balance on species i in phase α produces the equation

$$\frac{\partial}{\partial t} (\epsilon_{\alpha} \rho^{\alpha} \omega_i^{\alpha}) + \nabla \cdot (\epsilon_{\alpha} \rho^{\alpha} \omega_i^{\alpha} \mathbf{v}^{\alpha}) - \nabla \cdot \mathbf{J}_i^{\alpha} = S_i^{\alpha} + R_i^{\alpha} \quad (20)$$

where \mathbf{v}^{α} is the mass average velocity of the α phase [L/T], ω_i^{α} is the mass fraction of species i in the α phase [M/M], ϵ_{α} is the volume fraction occupied by the α phase, ρ^{α} is the mass density of the α phase [M/L³], \mathbf{J}_i^{α} is the non-advective transport of i in the α phase [M/L³T], S_i^{α} is the exchange of mass of species i due to interphase diffusion or phase change [M/L³T], and R_i^{α} represents an external source of species i to the α phase [M/L³T] (Abriola, 1988).

The first term on the left-hand side of equation (20) accounts for the accumulation of species i in the α phase, while the second term accounts for the movement of mass due to the advective flow of the α phase. The third term represents movement of i due to non-advective transport (i.e. dispersion and molecular diffusion). The terms on the right-hand side of equation (20) represent source or sink terms due to change of phase (i.e., interphase mass transfer) and chemical or biological transformations respectively.

In order to describe the flow and transport of a single contaminant component i , a mass balance equation must be written for each phase in which species i is present. Typically the phases in which a species may be associated with are a solid phase, an aqueous (water) phase, a vapor phase, and a non-aqueous phase liquid (NAPL) phase. These phases are represented by the letters s , w , v , and n in the transport equations.

If species i is present in the vapor phase, then the mass balance equation for the vapor phase is

3.5 Contaminant Transport Equations

$$\frac{\partial}{\partial t} (\rho^v \epsilon_v \omega_i^v) + \nabla \cdot (\rho^v \epsilon_v \mathbf{v}^v \omega_i^v) - \nabla \cdot \mathbf{J}_i^v = S_i^v + R_i^v \quad (21)$$

Similarly, if i is present in the NAPL, aqueous, and solid phases then the mass balance equations for these three phases are respectively

$$\frac{\partial}{\partial t} (\rho^n \epsilon_n \omega_i^n) + \nabla \cdot (\rho^n \epsilon_n \mathbf{v}^n \omega_i^n) - \nabla \cdot \mathbf{J}_i^n = S_i^n + R_i^n \quad (22)$$

$$\frac{\partial}{\partial t} (\rho^w \epsilon_w \omega_i^w) + \nabla \cdot (\rho^w \epsilon_w \mathbf{v}^w \omega_i^w) - \nabla \cdot \mathbf{J}_i^w = S_i^w + R_i^w \quad (23)$$

$$\frac{\partial}{\partial t} (\rho^s \epsilon_s \omega_i^s) + \nabla \cdot (\rho^s \epsilon_s \mathbf{v}^s \omega_i^s) - \nabla \cdot \mathbf{J}_i^s = S_i^s + R_i^s \quad (24)$$

In order to model the transport of species i in the subsurface for non-equilibrium conditions, all four mass balance equations must be solved simultaneously, along with a coupled set of flow equations. One flow equation is needed for each mobile phase—typically the aqueous, vapor, and NAPL phases.

If most of the contaminant mass in the unsaturated zone is associated with the NAPL phase and the vapor phase, then equations (23) and (24) can be eliminated. Assuming that the NAPL phase is immobile, diffusion of species i within the NAPL phase is negligible, and no appreciable degradation occurs, equation (22) reduces to

$$\frac{\partial}{\partial t} (\rho^n \epsilon_n \omega_i^n) = S_i^n \quad (25)$$

3.5 Contaminant Transport Equations

Assuming that diffusion within the vapor phase is minimal in comparison to advective vapor flow and no degradation of contaminants occurs in the vapor phase, equation (21) becomes

$$\frac{\partial}{\partial t} (\rho^v \epsilon_v \omega_i^v) + \nabla \cdot (\rho^v \epsilon_v \mathbf{v}^v \omega_i^v) = S_i^v \quad (26)$$

Equation (25) states that the change in mass of species i in the NAPL phase is due only to interphase mass transfer. Since the mass of i lost from the NAPL phase must be gained by the vapor phase,

$$S_i^v = -S_i^n \quad (27)$$

Since advective flow is assumed to occur only in the vapor phase, the rate of mass transfer from the NAPL to the vapor phase is the step that determines the time required for contaminant removal in this instance.

An expression must be derived to describe the interphase mass transfer term S_i^v . There are many theories that have been proposed to describe the mass transfer process. The simplest theory used to describe interphase mass transfer is known as the stagnant film theory (Sherwood et al., 1975). This theory assumes that a stagnant film layer between the interface of the two phases provides the only resistance to mass transfer. The mass transfer of species i through the stagnant film layer can be written as

$$J_i^v = K_L (\Delta C_i) \quad (28)$$

where J_i^v is the mass flux of component i from the NAPL phase to the vapor phase [M/L^2T], K_L is the mass transfer coefficient [L/T], and ΔC_i is the concentration

3.5 Contaminant Transport Equations

difference of i across the phase boundary $[M/L^3]$. According to the stagnant film theory, the mass transfer coefficient K_L is dependent on the diffusion coefficient of component i in the vapor phase and the thickness of the stagnant layer l .

The stagnant film theory is known to be a poor model of the actual mass transfer from a NAPL to a vapor or aqueous phase (Miller et al., 1990b). However, the general first-order formulation with a linear driving force is an adequate representation, which results from more conceptually satisfying formulations. The key point is that K_L is a function that is dependent upon the physical and chemical properties of the system under consideration. It must be determined by experimentation or estimated from literature correlations that account for the physical and chemical properties of the system.

Assuming that equilibrium exists at the boundary between the two phases present, equation (28) becomes

$$J_i^v = K_L (C_i^{v*} - C_i^v) \quad (29)$$

where C_i^{v*} is the saturated vapor concentration of component i in the vapor phase and C_i^v is the bulk phase concentration. In order to use equation (29) in the mass balance equations in place of the interphase mass transfer term S_i^v , K_L must be multiplied by the volume fraction of the vapor phase and the specific surface area a . The resulting expression used to describe the mass transfer term is

$$S_i^v = K_L a \epsilon_v (C_i^{v*} - C_i^v) \quad (30)$$

where a is defined as the interfacial surface area between the two phases per volume of porous media $[L^2/L^3]$. As discussed by Miller et al (1990b), the value of a is difficult to quantify in porous media due to the complex shapes exhibited at the

NAPL/vapor interface. Also, in the case of SVE the value of a will change with time as the mass of NAPL is reduced.

The concentration of species i in the α phase can also be expressed as

$$C_i^\alpha = \rho^\alpha \omega_i^\alpha \quad (31)$$

Substituting this expression for the concentration terms in equation (30) gives

$$S_i^v = K_L a \epsilon_v (\rho^v \omega_i^{v*} - \rho^v \omega_i^v) \quad (32)$$

The mass balance equation for the vapor phase, equation (26), becomes

$$\frac{\partial}{\partial t} (\rho^v \epsilon_v \omega_i^v) + \nabla \cdot (\rho^v \epsilon_v \mathbf{v}^v \omega_i^v) = K_L a \epsilon_v (\rho^v \omega_i^{v*} - \rho^v \omega_i^v) \quad (33)$$

Similarly, the mass balance equation for the NAPL phase becomes

$$\frac{\partial}{\partial t} (\rho^n \epsilon_n \omega_i^n) = -K_L a \epsilon_v (\rho^v \omega_i^{v*} - \rho^v \omega_i^v) \quad (34)$$

Equations (33) and (34) must be solved simultaneously to model the transport of component i in the unsaturated zone during the SVE process.

In order to solve the system of mass balance equations presented above, an expression must be derived for the mass average velocity of the vapor phase, \mathbf{v}^v , which satisfies the momentum balance. If the vapor phase is the only mobile phase present then the mass average velocity can be expressed by

$$\mathbf{v}^v = -\frac{k_v \rho^v g}{\mu_v} \nabla \left(\frac{P^v}{\rho^v g} + z \right) \quad (35)$$

3.5 Contaminant Transport Equations

where k_v is the intrinsic permeability tensor for the vapor phase, P^v is the vapor phase pressure, and the other terms are as previously described (Bear, 1979).

From equations (33) and (34) it can be observed that some expression must be developed to account for the change in NAPL mass and volumetric fraction with time as the SVE process proceeds. This is not a trivial task owing to the fact that the NAPL mass is usually distributed heterogeneously as individual blobs in a wide range of shapes and sizes (Mayer and Miller, 1991). Changes in NAPL mass will affect the rate of mass transfer to the vapor phase since the interfacial area between the phases will change. Some researchers have attempted to solve this transient problem for the case of NAPL dissolution by water in the saturated zone by assuming that the NAPL mass is uniformly distributed as spherical blobs and using a complex scheme to keep track of changing blob size and interfacial area (Powers et al., 1991). In addition, the reduction in the volumetric fraction of NAPL can cause an increase in the mass average velocity with time. The intrinsic permeability of the porous media will increase as a larger fraction of the pore space is available to advective air flow.

3.6 Vapor-Liquid Equilibrium Model

SVE can best be modeled using the differential equations for contaminant transport in the unsaturated zone. Due to the detailed information on subsurface conditions required to use these models, a more simplified approach can be used as a first-cut approximation. As mentioned in section 3.1, several researchers have developed simple equilibrium-based models to predict contaminant removal during the SVE process. Predicted removal rates based on equilibrium models usually represent the best case scenario for contaminant removal in the subsurface.

The key assumptions used in the development of the vapor-liquid equilibrium model presented in this section are:

3.6 Vapor-Liquid Equilibrium Model

- local equilibrium exists between the vapor and the NAPL phase;
- the NAPL is distributed uniformly in the porous media;
- air flow is uniform across the entire porous media cross section;
- the NAPL mixture behaves as an ideal solution;
- degradation is negligible; and
- the effluent air is saturated with vapors from all components present in the NAPL.

Because the mass transfer rates from pure VOC liquids are very high as compared to the pore velocities, the local equilibrium assumption seems to be valid for many situations. Johnson et al. (1990) estimated that the soil air becomes saturated and reaches equilibrium within a distance of 0.2 cm from the NAPL surface at a pore velocity of 1 cm/s. If the NAPL is not distributed uniformly and preferential air flow paths are formed, then contaminant removal rates may be overestimated using the vapor-liquid equilibrium model.

The differential equation used to account for the molar removal of a single NAPL constituent is

$$\frac{dN_i}{dt} = -QC_i^{v*} \quad (36)$$

where N_i is the total number of moles of component i [mol], Q is the volumetric vapor flowrate [L^3/T], and C_i^{v*} is the equilibrium molar concentration of i in the effluent vapor [mol/L^3]. The equation used to calculate C_i^{v*} for any component at time t , which is obtained by combining Raoult's Law and the Ideal Gas Law, is

$$C_i^{v*} = \frac{X_i P_i^{v*}}{RT} \quad (37)$$

3.6 Vapor-Liquid Equilibrium Model

where X_i , P_i^{v*} , R , and T are as previously defined. When P_i^{v*} is expressed in atmospheres and T in degrees Kelvin, equation (37) becomes

$$C_i^{v*} = 12.180 \frac{X_i P_i^{v*}}{T} \quad (38)$$

where C_i^{v*} is the concentration in moles per liter.

A finite difference approach can be used to approximate equation (36). Using an implicit method to approximate the time derivative, the finite difference algorithm for equation (36) is

$$N_i^{t+\Delta t} = N_i^t - \Delta t Q \frac{X_i P_i^{v*}}{RT} \quad (39)$$

where Δt is the time step [T], and X_i is evaluated at time t . The mole fractions of all constituents are updated after each time step. The new mole fraction of component i after the time step Δt is determined from

$$X_i^{t+\Delta t} = \frac{N_i^{t+\Delta t}}{N_T^{t+\Delta t}} \quad (40)$$

where N_T is the total number of moles of contaminant remaining in the porous media. The mole fractions of the less volatile components increase with time.

The total mass removal rate at time t for a NAPL containing n_c components is

$$R_m = Q \sum_{i=1}^{n_c} \frac{X_i P_{vi}^* M_i}{RT} \quad (41)$$

where R_m is the total mass removal rate [M/T]. The total mass removal rate declines with time, when more than one constituent is present, due to the decrease in total vapor pressure in the pore space.

3.6 Vapor-Liquid Equilibrium Model

The vapor-liquid equilibrium model was used to predict the time required to complete the experiments conducted during this research. Attempts were also made to model the experimental data using this simplified approach.

4 Materials and Methods

4.1 Introduction

Two different columns were used to conduct SVE experiments in the laboratory. Both columns were designed and built in the School of Public Health shop facilities at the University of North Carolina. Several experiments were conducted in each column.

The primary purpose of each experiment was to determine the concentration of organic chemicals in the vapor phase as a function of time. In the large column, temperature and air pressure were measured as well. The parameters varied between experiments included vapor flowrate and residual contaminant composition. Vapor flowrate and contaminant removal was induced in both columns by using pressurized nitrogen gas. Glass beads served as the porous media in all experiments.

Experiments to measure the mass transfer coefficient of toluene from a pure liquid to the vapor phase were also conducted. A small square glass column was used for these experiments.

4.2 Vapor Extraction Columns

4.2.1 General

The two columns used for SVE experiments were a round glass column and a much larger stainless steel column with a square cross section. The stainless steel column allowed for monitoring of temperature and pressure inside the column during an experiment. These two parameters could not be measured when the glass column was used.

4.2 Vapor Extraction Columns

Both columns were packed with glass beads in the size range of 0.25 mm to 0.425 mm in diameter (McMaster-Carr, Dayton, New Jersey). Natural porous media particles in this diameter range are classified as medium sand (Leeder, 1982). The bulk volume, porosity, and other parameters for both columns are summarized in Table 1.

Purified grade nitrogen gas from a pressure regulated tank was used in both columns to remove the contaminant vapors and induce the volatilization process. Nitrogen flowrates into the columns were measured with a glass rotameter (Gilmont Industries, Great Neck, New York).

Table 1. Column Characteristics

Parameter	Stainless Steel		Glass	
Bulk Media Volume	15.80	ℓ	1.85	ℓ
Pore Volume	6.57	ℓ	0.72	ℓ
Porosity	41.5	%	38.6	%
Mass of Glass Beads	24.07	kg	2.85	kg
Column Length	63.5	cm	30.0	cm
Cross Sectional Area	249.0	cm ²	62.0	cm ²

4.2.2 Stainless Steel Column

The larger and more versatile column used in conducting laboratory experiments was manufactured from a stainless steel sheet formed into a 15-cm by 15-cm square section that was 63-cm long (Figure 2). Very fine screens (100 mesh) were used to hold the glass beads in place. The stainless steel end caps which held the screens in place were designed for easy removal so that the porous media could be changed. All fittings used on the column were made of stainless steel.

4.2 Vapor Extraction Columns

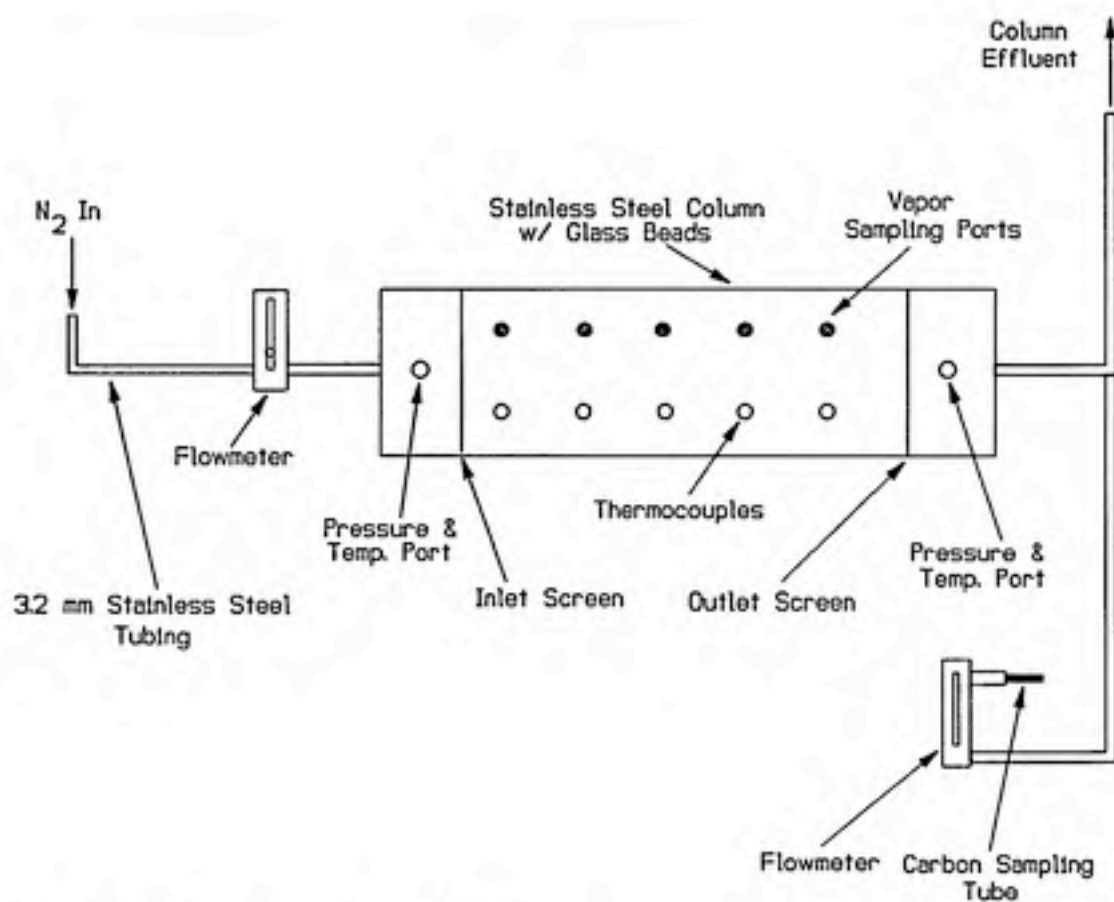


Figure 2. Stainless steel column apparatus.

Twelve ports were installed in the stainless steel column in order to obtain vapor samples and measure temperatures inside the system. Seven copper-constant thermocouples (Omega Engineering, Stamford, Connecticut) were inserted to measure temperatures within the glass beads and also at the column inlet and outlet. The five thermocouples measuring temperature inside the porous media were located at distances of 5, 18, 30, 43, and 56 cm from the inlet screen. One thermocouple was used to measure the room temperature. Vapor sampling ports were installed approximately 7 cm above the thermocouple ports. These five ports were equipped with Teflon-faced septa, which allowed for vapor sampling using a gas-tight syringe.

Pressure transducers (Omega Engineering) were installed in each end cap to monitor the pressure drop across the column. Column pressures were measured with an Omega DP2000 electronic pressure gauge, which was connected to the pressure transducers.

The column was operated in the horizontal position during an experiment for two reasons. By placing the column in the horizontal position, it was hoped that the distribution of contaminant would become more uniform. Secondly, because of the possibility of vapor leakage from the column, it was important that the entire apparatus be placed under the laboratory exhaust hood.

4.2.3 Glass Column

A glass column was used for conducting experiments on a smaller scale before using the larger column. Because of its smaller capacity, the duration of an experiment was much shorter in the glass column as compared to the stainless steel column, reducing the nitrogen requirements significantly.

The glass column was constructed from a 42-cm long section of 8.9-cm diameter glass tube (Figure 2). The Teflon end caps of the column were designed to create a more uniform vapor flow through the cross section. Approximately 75% of the total column volume was packed with glass beads before conducting experiments. The glass column was operated in the vertical position since it was not completely filled with glass beads.

4.3 Chemicals

The compounds used to residually saturate the glass beads, toluene (methylbenzene) and xylene (dimethylbenzene), are classified as aliphatic-aromatic hydrocarbons (Morrison and Boyd, 1973). These two compounds are insoluble in water, have low polarity, and are volatile. They were chosen for use in these experiments

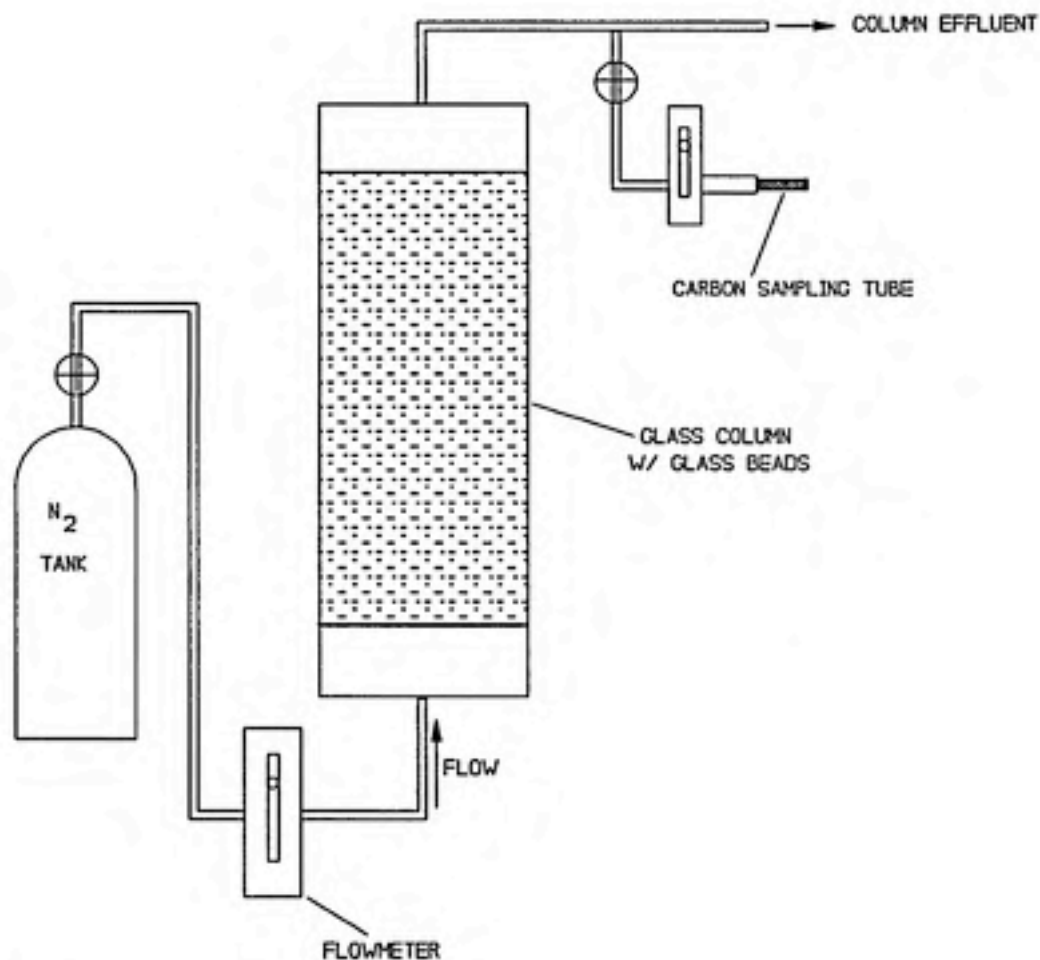


Figure 3. Glass column apparatus.

because of their presence in gasoline, which is often removed from the subsurface by SVE.

Both chemicals were purchased in reagent grade from EM Science. The liquid xylene was a mixture of m-xylene, p-xylene, and o-xylene isomers in mass proportions of approximately 1:4:1 as determined from gas chromatography analysis. Important properties of these and several other compounds commonly found in petroleum products are shown in Table 2.

Table 2. Properties of Common Petroleum Product Components

Compound	Vapor Pressure (atm)	Boiling Point (°C)	Aqueous Solubility (mg/ℓ)	Molecular Weight (g/mol)
isopentane	0.78	28	48.0	72.2
n-pentane	0.57	36	40.0	72.2
n-hexane	0.16	69	13.0	86.2
benzene	0.10	80	1780.0	78.1
n-heptane	0.046	98	3.0	100.2
toluene	0.029	111	515.0	92.1
n-octane	0.014	126	0.7	114.2
p-xylene	0.0086	138	198.0	106.2
m-xylene	0.0080	139	162.0	106.2
o-xylene	0.0066	144	175.0	106.2
dimethyl-ethylbenzene	0.0007	190	21.0	134.2

(from Johnson et al., 1990)

Carbon disulfide was used to desorb the contaminant mass adsorbed by the carbon sampling tubes during vapor phase sampling. The reagent grade carbon disulfide was purchased from Fisher Scientific.

4.4 Vapor Phase Sampling and Analysis

The most important parameter measured during the course of an experiment was the vapor phase concentration of the compound(s) present. The carbon adsorption method was used to determine contaminant concentrations in the vapor phase. Using this method, a small portion of the total vapor flow was allowed to pass through a small activated carbon trap, which was later desorbed using an organic solvent (Wallingford et al., 1988). One of the main advantages of the carbon adsorption method is that sensitivity can be increased by simply increasing the volume of vapor that flows through the trap. For example, longer sampling times can be used when vapor phase concentrations are low.

4.4 Vapor Phase Sampling and Analysis

Sorbent air sample tubes containing activated carbon (SKC, Inc., Eighty-Four, Pennsylvania) were used to sample the effluent vapors of both columns. These sample tubes contained two separate sections of carbon, 100 mg in the front section and 50 mg in the rear section. Sampling times were kept as short as possible to prevent the breakthrough of organic vapors to the rear section of the sampling tube. Typical sampling times ranged from 2 to 5 min. A sampling flowrate of 30 ml/min was used to insure complete adsorption of all vapors to the sample tubes. This flowrate was measured accurately using a flowmeter equipped with a micrometer valve (Gilmont Instruments, Great Neck, New York).

In order to extract the contaminants adsorbed during sampling, the front GAC sections were removed from the sampling tubes and placed in air-tight 5 ml vials. The GAC was desorbed with 2 ml of carbon disulfide containing 2000 mg/l of benzene as an internal standard. The vials containing the activated carbon and carbon disulfide were shaken for 30 min using a Lab-Line Instruments mechanical orbit shaker in order to insure complete desorption. Only a few rear sections of the sample tubes were desorbed to check for breakthrough. With the sampling times used, breakthrough was never experienced in any of the carbon tubes.

The carbon disulfide solutions from the desorption process were analyzed using a Hewlett Packard HP5890A gas chromatograph equipped with a flame ionization detector (Hewlett Packard, Avondale, Pennsylvania) and 30-m capillary column (J & W Scientific, Folsom, California). An oven temperature of 75°C was used along with a split ratio of 40:1. All compounds of interest eluted out of the capillary column in less than 5 min.

The equation used to calculate the concentration of compound *i* in the vapor phase is

$$C_i^v = \frac{C_i^l V_c}{Q_v t} \quad (42)$$

where C_i^l is the concentration in the CS_2 [M/L^3], V_c is the volume of CS_2 used for desorption [L^3], Q_v is the vapor sampling rate [L^3/T], and t is the sampling time [T]. C_i^l was determined from GC analysis using the internal standard method and an assumed desorption efficiency of 100%.

4.5 Experimental Procedure

A similar experimental procedure was used for SVE experiments conducted in both the glass and stainless steel columns. Before beginning an experiment, the column containing dry glass beads was weighed before being completely saturated with a pure organic liquid. Either pure toluene or a mixture containing 50% toluene and 50% xylene by volume was used to saturate the column. The columns were saturated while in the vertical position in order to leave as little trapped air behind as possible. The liquid was then allowed to drain out at a slow rate leaving behind a residual saturation in the glass beads. The mass of contaminant left behind was determined by re-weighing the column using a triple balance beam.

Instead of using a vacuum pump to remove the vapors from the porous media as is done in actual SVE systems, pure nitrogen gas from a pressure-regulated tank was used to induce flow. It was also easier to maintain a constant flowrate using pressurized nitrogen instead of a vacuum pump. Nitrogen gas was used instead of air in order to reduce the possibility of aerobic biodegradation during an experiment.

The volumetric flowrates used during these experiments correspond to pore velocities typical of SVE systems. The highest pore velocity to be encountered in the subsurface should be less than 1 cm/sec except in the immediate vicinity

4.5 Experimental Procedure

of a vapor extraction well (Johnson et al., 1990). The vapor pore velocities were estimated from the equation

$$v = \frac{q}{n} = \frac{Q}{nA} \quad (43)$$

where v is the pore velocity [L/T], q is the specific discharge [L/T], Q is the volumetric flowrate of nitrogen [L³/T], n is the porosity of the glass beads, and A is the total cross-sectional area of the column [L²]. The pore velocities used ranged from 0.40 to 2.90 cm/sec.

Once an experiment was begun, the column effluent was sampled at regular intervals in order to measure the change in vapor phase concentration with time. During the early stages of an experiment, the effluent was sampled more frequently since vapor phase concentrations changed more. In the stainless steel column, system temperatures and pressures were recorded as well. Nitrogen flowrate was monitored and adjusted when necessary in order to maintain a constant volumetric flow. Most experiments were conducted until the effluent concentrations fell below 1 mg/ℓ. The column was weighed after completing an experiment so the mass removal could be determined. In most experiments, >95% of all contaminant mass was removed by vapor extraction.

In order to remove the residual contaminant mass remaining in the glass beads after an experiment was completed, either nitrogen or air was flowed through the column for several days at low flowrates. When air was used, it was first flowed through a dessicant to remove any moisture present. The column was weighed again to insure that the porous media was completely dry.

Since the gas chromatograph was available for use, carbon sampling tubes were desorbed and analyzed during the course of an experiment. By determining the vapor phase concentrations in "real time," it was possible to adjust the vapor

4.5 Experimental Procedure

sampling times as the effluent concentrations decreased in order to improve sensitivity. It would have also been difficult to determine if a significant portion of the mass had been removed if the sampling tubes were not analyzed during the course of an experiment.

Several attempts were made to directly inject vapor samples taken from the sampling ports on the stainless steel column into the GC. The vapor phase concentrations obtained from direct injections were not reproducible and seemed erroneous. However, such measurements did have a qualitative value.

5 Results and Discussion

5.1 Experiments Conducted

5.1.1 Overview

A total of 12 experiments were conducted in order to study the SVE process in the laboratory. Major column leaks occurred during the course of two of these experiments, which adversely affected the vapor phase concentrations measured. Data from these two experiments are not presented here.

All vapor phase concentrations were calculated using an assumed carbon tube extraction efficiency of 100% for all compounds adsorbed. The vapor phase concentrations were used to calculate the total mass removed by SVE during an experiment. A balance beam scale was used to determine the total mass of the column both immediately before and after an experiment in order to independently measure the total mass of contaminant removed.

5.1.2 Glass Column Experiments

The conditions for the six glass column experiments performed are detailed in Table 3. Pore velocities of 0.394, 1.036, and 2.907 cm/s, which correspond to specific discharges of 0.15, 0.40, and 1.12 cm/s, were used for venting the contaminant vapors from the column. A pore velocity of 2.907 cm/s would be higher than expected in an actual SVE operation, except in the immediate vicinity of the well screen (Baehr and Hoag, 1988). This high pore velocity was used to determine if mass transfer from the NAPL phase to the vapor phase was sufficiently fast enough in order for

Table 3. Summary of Glass Column Experiments

Compound(s)	Experiment Number					
	G1	G2	G3	G4	G5	G6
	Toluene	Toluene	Toluene	Toluene & Xylene	Toluene & Xylene	Toluene & Water
Specific Discharge (cm/sec)	0.152	0.4	1.122	0.4	1.122	0.4
Pore Velocity (cm/sec)	0.394	1.036	2.907	1.036	2.907	1.036
Initial Mass (g)	55	55	53	59	55	77*
Total Moles	0.597	0.597	0.575	0.601	0.560	0.840*
% Residual Saturation	8.9	8.9	8.6	9.5	8.8	12.0*
% Mass Removed (calculated)	75.4	102.6	93	85.6	83.8	67.6*
% Mass Removed (measured)	92.7	98.2	98.1	98.3	98.2	98.0*
Total Moles Removed (calculated)	0.417	0.613	0.565	0.492	0.414	0.568*

* Toluene Only

local equilibrium conditions to exist at all pore velocities to be encountered in the subsurface.

All experiments were conducted using glass beads as the porous media. The glass beads were residually saturated with either pure liquid toluene or a toluene-xylene mixture except for experiment G6. In experiment G6, the dry glass beads were first residually saturated with distilled water, then with toluene. In addition to the 77 g of toluene, 116 g of water was retained in the column. In this experiment the nitrogen gas was first bubbled through a beaker of water in order to saturate it with water vapor before entering the column to prevent the evaporation of residual water from the glass beads.

5.1 Experiments Conducted

5.1.3 Stainless Steel Column Experiments

Conditions for the four SVE experiments conducted in the stainless steel column are detailed in Table 4. Pore velocities of 0.749, 1.118, and 1.296 cm/s were used. Higher pore velocities were not used in the stainless steel column because of the excessive quantities of nitrogen needed to maintain the flowrates required for the duration of an experiment. In addition, the higher flowrates created column inlet pressures that were near the maximum capacity of the pressure transducer (10 psig) installed in the end cap.

Table 4. Summary of Stainless Steel Column Experiments

	Experiment Number			
	SS1	SS2	SS3	SS4
Compound(s)	Toluene	Toluene	Toluene & Xylene	Toluene & Xylene
Specific Discharge (cm/sec)	0.538	0.464	0.311	0.464
Pore Velocity (cm/sec)	1.296	1.118	0.749	1.118
Initial Mass (g)	653	576	551	559
Total Moles	7.090	6.254	5.610	5.692
% Residual Saturation	11.5	10.2	9.7	9.8
% Mass Removed (calculated)	37.6	96.9	85.3	81.8
% Mass Removed (measured)	42.6	99.5	94.4	93.7
Total Moles Removed (calculated)	2.666	6.062	4.494	4.412

Two experiments were conducted where toluene was used to residually saturate the glass beads. Experiment SS1, the first experiment performed in either column, was stopped after only 13 hr due to the development of a major nitrogen leak. Only 43% of the mass was removed from the column during this time period. The

column was repaired and slightly modified in order to prevent future leaks before performing the second experiment. The column was residually saturated with the toluene-xylene mixture in experiments SS3 and SS4. Approximately 94% of the mass was removed by SVE during these two experiments.

From Table 4 it can be observed that a large mass of contaminant remained residually trapped in the glass beads. The amount of contaminant mass initially present in all four experiments was approximately 600 g as compared to about 55 g in the glass column experiments. The average residual saturation in the stainless steel column was 10.3% versus 8.9% in the glass column. Because the amount of mass to be removed from the stainless steel column was so much higher, the time required to complete an experiment was longer as compared to an experiment in the glass column. Experiment SS3, the longest experiment performed in the stainless steel column, was completed in 53 hr. The longest experiment conducted in the glass column, experiment G1, was finished in 23 hr.

5.2 Vapor Phase Concentration Profiles

5.2.1 Overview

The plots of vapor phase concentration versus time for the experiments conducted in both columns are presented in this section. As mentioned previously, the vapor phase concentrations were determined from GC analysis of the solvent (carbon disulfide) used to desorb the carbon sampling tubes. Assuming 100% adsorption of the contaminants from the vapor phase onto the carbon and 100% desorption of contaminants from the carbon to carbon disulfide probably underestimates the actual vapor phase concentrations.

5.2 Vapor Phase Concentration Profiles

5.2.2 Glass Column

For the experiments conducted in the glass column, the vapor phase concentration profiles for the removal of toluene by vapor extraction are presented in Figure 4. If the two phases are in equilibrium, then the saturated vapor phase concentration above pure toluene liquid should be near 111 mg/l at a temperature of 20°C as calculated from the equation

$$C_i^{v*} = 12.180 \frac{X_i P_i^{v*} M_i}{T} \quad (44)$$

where C_i^{v*} is the vapor phase concentration expressed in mg/l, M_i is the molecular weight of i in mg/mole, and the other terms are as previously defined in section 3.6. In Figure 4 the vapor phase concentration measured exceeds the saturated value of 111 mg/l for a period of time during all three experiments indicating the existence of local equilibrium conditions for at least part of the time. Because thermocouples could not be installed in the glass column, it is not known if the actual system temperature was above or below 20°C.

At the two highest specific discharges q used, the vapor phase concentration of toluene remained in the vicinity of the expected saturation concentration of 111 mg/l for a long period of time after going through a short period of stabilization. There is some fluctuation in the vapor phase concentration measured during this period of high effluent concentration. Either the vapor phase sampling procedure or changes in the mass transfer rate might have caused the large fluctuations observed. The experiment with the lowest specific discharge ($q=0.15$ cm/s) exhibited vapor phase concentrations that were noticeably lower than the other two experiments. During this particular experiment, it was difficult to obtain a steady vapor sampling flowrate. This may have been the reason for the low concentrations measured.

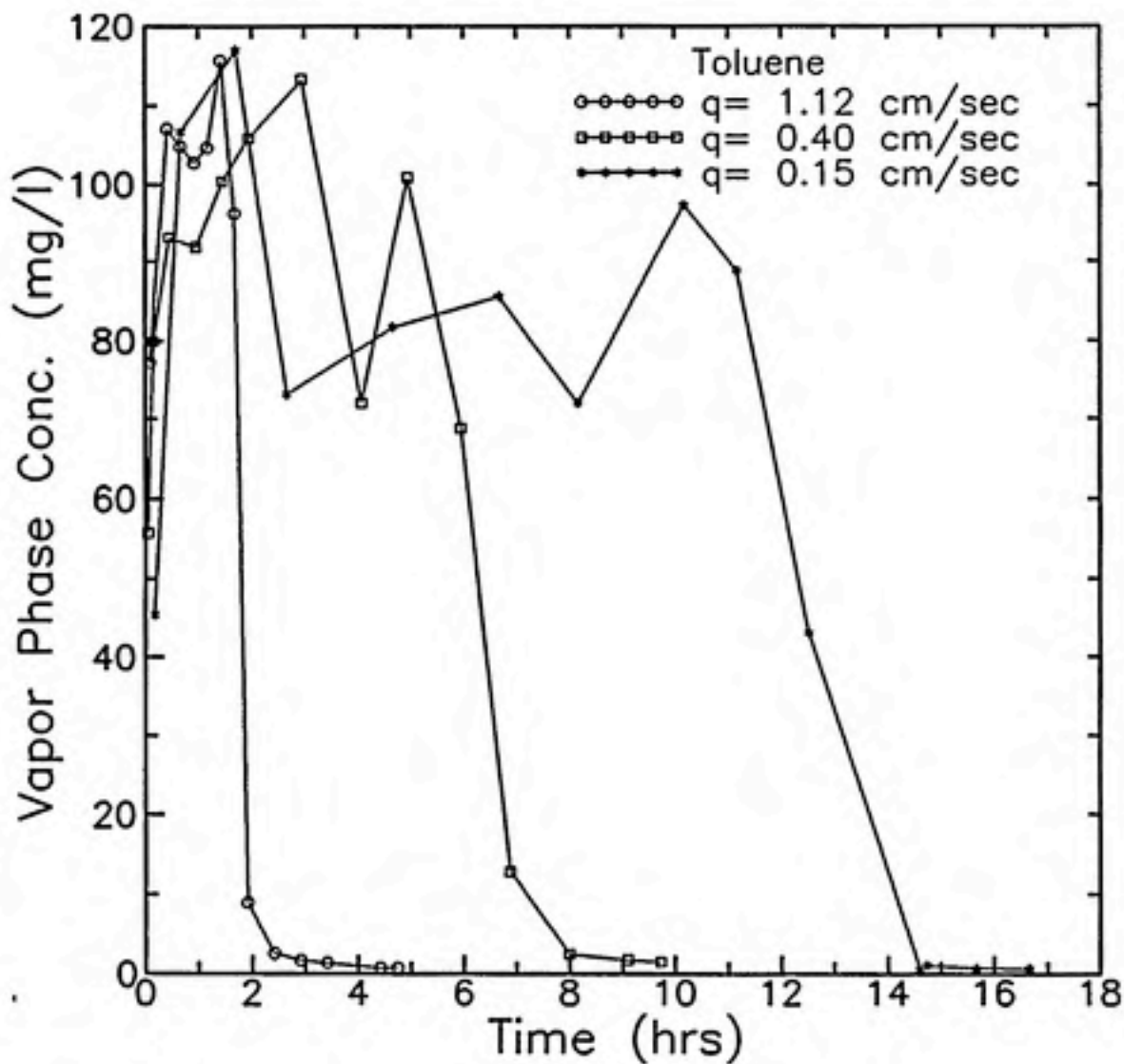


Figure 4. Vapor phase concentration of toluene as a function of time and specific discharge for glass column experiments.

In all three experiments, the vapor phase concentration of toluene fell rapidly to values slightly above zero. The period of time during which this large drop in concentration occurred was longer at the lower flowrates used. The sudden drop in vapor concentration occurred when approximately 90% of the initial toluene mass had been removed.

5.2 Vapor Phase Concentration Profiles

The concentration profiles for experiments G4 and G5, in which the toluene-xylene mixture was used to residually saturate the glass column, are shown in Figure 5. The total vapor phase concentration above the toluene-xylene mixture used in these experiments should be initially near 76 mg/ℓ at a temperature of 20°C if the two phases are in equilibrium. At the higher specific discharge ($q=1.12$ cm/s), the initial vapor phase concentration was much lower than expected. Sampling errors or the existence of non-equilibrium conditions in the column are two possible reasons for the lower concentration values measured. At the lower specific discharge, 0.40 cm/s, the initial vapor phase concentration was near the expected equilibrium value. Unlike in the experiments where toluene was the only contaminant removed, the total vapor phase concentration decreased gradually with time in experiments G4 and G5.

As discussed in section 3.6, the total vapor phase concentration should decrease gradually with time if the immobile liquid (NAPL) is a mixture containing more than one compound. The toluene-xylene mixture used in these experiments actually contained four compounds in measurable quantities: toluene, m-xylene, p-xylene, and o-xylene. The initial mole fractions of these four compounds were respectfully 0.536, 0.077, 0.297, and 0.090. As shown in Table 2, the three xylene isomers have slightly different vapor pressures and boiling points so they must be accounted for separately. The concentration profiles for the toluene and xylene components removed during experiment G4 are shown in Figure 6. The vapor phase concentration of toluene remained fairly constant before falling rapidly to near zero after 6 hr. Very little toluene was removed from the column after this time. The concentrations of the three xylene compounds remained fairly constant until the toluene concentration dropped rapidly. At that point, the vapor phase concentrations of m-, p-, and o-xylene increased substantially since their molar fractions increased. The vapor phase concentration of p-xylene was much higher than the other two xylene isomers

5.2 Vapor Phase Concentration Profiles

for most of the experiment since it was present in a higher mole fraction and had a higher vapor pressure. After 12 hr, the compound with the lowest vapor pressure, o-xylene, had the highest vapor phase concentration.

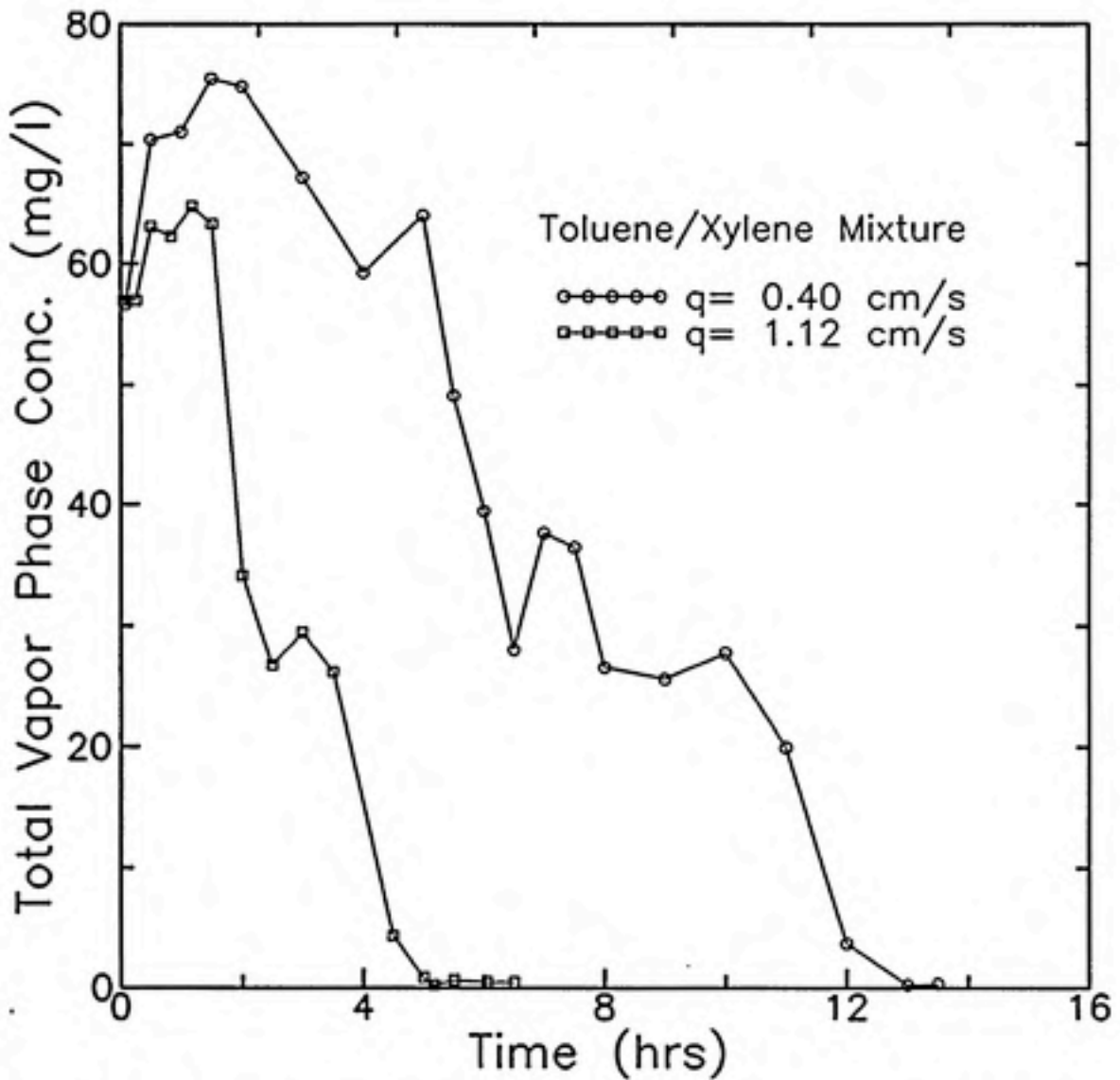


Figure 5. Vapor phase concentration as a function of time and specific discharge for the removal of toluene-xylene mixture from the glass column.

5.2 Vapor Phase Concentration Profiles

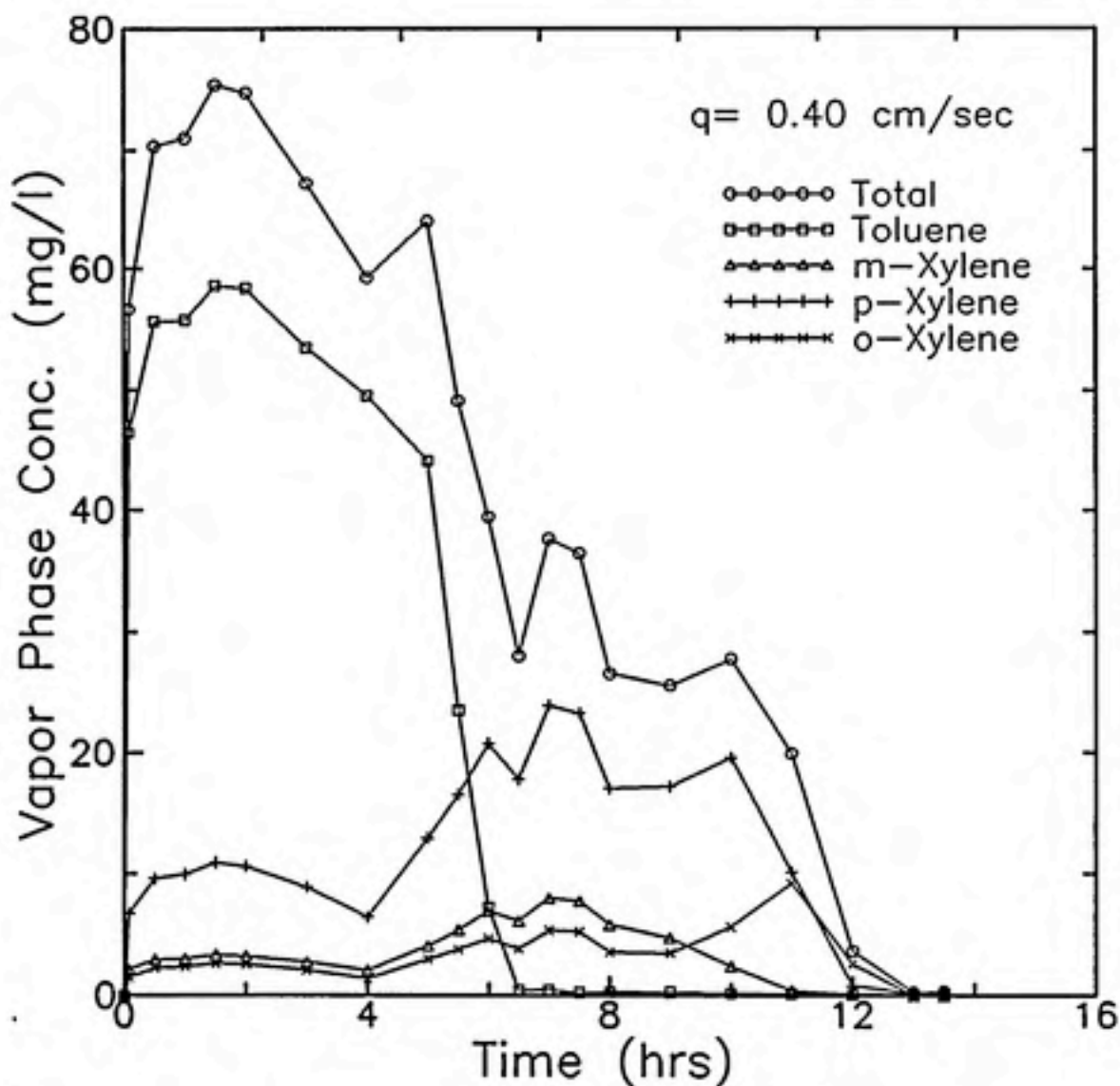


Figure 6. Vapor phase concentration as a function of time for each solute component during glass column experiment G4.

5.2.3 Stainless Steel Column

Only two experiments were performed in the stainless steel column with toluene as the sole contaminant. The vapor phase concentration profile for the first experiment conducted is not presented since the venting time was too short to remove

5.2 Vapor Phase Concentration Profiles

a significant amount of mass. The concentration profile for experiment SS2 is presented in Figure 7. The saturated vapor concentration value of 111 mg/l for toluene at 20°C was exceeded early in the experiment. This is to be expected since the average column temperature measured during this experiment was near 23°C. At a temperature of 23°C the saturated vapor phase concentration is approximately 129

5.2 Vapor Phase Concentration Profiles

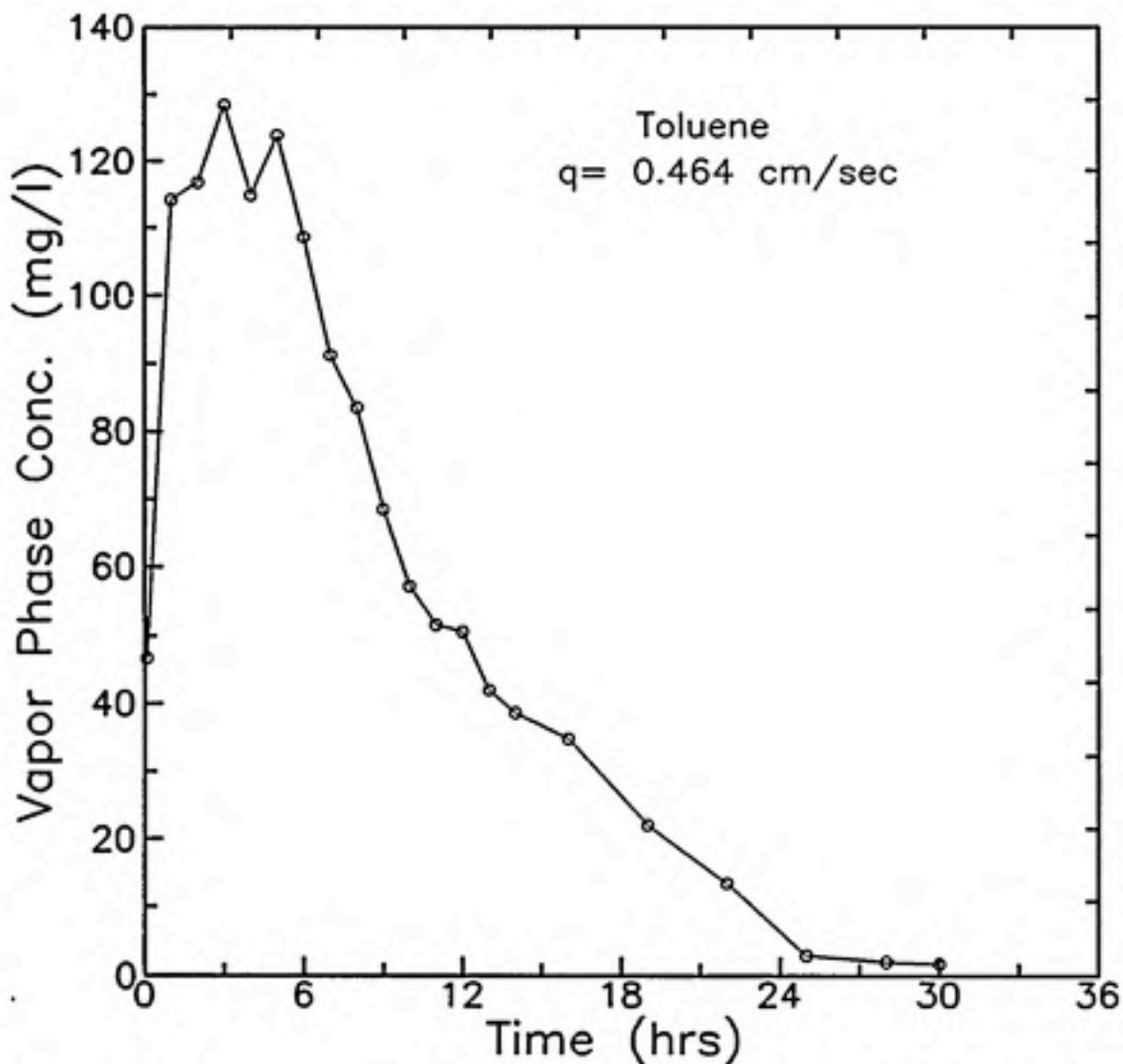


Figure 7. Vapor phase concentration as a function of time for stainless steel column experiment SS2.

mg/l.

The vapor phase concentration of toluene decreased from the maximum value after only 6 hr of flow and 47% of the toluene mass was removed. In the similar glass column experiment, the vapor phase concentration of toluene remained fairly stable and near the saturation concentration until about 90% of the mass was removed

before falling rapidly to near zero. This gradual decrease in toluene vapor concentration over an extended period of time may be an indication of non-equilibrium conditions occurring in the stainless steel column. Discussion of this point follows in a later section.

The stainless steel column was residually saturated with the toluene-xylene mixture in experiments SS3 and SS4. Figure 8 shows the concentration profiles for these two experiments. As expected, the total vapor phase concentration decreased with time as the remaining NAPL became less volatile. Both concentration profiles are very similar in appearance, since the specific discharges used were close (0.31 vs. 0.46 cm/sec).

5.3 Effect of Experimental Parameters on Contaminant Removal

5.3.1 General

Three parameters were varied during the course of these column experiments. The volumetric flowrate of nitrogen was varied in order to determine the effect of specific discharge (and pore velocity) on contaminant removal. The type of contaminant used to residually saturate the column was changed to study the effect of chemical properties, vapor pressure in particular, on removal rate. Finally, a single experiment was performed to evaluate the effect of moisture on the removal of the NAPL by including both an aqueous phase and toluene at residual saturation.

5.3.2 Vapor Flowrate

In general, the length of time required to remove a given amount of contaminant by SVE will decrease with increased flowrate. If equilibrium exists between the vapor phase and the NAPL phase, then doubling the flowrate will cut the removal time in half. The removal efficiency of the SVE process, amount of contaminant

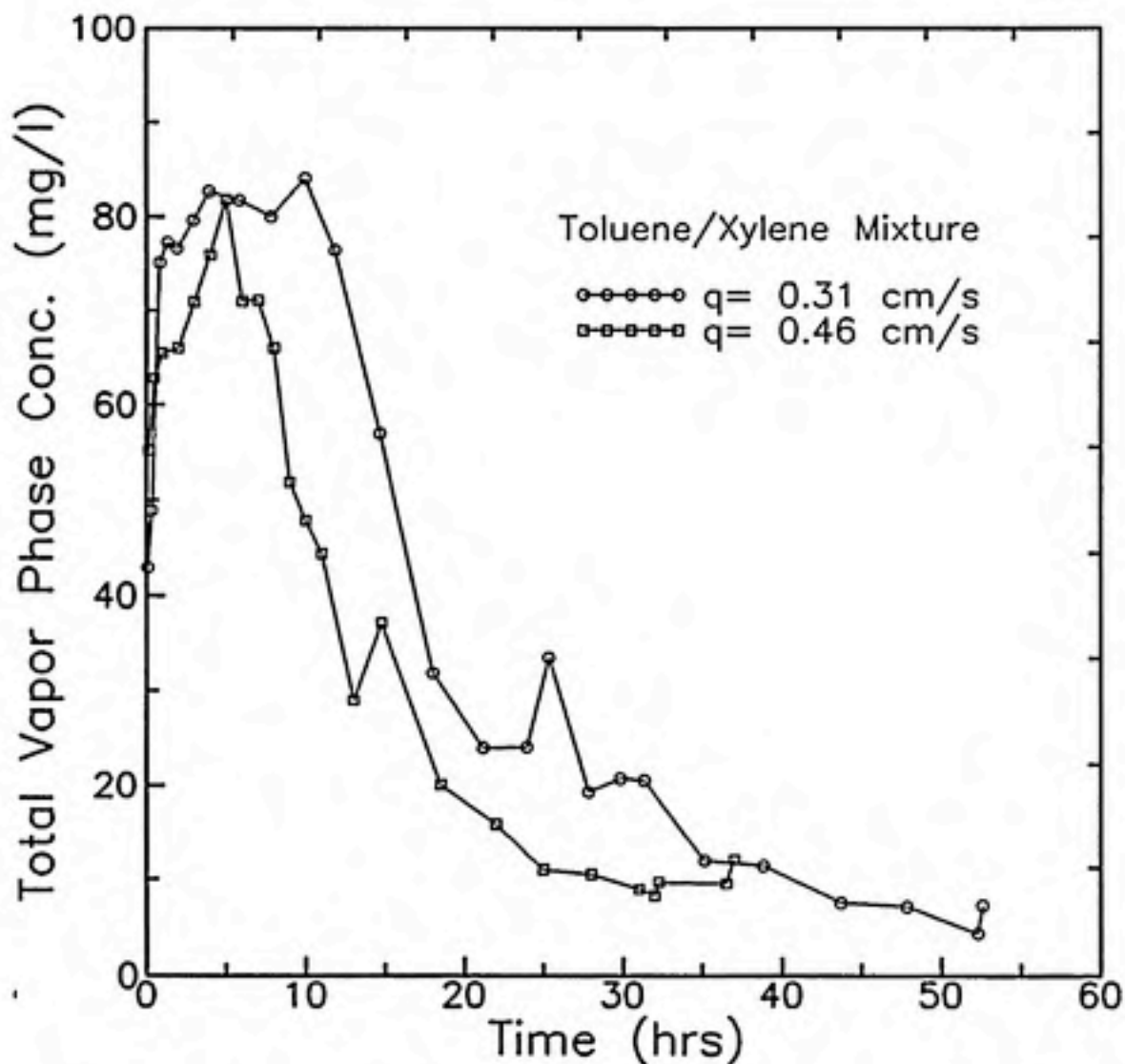


Figure 8. Vapor phase concentration as a function of time and specific discharge for the removal of the toluene-xylene mixture.

mass removed per volume of vapor extracted, will be independent of flowrate. Figure 9 shows how the specific discharge, which is the volumetric flowrate per cross-sectional area of media, affects the time required to remove a given number of moles of contaminant. The contaminant removed in this example is a mixture of toluene and p-xylene. For example, by increasing the specific discharge from 0.4 to

5.3 Effect of Experimental Parameters on Contaminant Removal

0.8 cm/sec the time required to remove 0.5 moles of contaminant is reduced from 8 to 4 hr. The data for Figure 9 were generated using the vapor/liquid equilibrium model described in section 3.6.

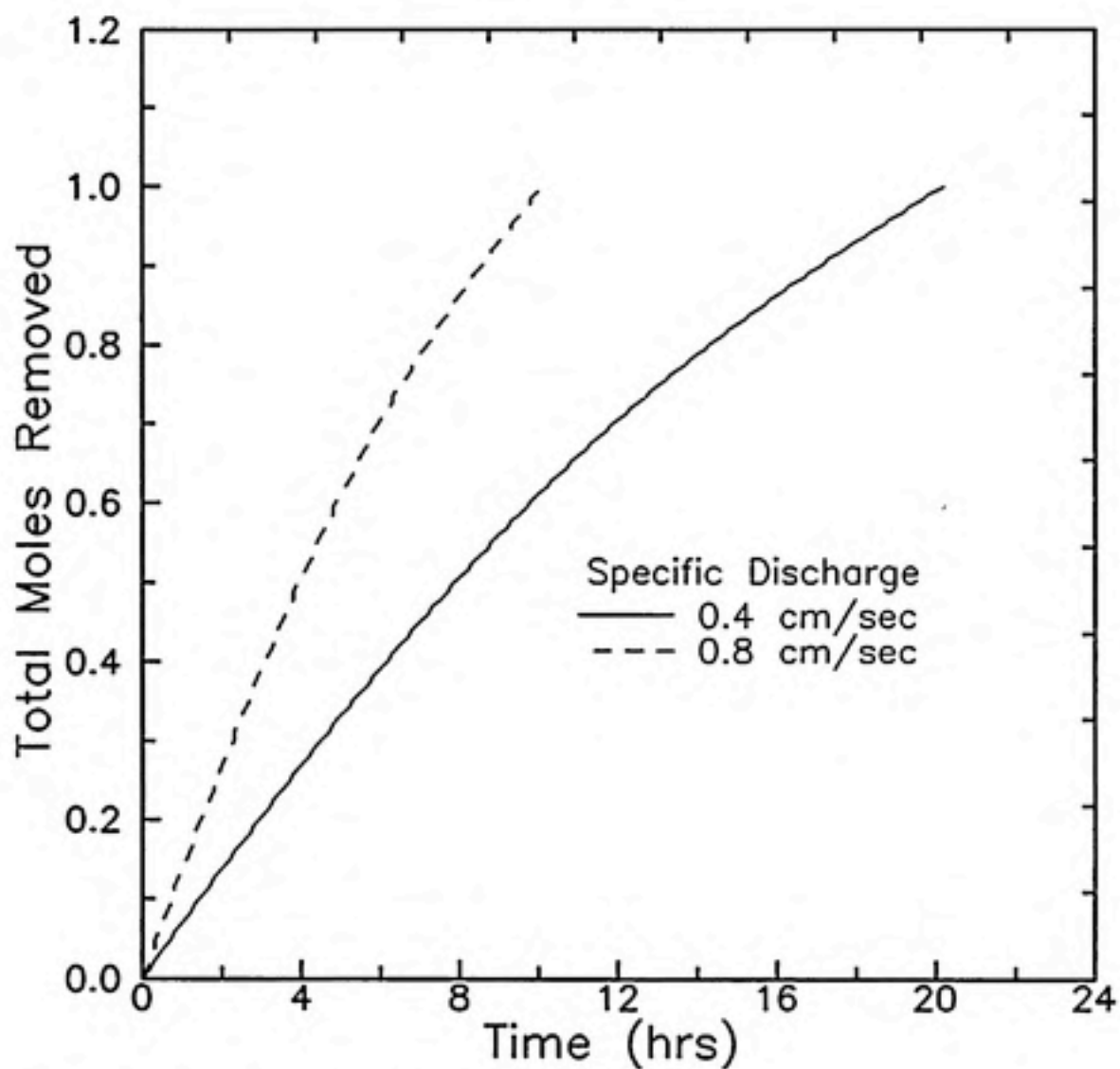


Figure 9. Equilibrium model prediction of contaminant removal as a function of time and specific discharge.

5.3 Effect of Experimental Parameters on Contaminant Removal

If mass transfer rates are reduced or molecular diffusion limitations occur in the porous media, then the vapor flowrate can affect the removal efficiency of the SVE process. Because the mass transfer rates from pure organic liquids to the vapor phase are very fast, equilibrium between the two phases should occur for the pore velocities typically found in the subsurface during SVE (Johnson et al., 1990; Lingineni and Dhir, 1990). Mass transfer rates might be reduced enough to cause non-equilibrium conditions to exist if the interfacial area between phases is reduced significantly due to contaminant removal (Hunt et al., 1988; Powers et al., 1991). The total volume of air that must be extracted to remove the residually trapped contaminants can increase substantially if reductions in mass transfer rates or diffusion limitations are causing deviations from local equilibrium.

Diffusion limitations can occur when the advective vapor flow is not uniform through the contaminated area. As mentioned in section 2.3, preferential flow paths can form in the subsurface due to the heterogeneous nature of porous media. The bulk vapor flow will be through the more permeable regions of the soil (e.g., sand and gravel layers, fractured zones). The contaminant mass adjacent to the areas of bulk flow will be removed rapidly and local equilibrium conditions may exist. Contaminants located in areas of little or no bulk flow, stagnant zones, will be removed more slowly. Organic vapors must be transported by molecular diffusion from the stagnant zones to the zones of bulk vapor flow in order to be removed by SVE (DiGiulio and Cho, 1990; Towbridge and Malot, 1990). Because of the tortuous path that vapors must take to reach the areas of bulk flow, diffusion can become the rate limiting step in the removal of contaminants by SVE. This is especially true when the moisture content of the soil is high or when the mass associated with the NAPL phase has been reduced significantly as in the latter stages of remediation.

One way to compare the effect of flowrate on contaminant removal efficiency is to plot the amount of mass removed versus the number of bed volumes, instead

5.3 Effect of Experimental Parameters on Contaminant Removal

of time. One bed volume is equivalent to the volume of air present in the column under initial conditions (i.e., before the NAPL is evaporated). Figure 10 is a plot of fractional molar removal versus bed volumes for two of the experiments in the glass column. From this graph it appears that the same number of bed volumes was required to obtain the same fractional removal of toluene from the column. In this instance, the vapor flowrate (specific discharge) had little effect on the removal efficiency until the later stages of the experiment. After approximately 90% of the toluene mass was removed, the two curves begin to deviate. This deviation is probably a result of vapor phase sampling error since the percentage of mass removed based on gravimetric analysis was about 98.2% in both experiments.

For the two experiments in the stainless steel column where the toluene-xylene mixture was used to residually saturate the glass beads, the number of bed volumes required to remove a given molar fraction of contaminant was slightly higher at the higher flowrate (see Figure 11). The removal efficiency was higher at the lower specific discharge of 0.31 cm/s. This would seem to indicate that diffusion and/or mass transfer limitations in the stainless steel column increased with increasing flowrate. Local equilibrium conditions may not have existed for a long period of time in either experiment.

5.3.3 Chemical Properties

The two chemical properties that are of most importance to the removal of contaminants by SVE are vapor pressure and Henry's constant. These two properties govern the partitioning of a compound to the vapor phase. The Henry's constant of a compound will be important only when the soil moisture content is high and a separated immiscible (NAPL) phase is not present in significant quantities (DiGiulio and Cho, 1990). During these experiments, partitioning to the vapor phase was

5.3 Effect of Experimental Parameters on Contaminant Removal

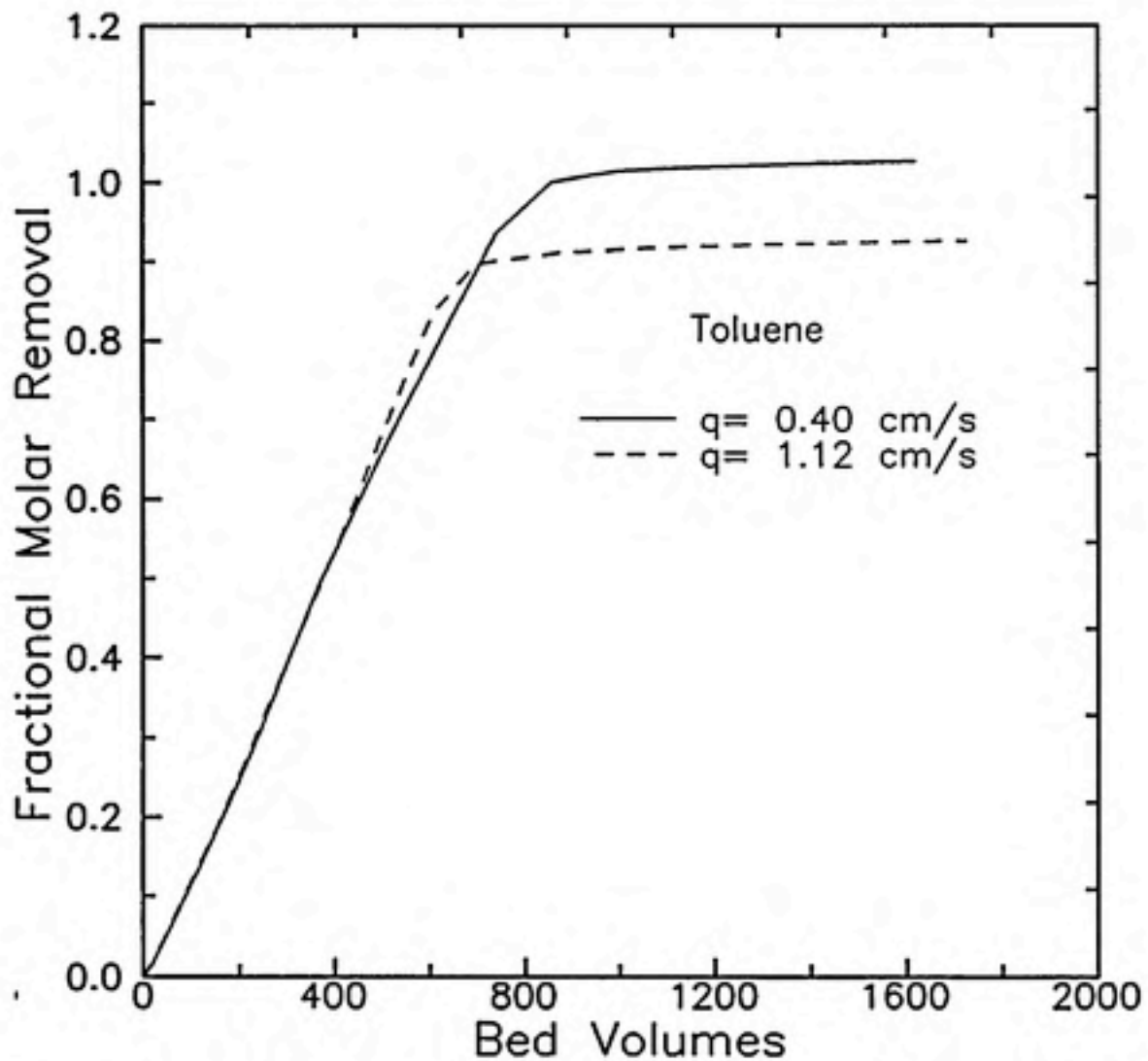


Figure 10. Mole fraction removed as a function of bed volumes of gas and specific discharge for glass column experiments.

governed mostly by contaminant vapor pressure since only the NAPL phase existed in the media.

The rate of contaminant removal from an SVE system is equal to the volumetric flowrate Q multiplied by the total vapor phase concentration in the effluent C_T^v . The

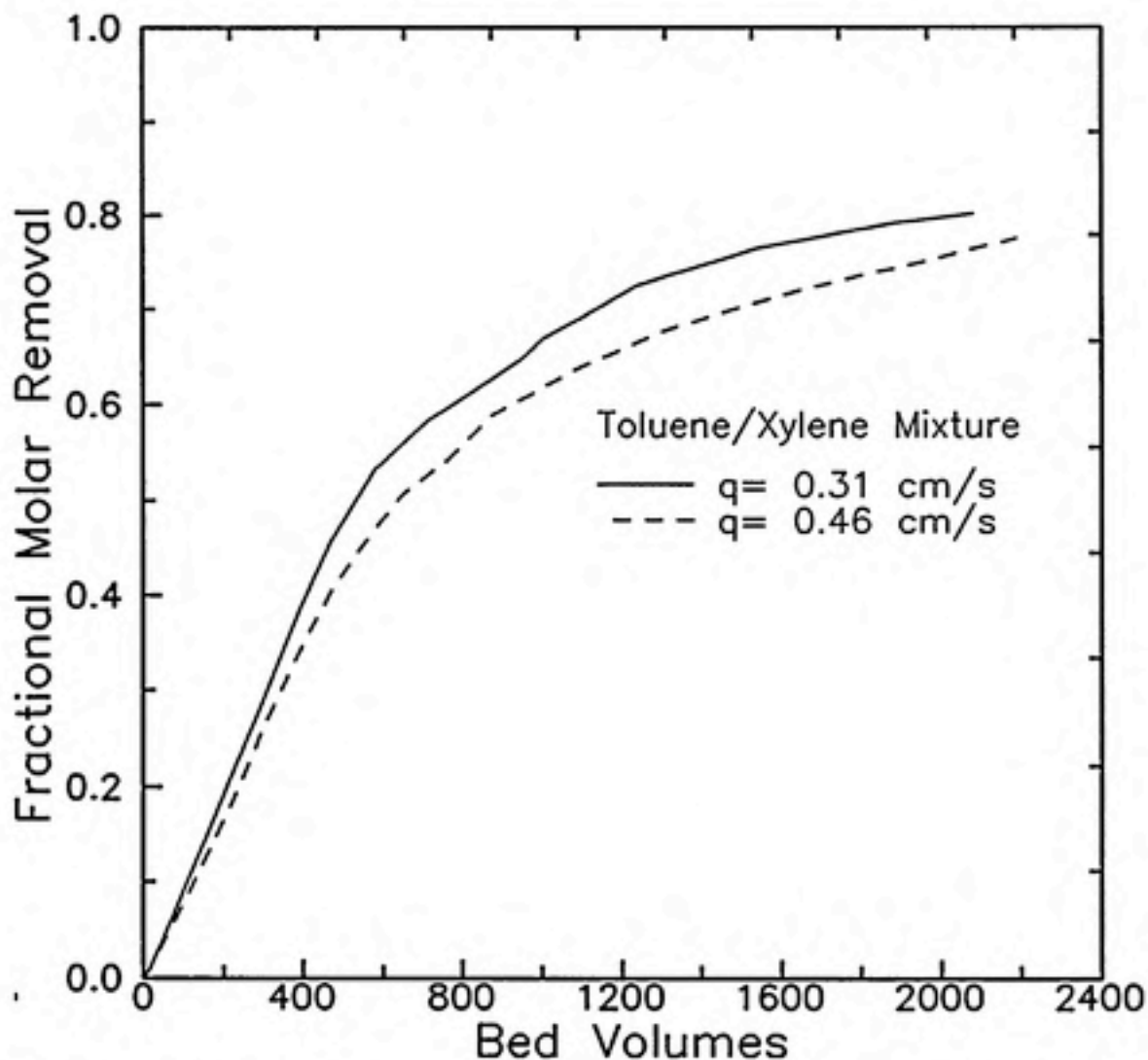


Figure 11. Mole fraction removed as a function of bed volumes of gas and specific discharge for stainless steel column experiments.

equation used to estimate the total vapor concentration in the effluent assuming that equilibrium exists between phases is

$$C_T^{v*} = 12.180 \sum_{i=1}^{n_c} \frac{X_i P_i^{v*} M_i}{T} \quad (45)$$

5.3 Effect of Experimental Parameters on Contaminant Removal

where the terms are as previously defined in section 5.2.2. Since C_T^{v*} represents the maximum concentration in the effluent at any time, the maximum removal rate occurs when equilibrium conditions exist in the system. The value of C_T^{v*} as well as contaminant removal rate should decrease with time, as the mole fractions (X_i) of the more volatile compounds with the higher vapor pressures (P_i^{v*}) are reduced, regardless of whether or not equilibrium exists between phases.

Two experiments conducted in the stainless steel column at the same specific discharge using different contaminants are compared in Figure 12. As expected, the mass removal rates in the experiment where the toluene-xylene mixture was used to residually saturate the column were lower. The vapor phase concentrations and mass removal rates in the column containing toluene only were initially much higher since toluene was the more volatile of the two contaminants. The vapor pressure of toluene is 0.029 atm at 20°C, while the vapor pressure of the toluene-xylene mixture is 0.019 atm. The vapor pressure of the toluene-xylene mixture remaining in the column decreases with time as the more volatile components are preferentially removed.

After about 20 hr, the mass removal rates were higher in the column containing the toluene-xylene mixture and continued to remain above 65 mg/min even after 36 hr. In the column containing toluene only, the mass removal rate was essentially zero after 24 hr. More time was required to remove the same amount of mass from the column containing the less volatile toluene-xylene mixture.

Only one experiment was conducted where the Henry's constant and therefore partitioning between the vapor and aqueous phase may have been important. In experiment G6, the glass beads were first residually saturated with water before adding toluene. Since the pure toluene has a solubility of 515 mg/l (Johnson et al., 1990), some of the mass partitioned into the aqueous phase. Assuming complete equilibrium between the aqueous and NAPL phases, the maximum mass of toluene

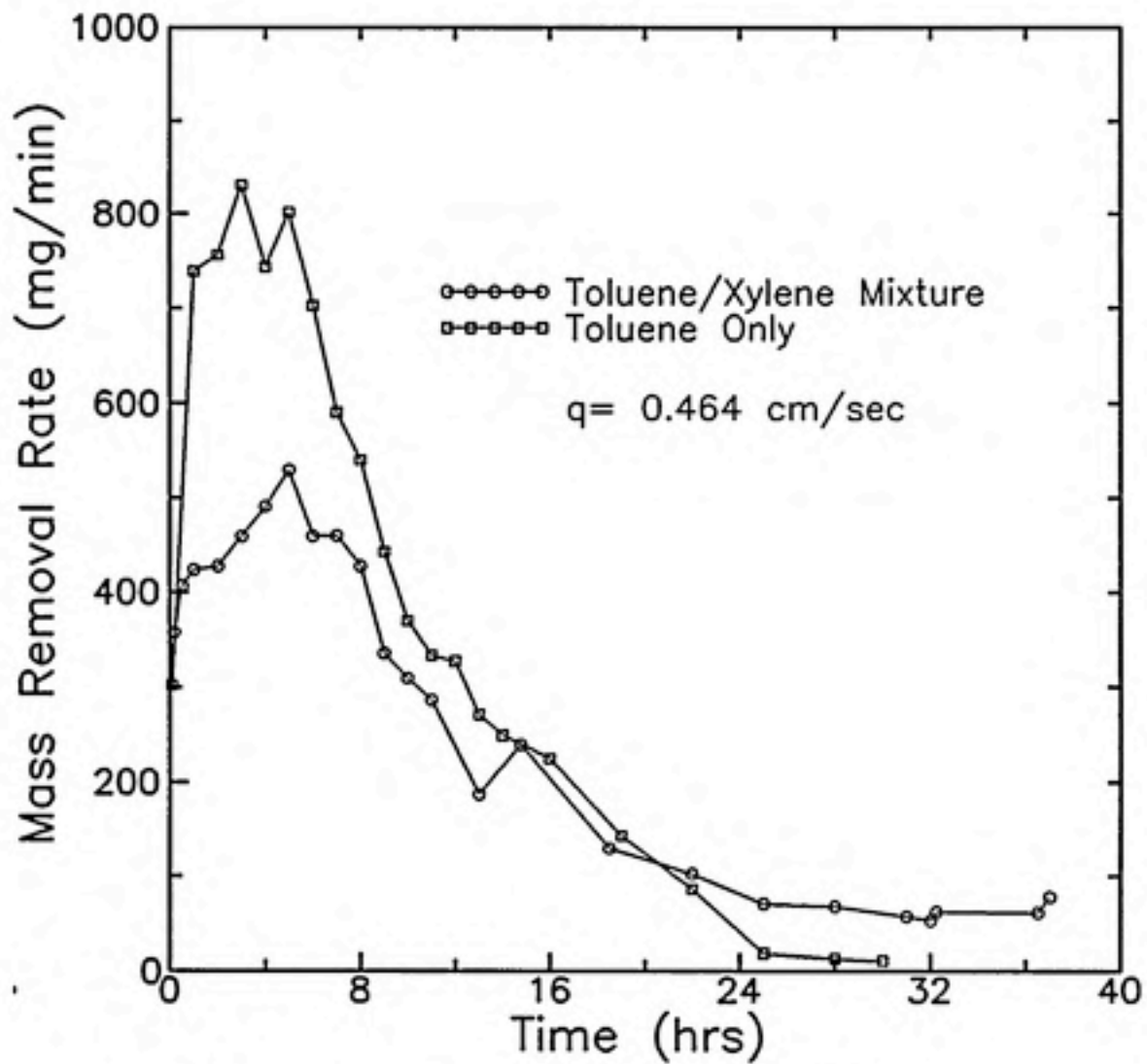


Figure 12. Effect of contaminant composition on mass removal rate.

in the aqueous phase would be about 59 mg. This is very small in comparison to the mass associated with the NAPL phase, so the partitioning between the NAPL and vapor phases was much more significant.

5.3 Effect of Experimental Parameters on Contaminant Removal

5.3.4 Moisture Content

If moisture is present in sufficient quantities in the porous media, then the removal of organic vapors by SVE may be hindered. In addition to reducing the volume of pore space available for advective vapor flow, the presence of an aqueous phase can cause mass transfer and diffusion limitations to occur. Since the diffusion coefficients for many organic chemicals are approximately four orders of magnitude higher in air than in water, increased moisture content can reduce the contaminant removal rate (DiGiulio and Cho, 1990; Stephanatos, 1990). The rate at which contaminant vapors diffuse from stagnant zones to areas of bulk advective flow is reduced by the presence of an aqueous phase. The condensation of moisture present in the influent air during the SVE process may also reduce the mass transfer rates of contaminants present in the soil (Lingineni and Dhir, 1990). The condensed moisture can form an aqueous film around the NAPL phase thereby increasing the resistance to mass transfer.

For glass column experiment G6, the column was first residually saturated with distilled water. The column was then saturated with pure toluene. The final residual saturations of toluene and water were 12.0% and 15.7% respectively. Figure 13 compares the change in vapor phase concentration with time for the experiment where the glass column contained toluene only, experiment G2, versus experiment G6. The same specific discharge was used in both experiments.

Because the total residual saturation was much higher in experiment G6, it is difficult to reach any conclusions on how the SVE process was affected by the presence of an aqueous phase. Since the residual saturation was higher in experiment G6, the actual vapor pore velocity was also higher. It appears that the removal rate of toluene was decreased slightly due to the water in the glass beads. The toluene vapors may have had to diffuse through the aqueous phase in order to be carried

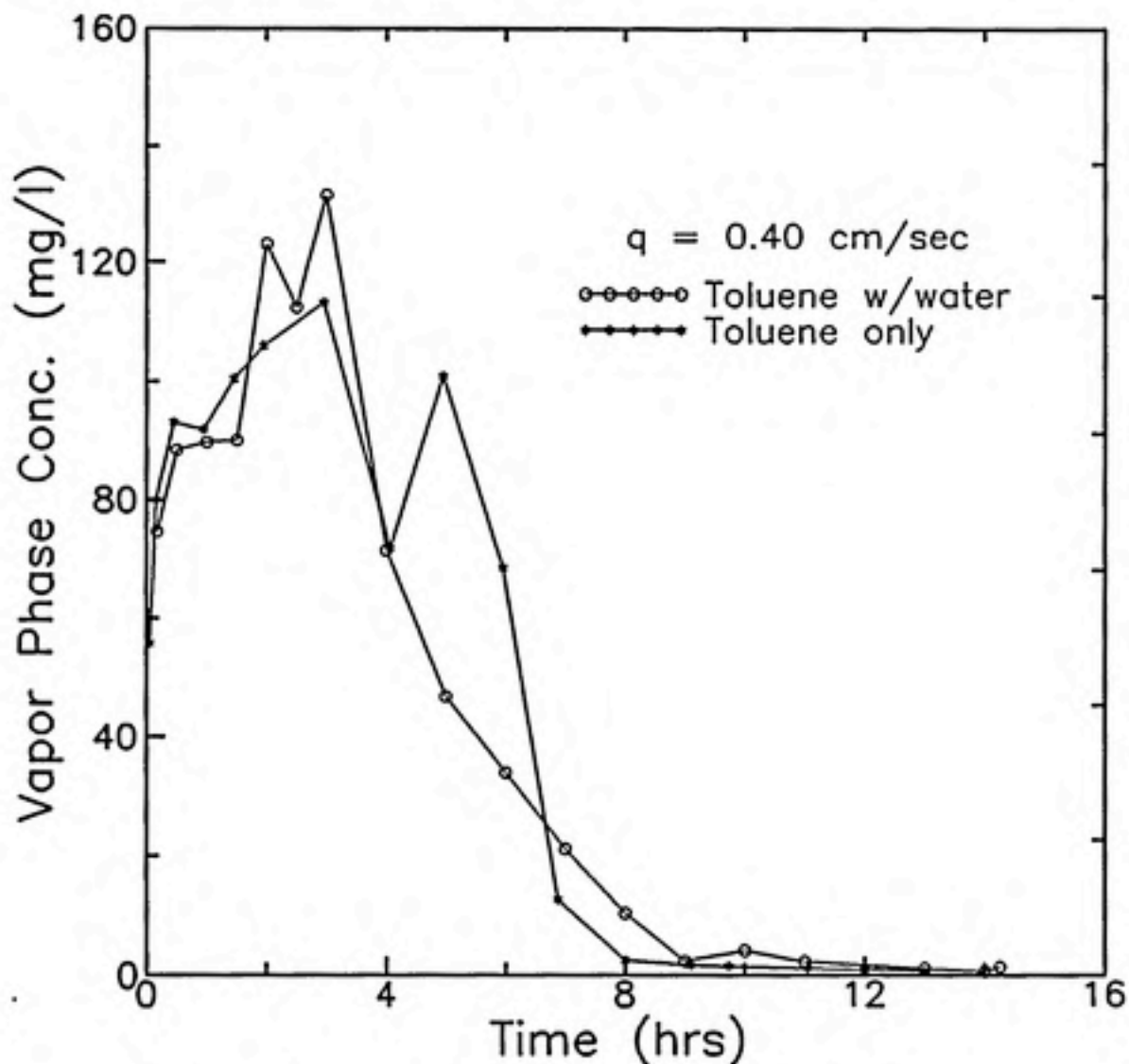


Figure 13. Effect of moisture on vapor phase concentrations.

away by the nitrogen. If the column was residually saturated with toluene first and then with water, the rate of toluene removal would probably have been reduced even more. An aqueous film would have surrounded some of the NAPL phase thereby reducing the mass transfer rate to the vapor phase.

5.4 Temperature Changes During SVE

5.4 Temperature Changes During SVE

One of the benefits of using the stainless steel column to conduct experiments was that temperatures could be measured during the vapor extraction process. Changes in air temperature can affect several key parameters in an SVE operation including gas density, gas viscosity, and vapor pressure (Hutzler et al., 1989). In addition, localized reductions in temperature may occur during the SVE process which can reduce the overall contaminant removal rate (Gannon et al., 1989; Lingineni and Dhir, 1990).

Gas viscosity increases as the gas temperature increases at low pressures and temperatures (McCain, 1973). This is opposite the response of liquid viscosity to changes in temperature. The effect of temperature change on viscosity and vapor volumetric flowrate can be approximated by

$$Q_T = Q_{T_0} \left(\frac{T_0}{T} \right)^{\frac{1}{2}} \quad (46)$$

where T_0 is the temperature in degrees Kelvin at the known flowrate Q_{T_0} (Johnson et al., 1990). During the course of these experiments the nitrogen temperature measured in the column inlet ranged from 20°C to 25°C. The viscosity of nitrogen varies very little within this temperature range, the average value being about 0.0175 centipoise. Based on equation (46), the flowrate at 20°C would be only 0.9% higher than at 25°C.

The vapor pressure of a compound is highly dependent on temperature. If equilibrium between the vapor phase and the liquid phase exists, then the saturated vapor phase concentration will increase with increased temperature as shown in Figure 14. The more volatile the compound or mixture of compounds, the greater the increase in vapor phase concentration per degree of temperature increase. For

5.4 Temperature Changes During SVE

example, between 20°C and 24°C, the range of temperature observed in the laboratory room, the saturated vapor phase concentration of toluene increases from 111 mg/l to 134 mg/l. In this same temperature range, the vapor phase concentration of the toluene-xylene mixture used in this research increases from 76 mg/l to 92 mg/l. Even if local equilibrium between phases does not exist, the vapor phase concentration in the effluent air along with the contaminant removal rate will increase with increased temperature. Figure 15 shows the predicted molar removal of a NAPL made up initially of 0.5 moles each of toluene and p-xylene at a specific discharge of 0.4 cm/sec using the vapor/liquid equilibrium model. To completely remove the NAPL by SVE, it would take 5 hr longer at 20°C than at 25°C. Since the efficiency of SVE is improved by increased system temperature, increased contaminant removal should be expected during the summer months when the temperature of the influent air and the media is higher.

The temperature data for the experiment where the toluene-xylene mixture was removed from the stainless steel column (SS3) is presented in Figure 16. The dimensions shown in the legend represent the distances of the thermocouples from the inlet screen in the stainless steel column. The temperature of the laboratory room air is also included.

From Figure 17 it can be observed that there is a minimum temperature front, a narrow region of lower temperature, moving through the column as the experiment proceeds. After 2.3 hr, the temperature at the first thermocouple is about 18.5°C, approximately 3.5°C lower than at the other four locations within the column. The temperature front reaches the second thermocouple after 4 hr producing a minimum temperature of 19.8°C. The temperature at the second thermocouple is about 2.5°C cooler than at the three locations ahead of the front. The temperature profiles for the first two thermocouples only are shown separately in Figure 17 for clarity. The minimum temperature front continues to move along the column, but has less

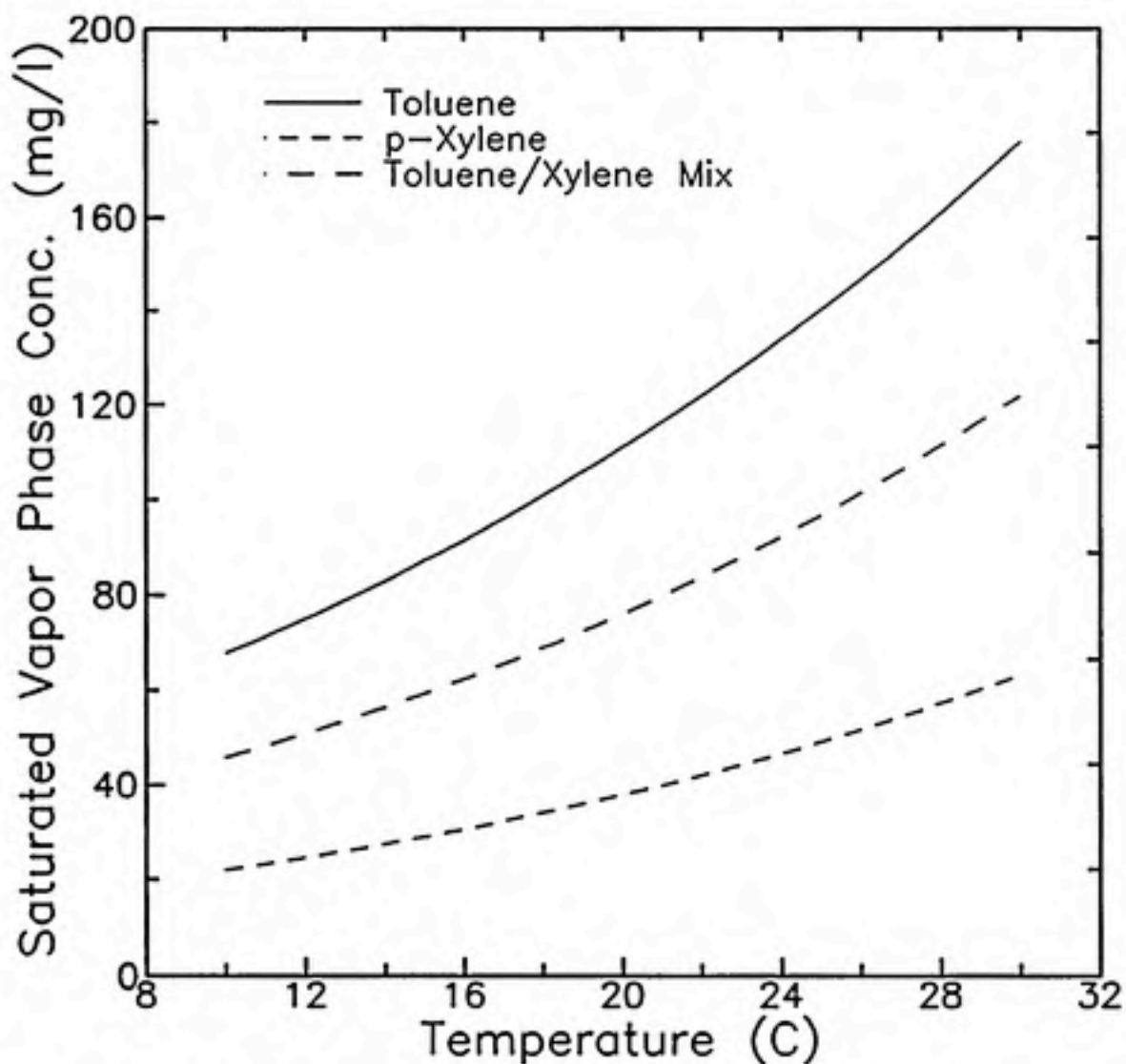


Figure 14. Saturated vapor phase concentration as a function of temperature and solute mixture.

effect on the local column temperature. After a major portion of the contaminant mass has been volatilized, the temperatures measured at all thermocouples are approximately equal. The measured column temperatures continue to increase or decrease depending on the temperature in the room.

The local reduction in column temperature is a result of the evaporation of liquid contaminant from the porous media. In order to evaporate a liquid, energy

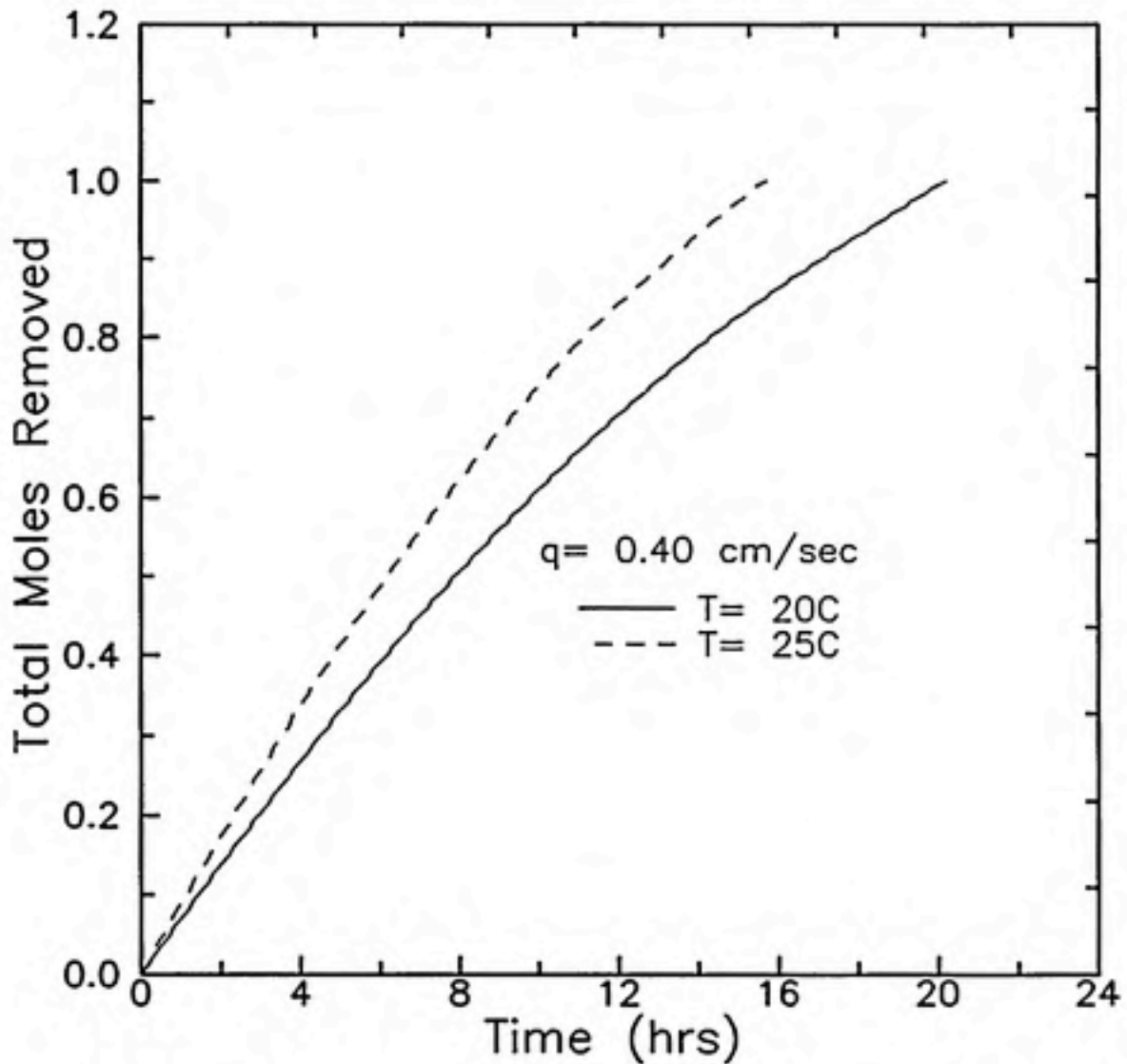


Figure 15. Equilibrium model predicted removal rate of toluene as a function of temperature.

in the form of heat must be provided to free liquid molecules from the intermolecular forces holding them in the liquid phase (Barrow, 1973). The amount of heat required for the conversion of a mass liquid to vapor at equilibrium is known as the heat of vaporization. During an experiment, the heat needed to vaporize the NAPL phase is provided by both the incoming nitrogen gas and the glass beads. As heat

5.4 Temperature Changes During SVE

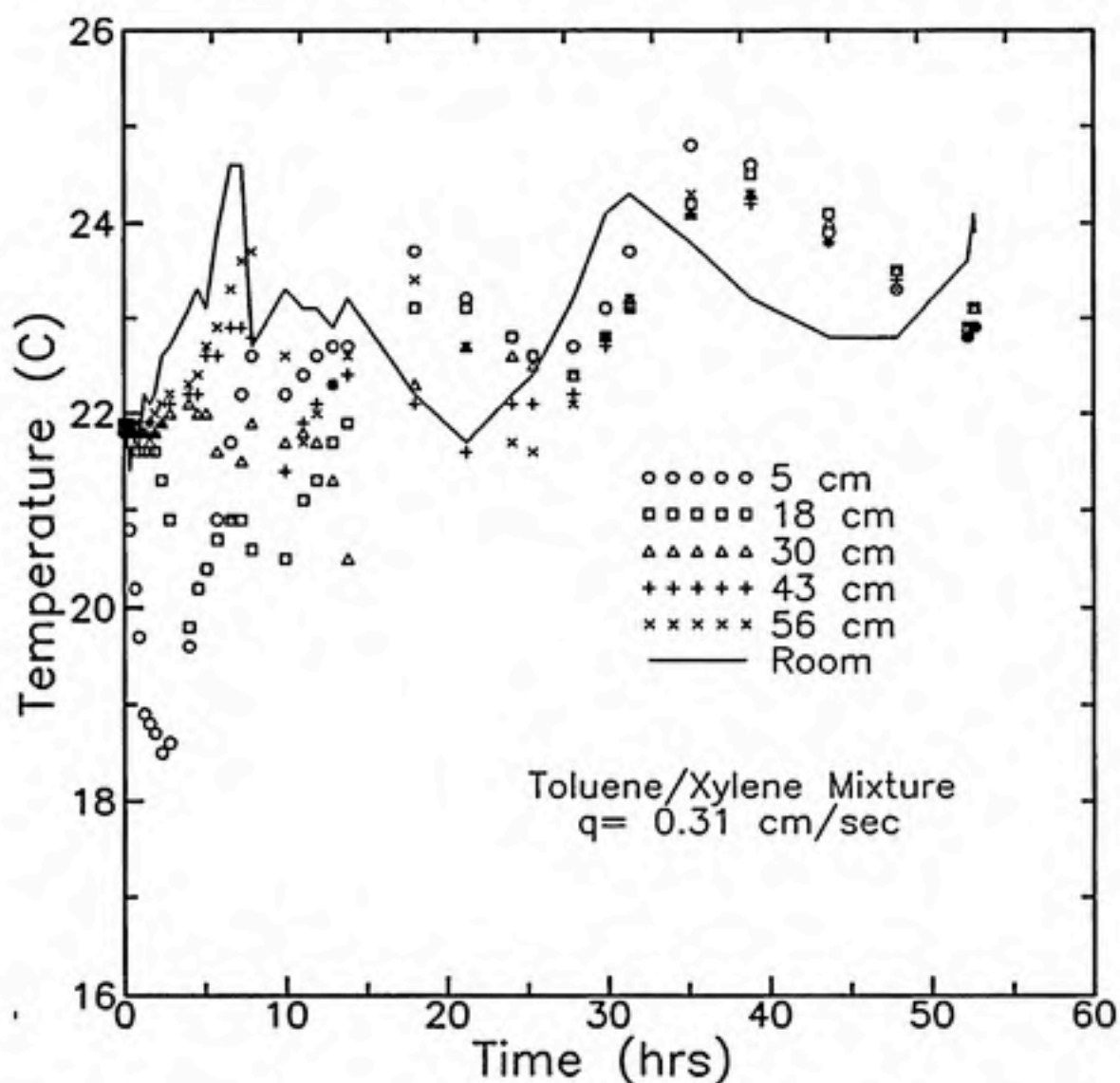


Figure 16. Column temperature versus location and time for experiment SS3.

is adsorbed by the NAPL, the temperature in the air space and the porous media decreases. Once the evaporation process is complete and all of the NAPL phase has been removed, the local temperature increases as heat is transferred from the nitrogen flowing into the column.

Since the evaporation of NAPL causes a reduction in local column temperature, it can be concluded from the shape of the temperature profile that the removal of

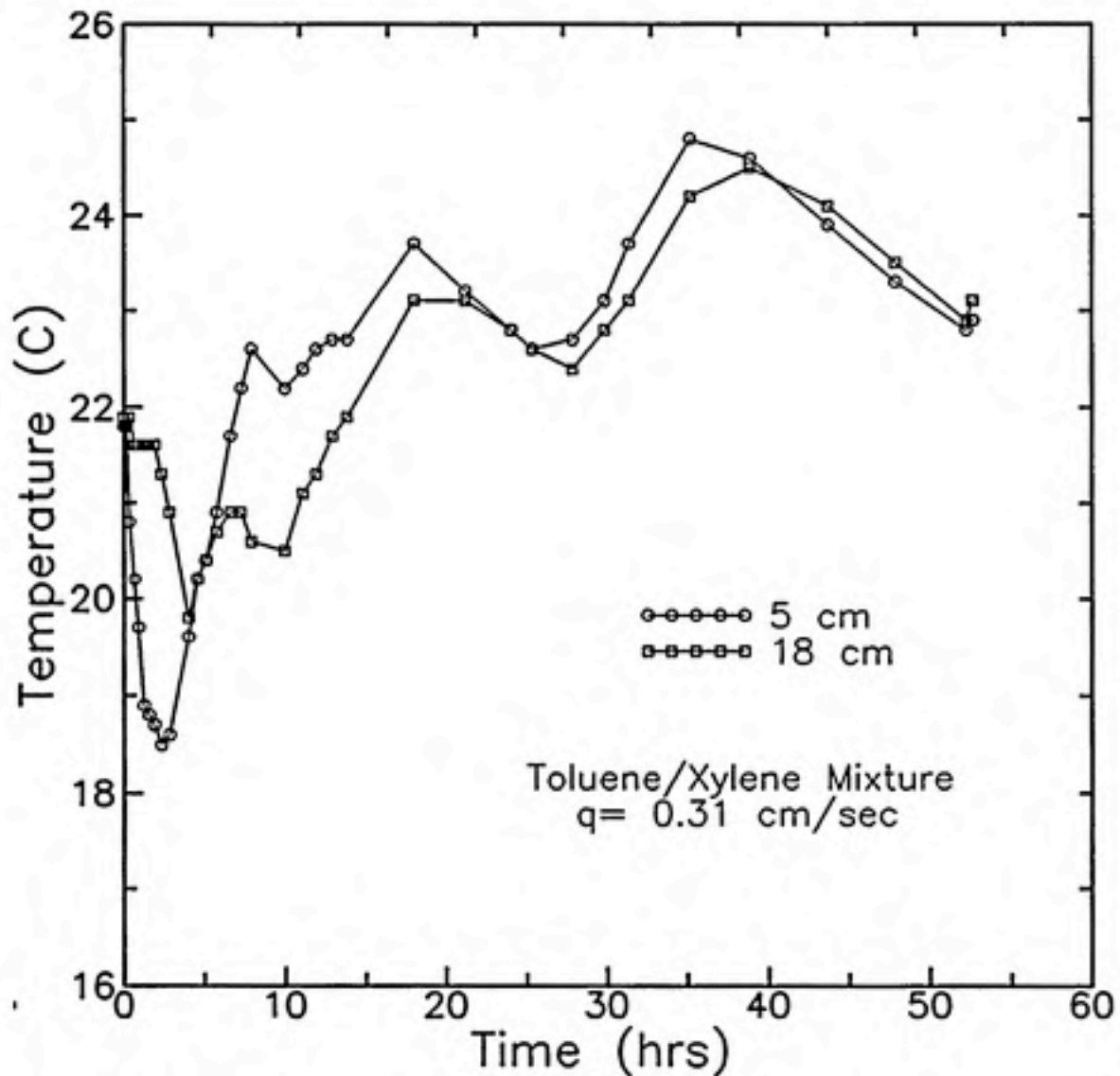


Figure 17. Column temperatures at the first two thermocouples for experiment SS3.

NAPL in this experiment is mostly limited to a region of only few centimeters wide. Very little NAPL removal occurs ahead or behind the temperature front. Gas chromatography analysis of vapor samples obtained from the sampling ports along the column showed that vapor phase concentrations behind the temperature front were much lower than ahead of the front.

5.4 Temperature Changes During SVE

The temperature profiles for the other experiment where the toluene-xylene mixture was used are shown in Figure 18. The temperature profiles obtained from this experiment appear similar in shape to those in experiment SS3. After 2 hr of flow, the minimum temperature recorded at the first point was on the average 4.4°C less than at the other measuring points. The temperature reductions due to vapor extraction were slightly higher in this experiment. In addition, the minimum temperature front moved slightly faster since a higher specific discharge (0.464 cm/s) was used during this experiment.

When toluene was used to residually saturate the column, the reduction in local column temperature was larger than in the experiments where the toluene-xylene mixture was used (see Figure 19). The reduction in column temperature was approximately 6.0°C at the first thermocouple. A larger reduction in local temperature is to be expected since toluene is more volatile than the toluene-xylene mixture and is evaporated at a much higher rate, which requires a faster rate of heat transfer. The minimum temperature front moved slightly faster in this experiment than in the other two experiments since a more rapidly evaporating contaminant was present. The minimum temperature front reached the first thermocouple after only 1.5 hr in this experiment as compared to 2.3 hr in experiment SS2 where the toluene-xylene mixture was being vented.

The temperature phenomenon observed in these three experiments were also observed in experiments conducted by Lingineni and Dhir (1990). Using a column residually saturated with ethyl alcohol, they observed much higher reductions in column temperature. Temperature reductions of up to 15°C were recorded. These high reductions in column temperature were a result of the high heat of vaporization of ethyl alcohol and the high flowrates used. The flowrates used corresponded to pore velocities as high as 38 cm/s, much higher than to be expected in an actual SVE operation.

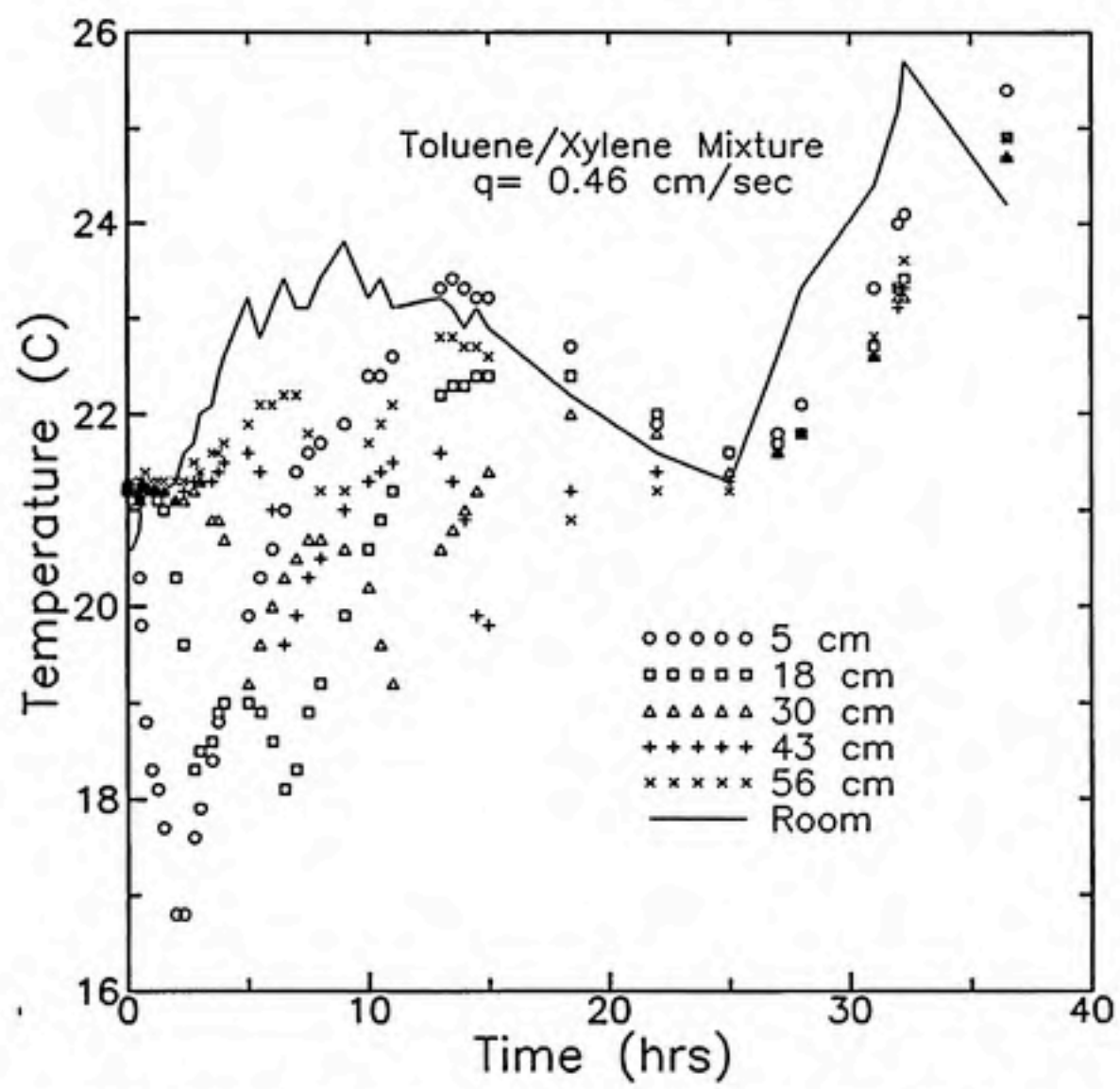


Figure 18. Column temperature versus location and time for experiment SS4.

The reduction in local media temperature could reduce the efficiency of the SVE process. According to Lingineni and Dhir, the reduction in temperature could cause the moisture in the incoming air to condense behind the evaporative front. If an immiscible phase is still present behind the front, then the water that condenses out of the air could reduce the mass transfer rate (evaporation rate) by forming a layer above the immiscible phase. Because relatively dry nitrogen gas was used

5.4 Temperature Changes During SVE

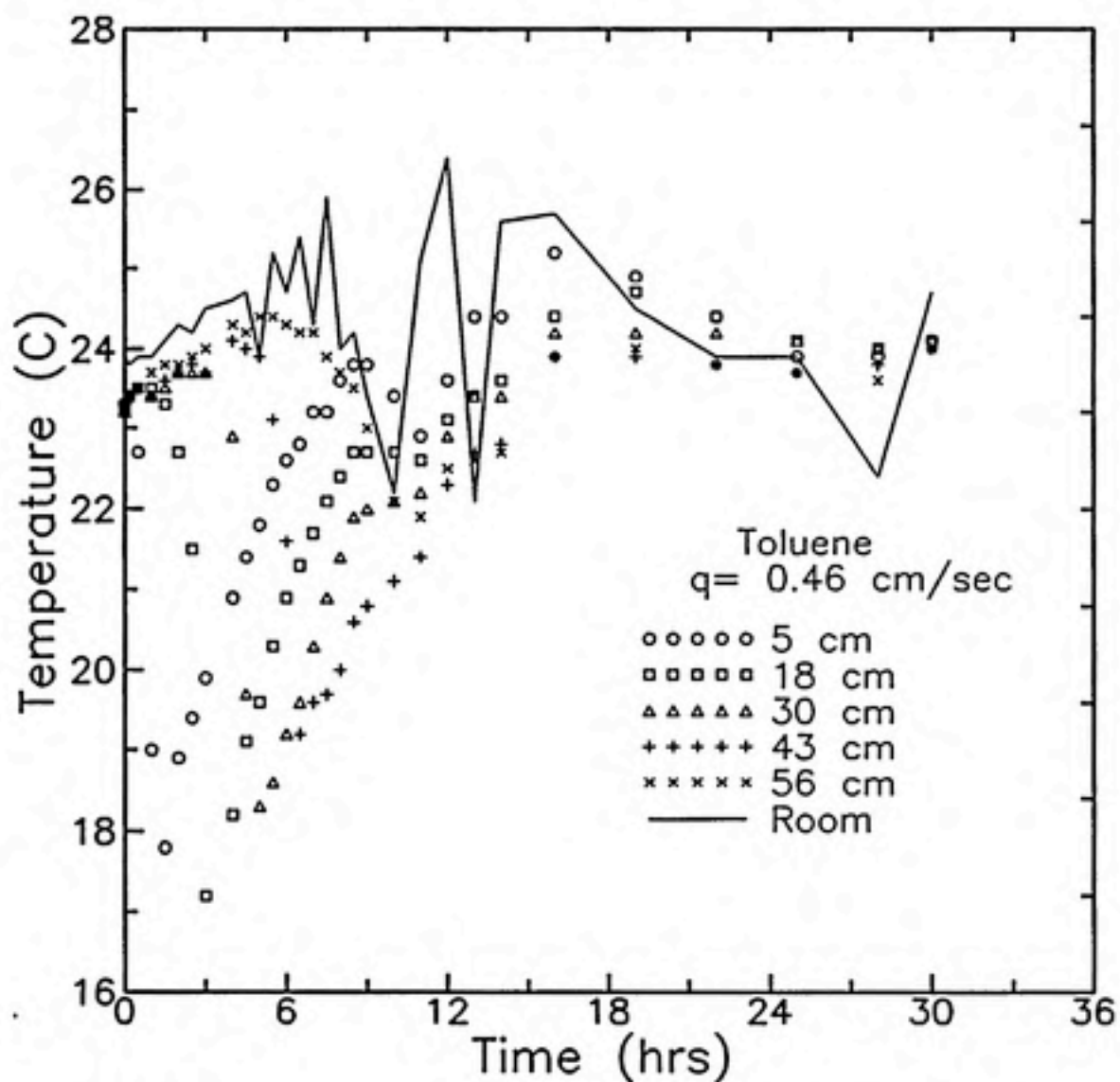


Figure 19. Column temperature versus location and time for experiment SS2.

during these experiments, it is highly unlikely that mass transfer rates were affected by condensation of moisture from the nitrogen.

5.5 Column Pressure

During the experiments conducted in the stainless steel column, the air pressures were measured at both the column inlet and outlet. The pressures were recorded at the same time temperature measurements were taken. The recorded pressures for experiment SS4 are shown in Figure 20.

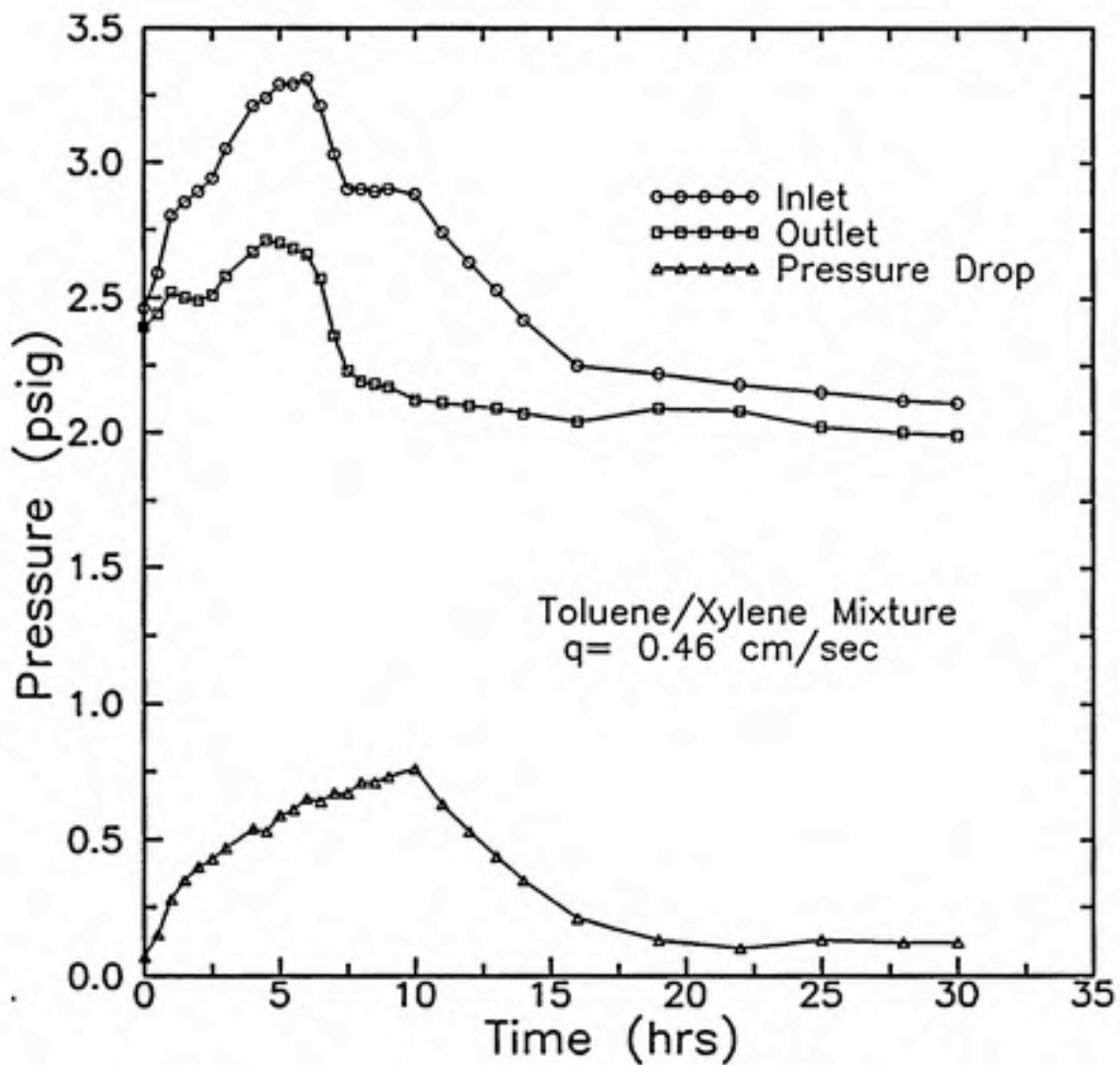


Figure 20. Column pressure as a function of time and location for experiment SS4.

5.5 Column Pressure

Interestingly, the measured pressures increased with time during the first 5 hr of the experiment. Pressures should not rise during the course of an experiment unless steady state conditions have not been established. Since the glass beads used are highly porous and permeable, steady state conditions should have been established rapidly. The pressures at both the inlet and outlet begin to decrease steadily before stabilizing after about 15 hr.

The pressure drop, difference between inlet and outlet pressure, increased steadily during the first 10 hr before slowly decreasing and approaching a steady state. The pressure drop across the column should decrease slightly with time as the contaminant is removed. As NAPL is removed, the air permeability of the porous media should increase as the fraction of the pore space containing air increases. The nitrogen flowrate through the column did increase slightly during the course of an experiment as contaminant was removed and had to be readjusted often in order to maintain a constant specific discharge and pore velocity.

5.6 Modeling Efforts

One of the main objectives of this research was to determine whether or not the assumption of local equilibrium between phases is valid during the SVE process. Many researchers have concluded that equilibrium should exist between phases at the pore velocities encountered in the soil during SVE (Thorton and Wooten, 1982; Marley and Hoag, 1984; Johnson et al., 1990). Some researchers report of mass transfer and diffusion limitations which will prevent equilibrium from occurring (Hutton, 1989; Rainwater et al., 1989; Gierke et al., 1990).

As discussed in section 3.6, a vapor-liquid equilibrium model was developed in order to model the SVE process in the laboratory columns used during this research. A FORTRAN computer program called EQUIL was written to model the laboratory process. The program predicts the removal of pure organic liquids from

porous media. Partitioning from the aqueous and solid phases to the vapor phase is not included in this model. The removal of up to 50 different compounds can be accounted for using this program.

Sample data output is provided to show how the vapor-liquid equilibrium model predicts NAPL removal. Figure 21 presents data generated by the program EQUIL for three different NAPL's at a specific discharge of 0.25 cm/sec and a temperature of 20°C. Initially, there is a total of one mole of contaminant present in the system in each case. For the case where the NAPL is composed of a single constituent (i.e., toluene), the model predicts a constant contaminant removal rate. The total number of moles removed is linearly related to the time of flow since the model predicts a constant effluent concentration of toluene, 111 mg/l. When the NAPL is composed of two constituents (i.e., toluene and p-xylene), the model predicts a non-linear molar rate of contaminant removal since the equilibrium vapor phase concentration is decreasing with time. The higher the initial mole fractions of the more volatile components, toluene in this case, the higher the removal rate. It should be noted that with this model, as long as any amount of contaminant mass is present in the system, equilibrium between phases is assumed. The mass removal rate reaches zero only when all contaminant has been evaporated from the system.

In order to determine if the assumption of equilibrium between the NAPL and vapor phase was valid for the experiments conducted, the EQUIL program was used to compare predicted and observed molar removal rates. The data for the second glass column experiment (G2), q equal to 0.4 cm/s, is presented in Figure 22. The predicted removal agrees fairly well with the actual removal indicating the probable existence of vapor-liquid equilibrium.

A comparison of modeled versus actual data for the toluene experiment conducted in the stainless steel column is presented in Figure 23. Initially, the measured toluene removal agrees very well with the modeled data. After about half the

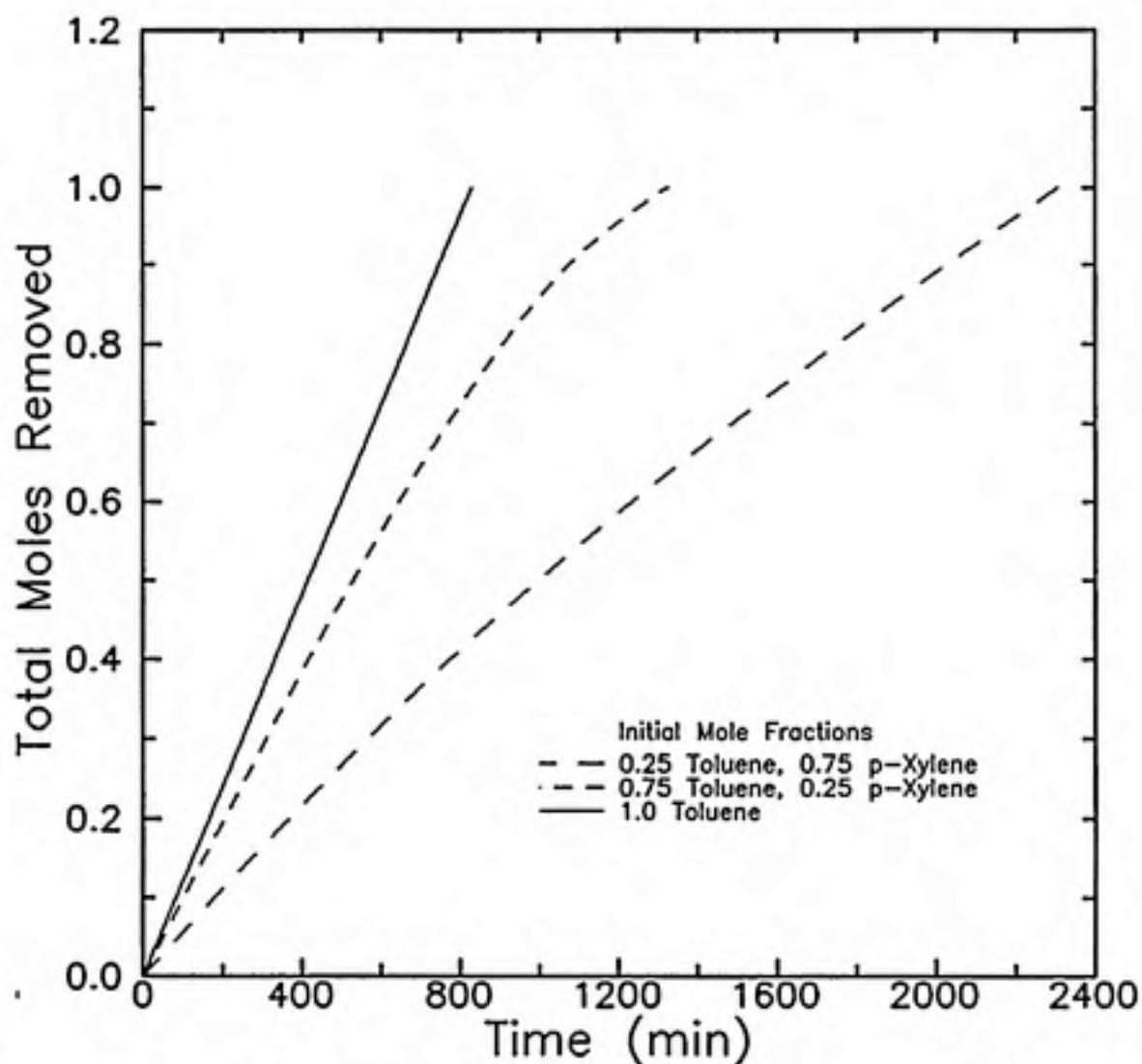


Figure 21. Equilibrium model predicted molar removal as a function of time and mixture properties.

toluene is volatilized, deviation from equilibrium is quite apparent. The contaminant removal rate begins to decline steadily. Since the specific discharge used in this experiment was very similar to the specific discharge used in the corresponding glass column experiment, deviation from vapor-liquid equilibrium was not expected. One possible cause for the existence of non-equilibrium conditions in the stainless steel

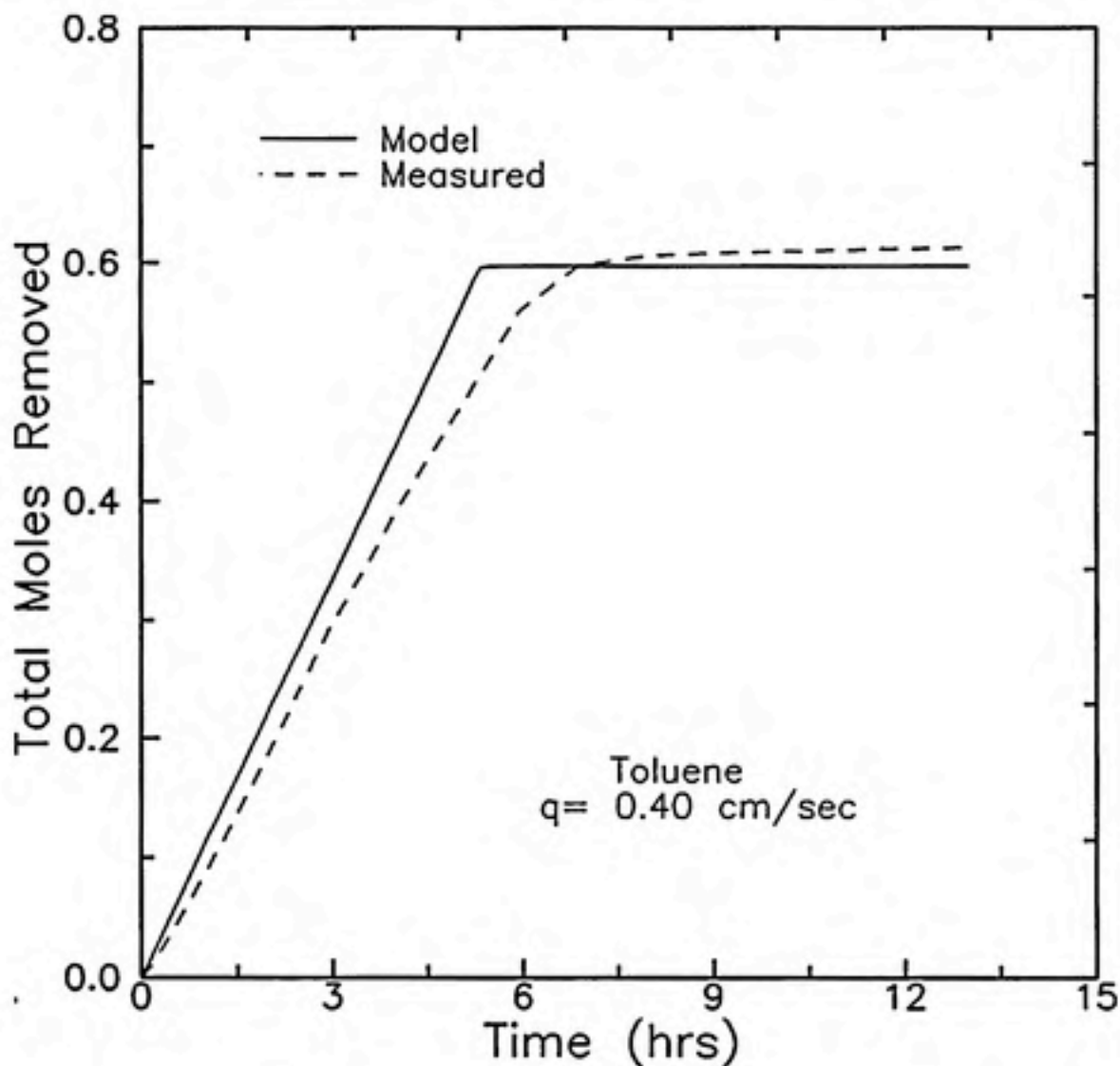


Figure 22. Comparison of measured and predicted molar removal for experiment G2.

column is the preferential flow of nitrogen through the glass beads. If the nitrogen does not flow uniformly through the porous media then molecular diffusion may be the rate limiting step for vapor removal. A tracer test was performed on the stainless steel column to test this theory (see Section 5.8).

Determining whether or not the assumption of local equilibrium between phases was valid during the experiments where the toluene-xylene mixture was volatilized

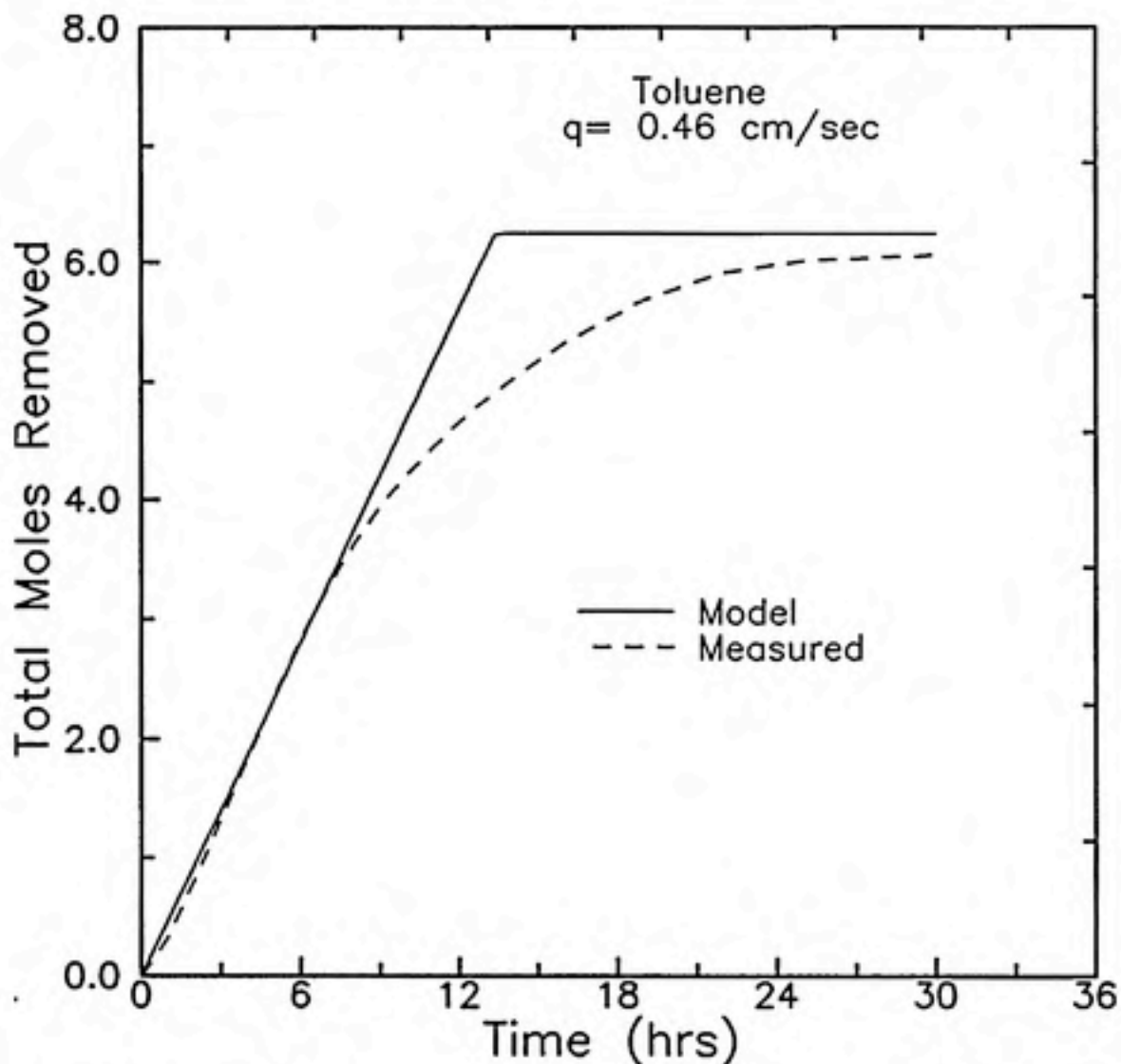


Figure 23. Comparison of measured and predicted molar removal for experiment SS2.

from the columns was slightly more difficult due to mass balance problems. From Tables 5-1 and 5-2, it should be noted that the difference between the calculated value of percent mass removed and the measured value was significantly larger when the toluene-xylene mixture was used. The measured value was determined from measuring the difference in column mass before and after an experiment using a balance beam scale. Since the balance beam scale was proven to be accurate, the

mass balance problems were a result of either the analytical methods used or the loss of mass through the system.

The assumption of 100% efficiency in carbon sampling tube extraction may account for a portion of the mass balance problem. A series of experiments were performed to determine the extraction efficiencies of toluene and xylene. Using the same method as Corn (1989), the calculated extraction efficiencies for toluene and xylene were 98% and 96% respectively, much higher than expected. Both Szatkowski (1990) and Corn reported an extraction efficiency of 90% for toluene. The difference between the calculated and measured amount of mass removed cannot be accounted for if the extraction efficiencies are as high as determined from the extraction efficiency experiments conducted during this research.

Since the assumption of 100% extraction efficiency does not seem that unreasonable, then there has to be some other cause for the mass balance problems observed. Contaminant mass had to be lost somewhere in the experimental apparatus. Great care was taken to prevent any vapor leakage from the stainless steel fittings and tubing used to carry the influent and effluent out of the column. Based on flowrate measurements at the column inlet and outlet, vapor leakage was believed to be minimal. One possible source of mass loss is the Teflon tubing used to carry a small amount of the total effluent flow to the apparatus used to obtain vapor samples. Since some of the vapor can diffuse through Teflon, some of the mass may have been lost before being adsorbed by the carbon. An experiment was performed without using the Teflon tubing in order to test this theory. Mass balance was improved only slightly by eliminating the Teflon tubing leaving the source of the mass balance problem still unresolved.

The measured molar removal data agreed fairly well with the vapor-liquid equilibrium model during the early stages of glass column experiment G4, for which a toluene-xylene mixture was used (Figure 24). The two curves start deviating from

5.6 Modeling Efforts

one another after a sizable portion of the toluene has been removed providing some indication that the concentrations measured for the xylene components are too low. In Figure 25, the molar removals of toluene and xylene are plotted separately. The measured molar removal for toluene agrees much better with the equilibrium model than does the measured removal for xylene. This can somewhat be explained by the fact that xylene is more strongly sorbed to GAC than toluene (Wallingford et al., 1988). As found in the extraction efficiency experiments, the extraction efficiency for xylene was slightly lower than for toluene. In order to gain a better understanding of why the mass balance was much lower when the toluene-xylene mixture was vented, an experiment should be conducted with only one of the xylene isomers (i.e. p-xylene) present in the column.

An attempt was made to correct the measured data in order to get complete mass balance. By multiplying all of the measured toluene vapor phase concentrations by 1.10 and all the concentrations of the xylene components by 1.25, the adjusted mass balance was approximately 100% (see Figure 26). This exercise yielded a relatively good agreement between the experimental data and the model predictions. The remaining discrepancy is consistent with an equilibrium modeling error that would result from using too low a temperature. A temperature of 20°C was used for these simulations, a higher temperature may have existed during this experiment.

Similar mass balance problems were encountered in the stainless steel column when the toluene-xylene mixture was used. During experiment SS4, the measured data and modeled data are in agreement initially as shown in Figure 27. As in the other stainless steel column experiments, non-equilibrium conditions existed after a portion of the mass was removed. Because of mass balance problems, it appears that local equilibrium existed for a shorter period of time than in the experiment where toluene alone was removed by vapor extraction.

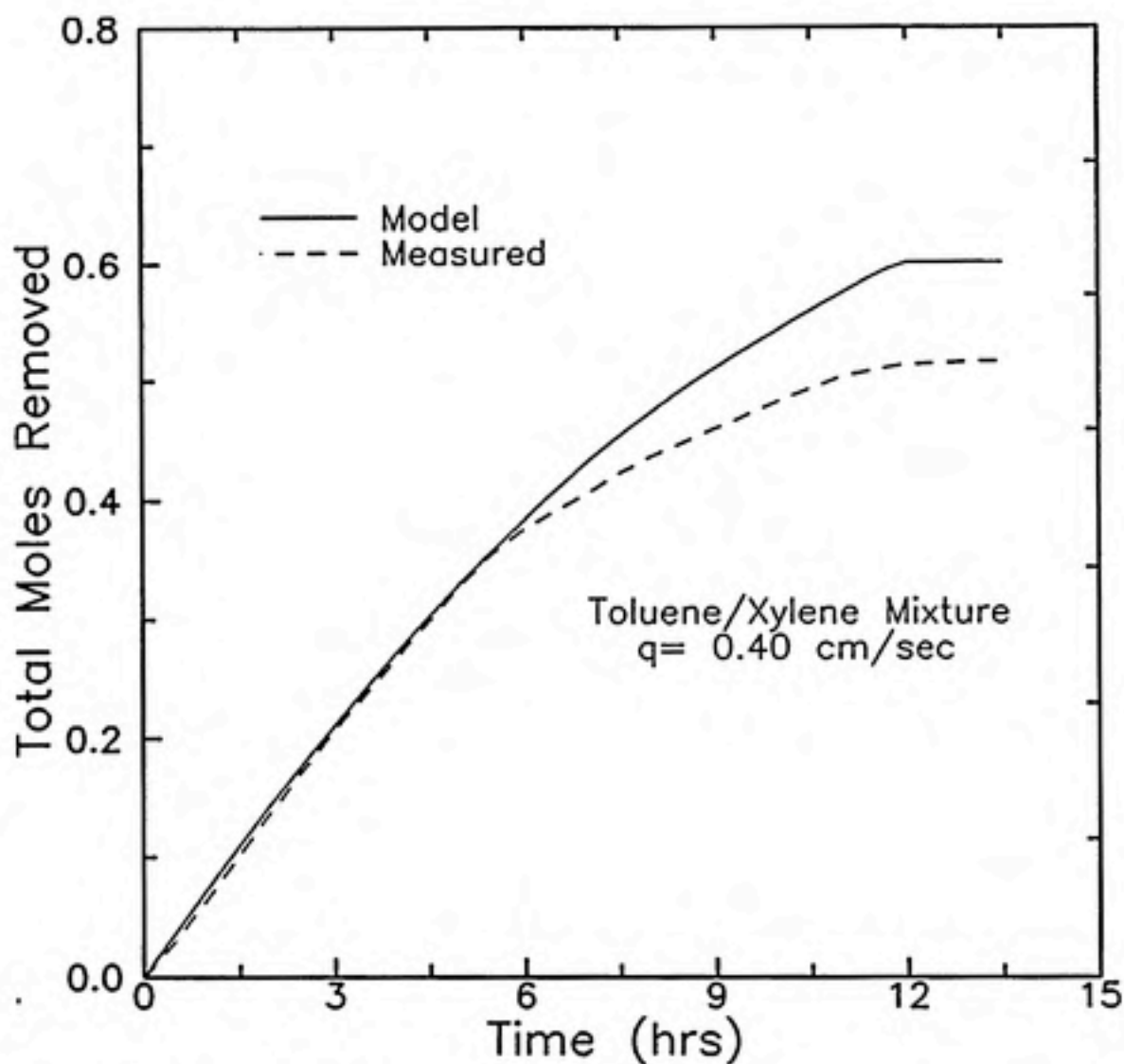


Figure 24. Comparison of measured and modeled molar removal for the toluene-xylene mixture in experiment G4.

5.7 Mass Transfer Rate Experiments

Based on experimental evidence from this work and the work of other researchers, the assumption of local equilibrium between the vapor phase and the NAPL phase seems reasonable at the pore velocities typically found in the subsurface during SVE. The mass transfer coefficients and thereby the mass transfer rates

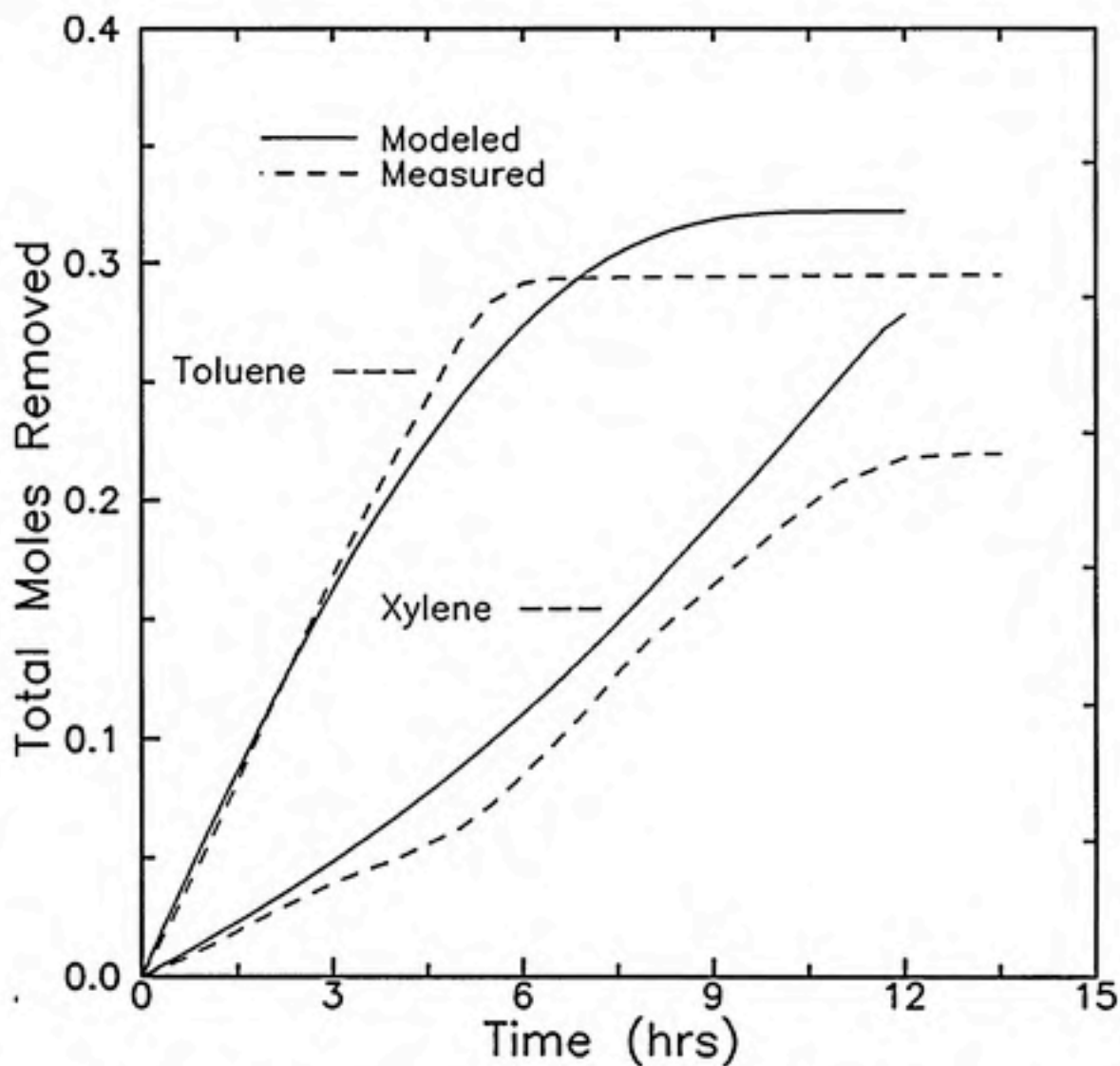


Figure 25. Comparison of measured and modeled molar removal for toluene and xylene components in experiment G4.

are high enough for equilibrium to exist. Deviations from equilibrium can occur, but probably as a result of diffusion limitations that can exist in heterogeneous media or in media with variable degrees of fluid saturation.

An attempt was made to measure the mass transfer coefficient for toluene in the laboratory. A small square glass column of 5.20-cm long and 6.3-cm² in cross

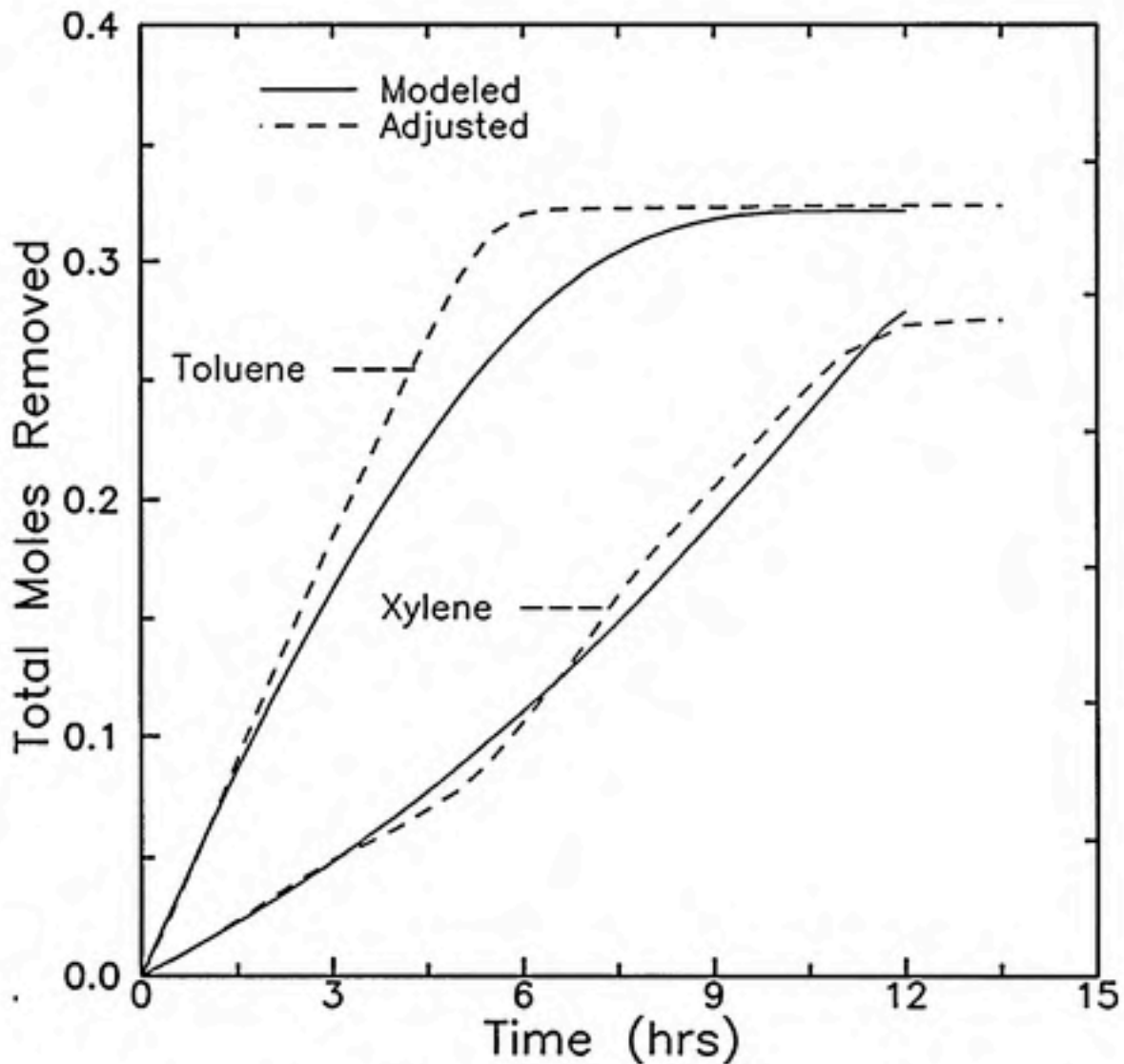


Figure 26. Adjusted experimental molar solute removal compared to model predictions for experiment G4.

sectional area, similar to the column used by Szatkowski (1990), was used to conduct this experiment. The column was filled with 11.2 ml (9.7 gm) of toluene. Nitrogen gas was flowed across the top of the toluene surface at a linear velocity of 0.8 cm/s.

After 2.5 hr of flow, 2320 mg of toluene had been removed from the column by the nitrogen. The average vapor phase concentration of toluene was 103 mg/l

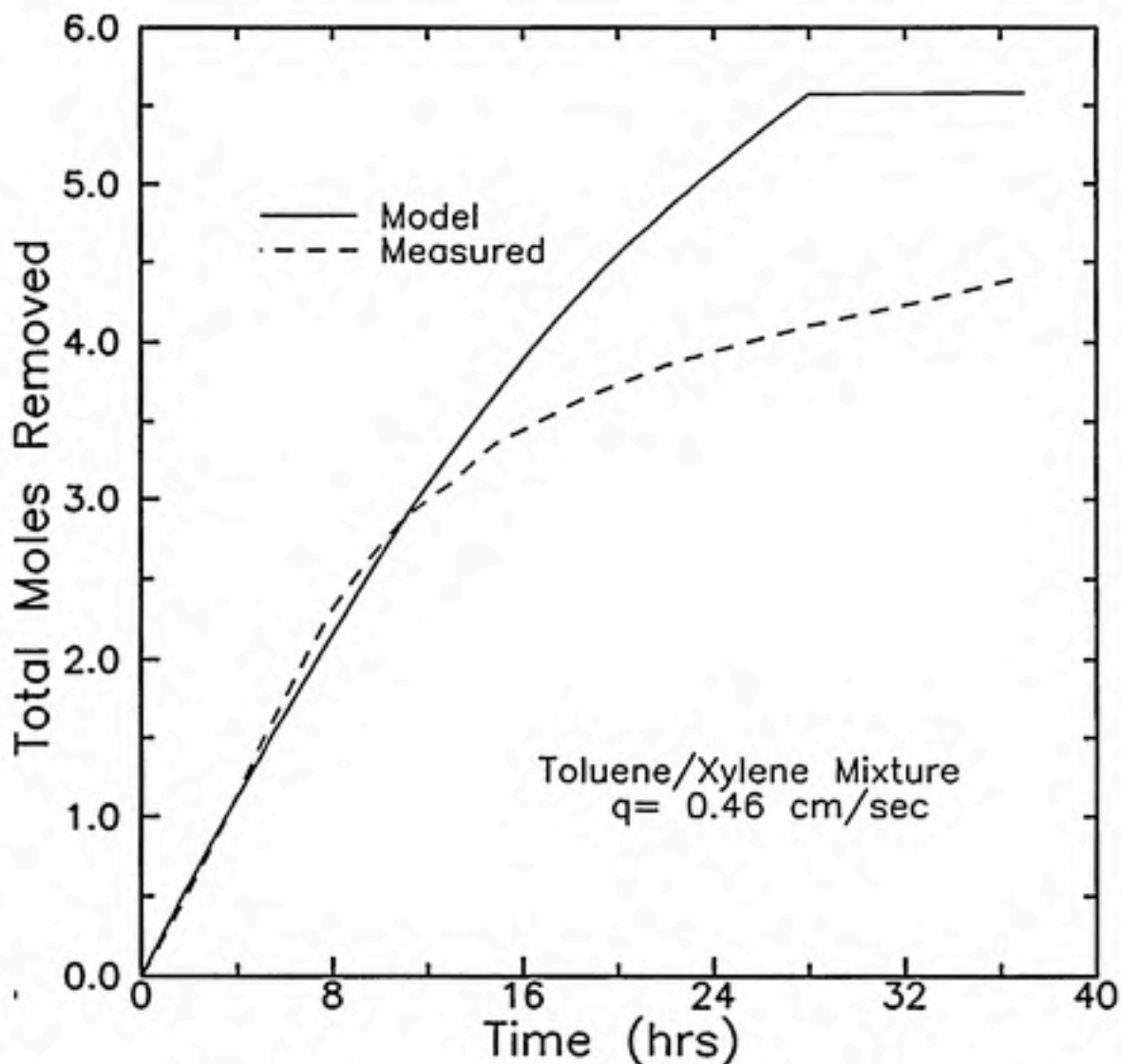


Figure 27. Comparison of measured and modeled molar removal for the toluene-xylene mixture in experiment SS4.

during this period. Since the average vapor phase concentration is so close to the expected equilibrium value of 111 mg/l, the mass transfer coefficient calculated from this experiment would be subject to large error (Miller et al., 1990). Either a shorter column or a higher vapor phase velocity would be needed to insure mass transfer along the entire column length and to obtain an accurate value of K_L . An

attempt was made to use a higher vapor phase velocity, but a severe leak developed in the column. A better method needs to be developed in order to measure the mass transfer coefficients from pure organic liquids.

5.8 Stainless Steel Column Tracer Test

In order to determine the probable cause for the observance of non-equilibrium conditions in the stainless steel column experiments, a liquid tracer test was conducted. A gas tracer was not used because the equipment required was not readily available. A conservative tracer, sodium azide, was dissolved in water and then pumped through the column at an average flowrate of 102.7 ml/min which corresponded to a pore velocity of 1.031 cm/min. The column effluent concentration was measured using an ultra-violet (UV) spectrophotometer.

The two main mechanisms by which a solute migrates through porous media are bulk advective flow and hydrodynamic dispersion. Hydrodynamic dispersion is a result of both mechanical dispersion, which is caused by variations in pore velocity on the microscopic scale, and molecular diffusion (Bear, 1979). The key parameters determined from a tracer test are the hydrodynamic dispersion coefficient (D_h) and the intrinsic longitudinal dispersivity (α_L). When molecular diffusion is negligible as compared to advective flow, α_L can be multiplied by the average pore velocity to obtain D_h .

An analytical solution to the advective-dispersive (AD) equation was used to determine D_h and consequently α_L . According to Bear, an approximate solution to the AD equation for a conservative tracer is

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{L - vt}{2(D_h t)^{1/2}} \right) \quad (47)$$

5.8 Stainless Steel Column Tracer Test

where $\frac{C}{C_0}$ is the normalized effluent concentration, L is the column length, v is the average pore velocity (L/T), t is the time, and erfc is the complimentary error function.

The value of D_h was estimated by fitting the analytical solution above to the experimental data (see Figure 28). A hydrodynamic dispersion coefficient of approximately $2 \text{ cm}^2/\text{min}$ was calculated using this approach. This corresponds to a longitudinal dispersivity (α_L) of 1.94 cm. The calculated value of α_L is high as compared to values measured by other researchers in glass beads of similar size (Poirier-McNeill, 1989).

Because of the slightly higher value of α_L measured in this tracer test, there is some indication of the existence of preferential flow paths through the stainless steel column. During a SVE experiment, the nitrogen is probably not flowing uniformly through the column thereby causing the effluent vapor concentration to be less than the expected equilibrium value. Vapor phase diffusion of contaminants from the areas in the column of little vapor flow to the areas of preferential flow becomes the rate limiting step for contaminant removal as an experiment progresses.

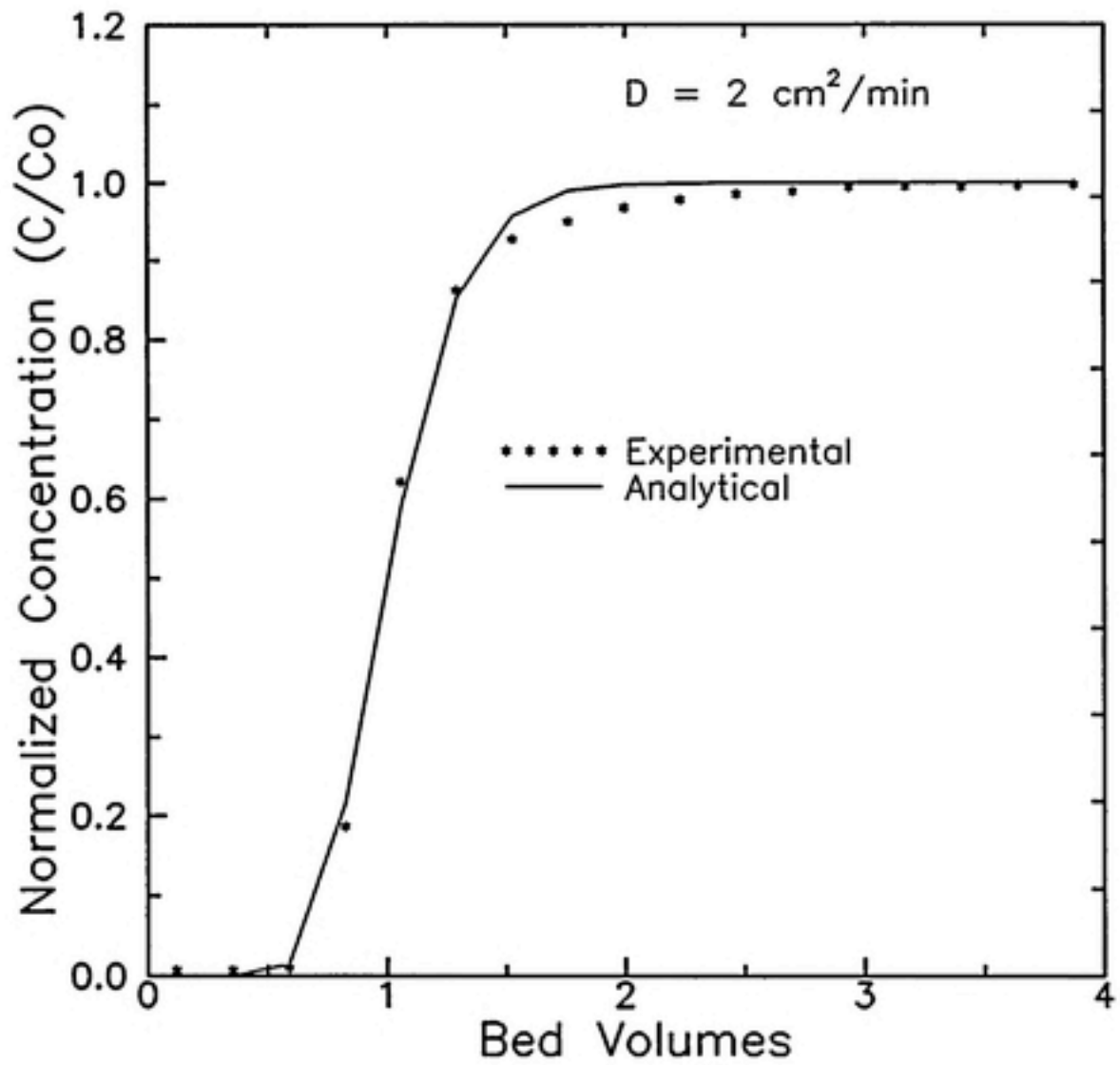


Figure 28. Breakthrough Curve for Tracer Test

6 Conclusions and Recommendations

6.1 Conclusions

1. The assumption of local equilibrium between the NAPL phase and the vapor phase is valid for the pore velocities to be encountered in the subsurface during SVE.
2. The reason for the existence of local equilibrium during the SVE process is that the rate of mass transfer from a pure organic liquid phase to the vapor phase is very high as compared to typical vapor velocities in porous media.
3. Deviations from local equilibrium can occur if the mass of NAPL is reduced significantly thereby reducing the interfacial area available for mass transfer.
4. The molecular diffusion of organic vapors from stagnant zones to areas of bulk advective flow can cause non-equilibrium conditions to develop in the porous media.
5. Diffusion can become the rate limiting process when the porous media contains heterogeneities that cause preferential flow paths to be formed or when the contaminant is not uniformly distributed.
6. In order to most efficiently remove contaminants in the subsurface by SVE, the highest possible flowrates should be used initially when mass transfer is fast enough for local equilibrium conditions to exist. Once a significant portion of the contaminant has been removed and mass transfer or diffusion limitations cause non-equilibrium conditions, then a lower flowrate should be used in order to save on power costs and reduce the volume of air requiring treatment.
7. Local reductions in temperature are apparent as contaminants are volatilized during the SVE process. Whether or not the reduction in media temperature

during an actual SVE installation will adversely affect the removal of contamination is still in question.

6.2 Recommendations

1. The lab apparatus should be improved in order to insure better mass balance.
2. If the stainless steel column is used in future experiments, then another source of vapor removal should be sought. Because nitrogen must be obtained in large quantities from an outside source, it would be more convenient to use an air compressor equipped with a device for removing water vapor from the air.
3. Experiments should be conducted using a more realistic porous media such as sand.
4. An experimental apparatus should be developed in order to determine the mass transfer coefficients of the contaminants commonly removed by SVE.
5. A multiphase flow and transport model should be used to simulate the mass removal, temperature, and pressure data collected in the stainless steel column experiments.

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