FORCED AIR VENTILATION FOR REMEDIATION
OF UNSATURATED SOILS CONTAMINATED BY
VOC

(U.S.) Environmental Protection Agency
Ada, OK

May 91

FORCED AIR VENTILATION FOR REMEDIATION OF
UNSATURATED SOILS CONTAMINATED BY VOC

by

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-91/016	2.	3. PB91-181750

4. TITLE AND SUBTITLE
FORCED AIR VENTILATION FOR REMEDIATION OF UNSATURATED
SOILS CONTAMINATED BY VOC

5. REPORT DATE May 1991

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Jong Soo Cho

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Robert S. Kerr Environmental Research Laboratory
U.S. Environmental Protection Agency
P.O. Box 1198
Ada, OK 74820

10. PROGRAM ELEMENT NO.
ABWD1A

11. CONTRACT/GRANT NO.
INHOUSE

12. SPONSORING AGENCY NAME AND ADDRESS
Robert S. Kerr Environmental Research Laboratory
U.S. Environmental Protection Agency
P.O. Box 1198
Ada, OK 74820

13. TYPE OF REPORT AND PERIOD COVERED
Project Report

14. SPONSORING AGENCY CODE
EPA/600/15

15. SUPPLEMENTARY NOTES

Project Officer: Jong Soo Cho   FTS: 743-2353

16. ABSTRACT
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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field, Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	90
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77)   PREVIOUS EDITION IS OBSOLETE

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QUALITY ASSURANCE STATEMENT

All research projects making conclusions or recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project was conducted under an approved Quality Assurance Project Plan. The procedures specified in this plan were used with the following exceptions: The QA/QC plan for field pneumatic tests was not made and the original QA/QC plan was not updated. The calibration of pressure gauges was not conducted and a calibration chart for the pitot tubes supplied by the manufacturer was used. Soil air pressures relative to the atmospheric pressure were measured and the pressure changes with distance from the wells were observed. The pressure gauges in the range of less than 1 inch water were very sensitive to the atmospheric pressure and unreliable under windy conditions. The reproducibilities of the gauges in higher ranges were good and the repeated measurement could replicate the trend of pressure changes. Information on the plan and documentation of the quality assurance activities and results are available from the author.

ABSTRACT

Many cases of soil vacuum extraction(SVE) applications in the field have been reported, but very few systematic studies about physical and chemical processes in soil air are found. Parameters which were expected to control the removal process of VOCs from contaminated soil during the SVE operation were studied by means of numerical simulations and laboratory experiments in this project.

Experimental results of SVE with soil columns in the laboratory indicated that the removal efficiency of VOCs from soil columns was a complicated function of air flow and the hydrogeometry inside. The partition process between air and the immobile liquid was not an equilibrium one, and the interfacial mass transfer varied with the residual amount of VOCs in the soil. Additional experiments under various conditions should be conducted to obtain further insight into the SVE process.

Two computer models were developed to study soil air and VOC movement during the SVE process. The first one was an analytical approximate model which could be used for the simulation of air movement in SVE operation with multiple wells in homogeneous soil media. The second one was a numerical model in three-dimensional geometry which used a finite difference solution scheme. A simple pneumatic pump test was conducted, and parts of test data were used for the validation of the simple analytical model.
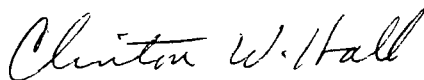
This report covers a period from June 1988 to December 1990 and work was completed as of December 31, 1990.

FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes indigenous to the soil and subsurface environment, for the protection of this resource.

This report describes research conducted to develop, evaluate, and demonstrate the efficacy of forced air ventilation of VOCs from unsaturated soils. The research assesses evaporation of VOCs under artificially driven pressure gradients as a means of removing VOCs, which are widely encountered as ground water pollutants.

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ABBREVIATIONS AND SYMBOLS

Abbreviations

ADI : Alternative Directive Implicit

FID : Flame Inonization Detector

PVC : Polyvinyl Chloride

scfm : standard cubic feet per minute

SVE : Soil Vacuum Extraction

TCE : Trichloroethylene

VOC : Volatile Organic Contaminant

Symbols

atm : atmospheric pressure

cp   : centipoise

H   : Henry's law constant

Kpa : Kilopascal

L   : soil column length

x   : x coordinate in rectangular coordinate system
       longitudinal direction of soil column

z   : z coordinate in rectangular coordinate system
       vertical direction in three-dimensional models

Δ : linear increment

∇ : gradient operator

∂ : partial differential operator

ACKNOWLEDGEMENT

SECTION 1

INTRODUCTION

Fuel leakage and spills are the most frequent sources of soil and ground-water contamination at service stations and underground storage tank areas. A large portion of released hydrocarbon infiltrates the subsurface and remains bound under capillary pressure as residual immiscible phase liquid. The residual hydrocarbon serves as a continuous source for groundwater contamination. Therefore, the reclamation of the contaminated aquifer should include removal of the long-term contamination source. The clean-up of soil contaminated by Volatile Organic Contaminants (VOCs) is generally an expensive operation due to the high cost associated with excavation, transportation and disposal. Classical methods such as soil removal, forced percolation, encapsulation, or trenching are frequently impossible or prohibitively expensive, especially in the midst of an industrial or residential area.

An alternative method to remediate soils is by the use of the soil vacuum extraction (SVE) system. This process has proven to be inexpensive and effective for the clean up of soil and ground-water contaminated by solvents and volatile components of petroleum products (Bennedsen, 1987; Jafek, 1986; Agrelot et al., 1985; Malot, 1985). The cost of installation and operation of an SVE system is usually lower than the cost of other methods (Hinchee et al.,1987). Another major advantage is that this method is an in-situ process. The contaminated soil remains in place and is not transported and disposed of in other locations. The SVE system is also used for the removal of methane gas originated in landfills (Moore et al., 1982). Practical applications of the SVE system have been reported for the control of methane gas migration from landfills (Moore et al., 1979). Methane and carbon dioxide generated by microbial decomposition of organic materials can migrate a long distance from the landfill and can build up to explosive levels. The SVE wells, sometimes with interdiction walls, are installed to prevent the migration of methane gas (Mohsen et al., 1980).

Many field applications have been reported since early 1980 (Bruckner, 1987; Bruckner and Kugele, 1985; Glynn and Duchesneau, 1988; Hutzler et al.,1988). In spite of many field applications, very few scientific or systematic studies have been reported. Therefore, the design of the SVE system has

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been mainly dependent on experience and rough estimations. Sometimes, prototype or pilot-scale systems are used to obtain design parameters such as well depths, well spacings, and extraction rates (Hutzler et al., 1988). Field operations and pilot scale studies can be found in several review reports (Dynamac, Inc., 1986; Oak Ridge National Laboratory, 1989; Hutzler et al., 1988).

This project investigated the movement of VOCs in soil air during the SVE applications. Several physical and chemical processes are involved in the movement of VOCs in soil air, including convective and diffusive transport, interfacial mass transfer between immiscible phases, and biological/chemical transformations. Physical and chemical properties of soils and VOCs are expected to control these processes. The ultimate goal of this project was to obtain knowledge on relationships among the various properties and processes of VOC transport in soil air. These relationships were integrated in computer models. This report includes laboratory experiments and field tests of the SVE system under relatively simple conditions. The model development procedures are also included in this report. Vigorous validations of models are recommended prior to public distribution.

This report consists of several sections. Section 2 includes the summary of the conclusions of this project and recommendations for future research. In section 3, background review of the SVE research and model development is included. In sections 4 and 5, mathematical expressions of processes involved in SVE are derived and analyzed. In section 6, soil column experiments conducted in the laboratory are reported. In sections 7 and 8, development of two models and a field pneumatic pump test are included.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

From the experiments in laboratory, field tests, and development of models in this project, the following conclusions are drawn:

(1) From analyses of experiments and model simulations, very valuable information could be obtained. The observation of simulated results based on soil column experimental conditions showed several physical and chemical properties influencing the efficiency of the SVE operation. Among VOC chemical properties, the vapor pressure was the most sensitive factor that controlled the efficiency of total operations.

(2) Air flow rate and liquid distribution were very important parameters which controlled the removal rate of VOCs from soil columns. A conceptual model was proposed to describe the evaporative process of VOCs from the residual liquid in soil pores.

(3) The pneumatic pump test gave very important information for design of SVE systems, including the zone of influence, soil characterization and pumping efficiencies.

(4) Two computer models for soil air flow and VOC transport in the SVE system were developed. The analytical solution model developed was very simple and easy to use. Simulations of pneumatic pump tests with this model revealed that the model generated reasonable results and could be used as an initial design tool. A fully three-dimensional finite difference model was developed. Various solution methods have been tried and explicit schemes were selected to reduce the computational time and memory requirements. A graphical postprocessor was attached to enhance the visualization of output results.

The proposed future works are as follows:

(1) A large number of studies on mass transfer have been reported in engineering literature, but very few pertain to soil systems. Soil particles and pore sizes are not uniform and the Reynolds' number is usually less than 0.1 in soil systems. The extrapolation of empirical correlations to unmeasured operating conditions is not desirable, and further studies are required to obtain more precise correlations suitable for soil systems. More experiments are suggested with modified columns and procedures for quantitative analyses.

(2) The proposed model for VOC removals from soil pores needs to be verified through additional experiments.

(3) Research on the enhancement of SVE by increased temperature is also proposed to achieve better efficiency of SVE operations.

(4) Pneumatic pump tests are recommended under various operating conditions before full scale implementations of SVE systems. Tracer gas tests will help further.

(5) A main reason for the lack of field scale model developments is the expense of the model validation with field scale data. It is very costly to perform tests for the model validation, but this is a very necessary step. A simple pneumatic pump test, like the one reported in this project, will give very important information for model validation and optimal design of the SVE system.

(6) Additional refinement and validation of the analytical solution model are necessary for further field applications. The finite difference model is still in the developmental stage and needs a rigorous validation through numerical experimentations and comparison with field data. In addition to the validation, alternative schemes should be tested to accelerate the computation.

SECTION 3

BACKGROUND REVIEW

In this section, a small number of background reviews of the SVE process study are included. Reviews are limited to the areas of laboratory research and mathematical model development.

Several laboratory experiments involving convective transport due to air flow inside soil pores have been reported since 1980. Before this time, research involving soil gas movement was restricted to diffusional transport. Laboratory research is often performed with small soil columns. Marley and Hoag (1984) and Baehr et al. (1989) used soil columns to measure the removal rate of gasoline from contaminated soil. They reported experiments on the removal rate of partially saturated gasoline in the capillary fringe above the water table by steady air flow. More than 99 % removal of gasoline initially present was observed in a reasonably short time. Aware, Inc. (1987) conducted soil column experiments to evaluate the SVE process with various contaminant conditions and soil types. They reported 40 to 90% removal of the initial amount of VOCs applied in less than 8 days of operation in the temperature controlled environment. They concluded that there is the possibility of success in contaminated soil cleaning with the SVE process. Rainwater et al. (1988 a, b) reported large-sized soil column experiments to study the volatilization mechanism in porous media and provided removal rate data of hydrocarbon mixtures with a preliminary modeling effort. They concluded that the presence of the residual water in porous media significantly retarded the diffusion of the hydrocarbon vapor and slowed the removal process.

Since soil column experiments are one-dimensional, they are easy to analyze. But it is difficult to replicate three-dimensional field conditions with one-dimensional soil columns. It is reasonable to conduct large three-dimensional experiments with sand boxes or tanks. Texas Research Institute (Thornton and Wootan, 1982; Wootan and Voynick, 1984) reported experiments with large sand boxes. They studied the removal of gasoline product floating above a water table using the SVE process and showed the possibility of the field scale application. A large volume of gasoline spilled in sand tanks was removed by air flow and a remarkable amount of gasoline was also degraded by microbial activity.

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Johnson (1989) reported a large physical model study to examine the effectiveness of an SVE system. He observed high hydrocarbon vapor concentration in soil air just after gasoline spillage. Water table fluctuation made the hydrocarbon concentration decrease due to the entrapment of hydrocarbon in the capillary fringe. He indicated the low efficiency of the SVE application for the removal of the entrapped gasoline residual.

Many computer models have been developed for experimental data analyses. A one-dimensional model was developed by D.J. Wilson et al. (1988) for analysis of AWARE, Inc.'s soil column experiment (1987). This simple model was used for analysis of soil column experiments and later expanded to two-dimensional rectangular and cylindrical coordinate systems for analysis and design of field scale operations. This model used site-specific partition coefficients and a finite-difference scheme with a relaxation method to solve partial differential equations. A two-dimensional, finite difference model was reported by D.E. Wilson et al.(1987) for simulations of sand-box experiments performed by the Texas Research Institute (Wootan and Voysnick, 1984). This model included the air flow and transport of gasoline components evaporated from free product over the water table. The floating gasoline product in the capillary fringe above the water table was treated as a constant flux boundary due to evaporation.

Air flow and VOC transport in the soil system are considered as the two main processes in SVE systems. Some models have been developed to treat the air flow only. Initially in designing an SVE system, the air flow model is sufficient. For the prediction of clean-up time, a model developed to describe both processes is necessary. A two-dimensional model with the axial symmetry assumption which was limited for the single venting well was presented by Kemblowski (1989). Analytical solutions of soil air pressure distributions were obtained in porous media confined by impervious boundaries. Only the radial directional flow to the well was considered. In field applications of the SVE process, multiple wells are expected to show three-dimensional configurations of the air pressure and flow velocity distributions. Therefore, only a three dimensional model incorporating various well locations and lengths of screened well sections can provide an optimal design. Because of the large memory and computational time, three-dimensional models developed for SVE systems are rare. Colorado State University (Sabadell et al., 1988) reported a three-dimensional air flow model with the finite difference method. Their model was tested with limited field data.

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The similarity of the physical processes of SVE and ground-water pumping led to the idea of utilization of a ground-water model as an aid in the design of soil vacuum extraction systems. Massmann (1989) compared the soil air flow equation with the ground-water flow equation. The difference between these equations was the air compressibility which made the flow equation nonlinear. The equation could be linearized by substituting the density of air with an initial or averaged value. The maximum computational error in pressure distribution due to the linearization was estimated to be 7% when the applied vacuum pressure was 0.5 atm. Computational error was negligible with the applied vacuum of 0.2 atm or less. He concluded that computational error was negligible in the range of applied vacuum pressure in field operations and the use of a ground-water model was a reasonable tool in the design of a SVE system when an appropriate soil air flow model was not readily available. Application of a ground-water flow model for simulations of the air pressure and flow velocity distributions of an SVE system was reported by Cho and DiGiulio (1990).

SECTION 4
PROCESS OF SOIL VACUUM EXTRACTION

The basic principle of SVE is very simple. Air flow is induced in the subsurface by a pressure gradient applied through vertical wells or horizontal trenches. The flowing air sweeps out VOCs by vaporizing highly volatile components from soil pores and the contaminated soil air is collected by extraction wells. Effluent air from extraction wells is often treated by off-air treatment systems, e.g. an activated carbon tank or catalytic converters. A typical SVE system consists of air pumps or blowers connected to a series of wells located in contaminated soil. The lower pressure inside the extraction well generated by pumps causes soil air to move to the well. Sometimes air injection wells are added for the further control of air flow.

VOC transport in convective and diffusive modes is considered as the main physical process. When there is an induced pressure gradient, the bulk phase of soil air moves and carries a large amount of VOCs in the convective transport mode. Especially in the close vicinity of wells and trenches, a large pressure gradient is developed and the convective transport dominates the movement of VOCs. At remote areas from wells, the pressure gradient becomes very small. VOC transport in this remote area is expected to be slow because of the diffusive transport. In addition to the convective and diffusive movements, VOC transport in soil air during SVE is expected to be influenced by other processes including the partition process among gas, liquid and solid soil matrices, and biological/chemical transformations. In this project, biological/chemical transformation processes of VOCs were not studied.

Soil Air Flow

The VOC concentrations in soil air are usually low and the changes in thermodynamic and transport properties of soil air due to the VOC concentrations are not significant. Therefore, air flow can be considered independent of the VOC concentration in soil air and treated explicitly from VOC transport. In cases where the property changes due to the high concentrations of VOCs in soil air are significant, iterative or updating procedures at each time step should be used to solve the coupled equations.

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Three basic equations are considered in the description of air flow, the mass balance equation of soil air, the flow velocity due to pressure gradients, and the equation of state. Detailed derivation of these equations is given in Massman (1989) and D.E. Wilson, *et al* (1987). The mass balance of soil air is expressed by the equation of continuity.

$$\phi_a \frac{\partial \rho_a}{\partial t} = - \nabla \rho_a V \qquad (4-1)$$

where the ϕ_a is the air filled porosity in soil, ρ_a is the density of soil air, and V is the velocity vector of air flow.

The air flow velocity due to pressure gradient can be expressed by Darcy's law when the slip flow is negligible. In the case of air flow in sand and gravel, the slippage of air on the soil wall is negligible (Massman, 1989) and Darcy's law for the flow in porous media can be applied.

$$V = - \frac{\kappa_a}{\mu_a} \nabla p \qquad (4-2)$$

where κ_a is the soil-air permeability tensor and μ_a is the viscosity of air.

The density of air is a function of the pressure and temperature. The relationship among these parameters is expressed by the equation of state. One of these equations of state is the ideal gas law, which is simple and applicable only for the gas at low pressure. The ideal gas law can be used because the operating pressure of the conventional SVE system is close to ambient or lower. The ideal gas law for soil air is

$$\rho_a = \frac{p \ MW}{R \ T} \qquad (4-3)$$

where MW is the molecular weight of soil air, R is the ideal gas law constant, and T is the absolute temperature.

By combining equations (4-1),(4-2), and (4-3), a general soil air flow equation can be obtained.

$$\phi_a \frac{\partial (\frac{MW}{R} \frac{p}{T})}{\partial t} = \nabla (\frac{\rho_a \kappa_a}{\mu_a} \nabla p) \qquad (4-4)$$

This air flow equation is nonlinear because the air density, ρ_a, in the right hand side of the equation is a function of pressure.

VOC Fate and Transport

VOCs can be present in the subsurface soil in five basic ways: (1) as a residual immiscible liquid phase in the soil pore spaces, (2) as a floating product above the water table in the case of light hydrocarbon and as a pooled or continuously migrating liquid of the dense nonaqueous phase moving continuously to the bottom of the ground-water, (3) as a vapor in soil air, (4) as dissolved components in soil pore water and ground-water, and (5) as adsorbed hydrocarbons on soil particles surfaces. When soil air remains undisturbed after spillage and infiltration to the subsurface, it becomes saturated by VOC vapors evaporated from the liquid phase. This highly saturated air will be removed initially after SVE starts. As vapors are purged from soil pores, the concentration of VOCs in soil air begins to decrease as the process shifts away from equilibrium. At this stage, the interfacial mass transfer between the liquid and flowing air is expected to control the removal of VOCs from soil. Flowing air in the SVE system moves much faster than the liquid phase inside soil pores. Therefore, the residual immiscible liquid, soil pore water, and solid particles are considered as immobile phases in model developments.

The following mathematical descriptions of the VOC movement in soil air are proposed. The convective transport by bulk air flow and diffusive transport due to the concentration gradient are the major transport processes. The mass flux of the VOC component A is

$$N_A = c_A V - \phi_a D \nabla c_A \qquad (4-5)$$

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where c_A is the concentration of the component A in soil air, V is the velocity vector of air flow, ϕ_a is the air filled porosity in soil, and D is the diffusivity.

The mass balance of the component A in soil air becomes

$$\phi_a \frac{\partial c_A}{\partial t} = -\nabla N_A + S_a$$
$$= -\nabla c_A V + \nabla \phi_a D \nabla c_A + S_a \qquad (4\text{-}6)$$

where S_a is the source/sink term of soil air.

The mass balance of the component A in the immobile phase becomes

$$\phi_I \frac{\partial C_A}{\partial t} = -S_I \qquad (4\text{-}7)$$

where ϕ_I is the pore volume occupied by the immobile phase, C_A is the concentration in the immobile phase, and S_I is the source/sink term for the immobile phase.

The source/sink terms both in the mass balance of component in soil air and the immiscible phase include the interfacial mass transfer and biological/chemical transformations. The interfacial mass transfer of VOCs from the immobile phase to flowing air in soil pores will be a source term of VOCs in soil air and a sink term of VOCs in the immobile phase. When soil pores contain static soil air, soil air is at equilibrium with the liquid phase. Equilibrium concentrations in both phases can be related by Raoult's law between nonaqueous liquid hydrocarbon and air. For the equilibrium between aqueous phase and air, Henry's law is used when the solubility of the VOC is low (Trowbridge and Malot, 1990). This equilibrium state of the VOC in soil pores is achieved when contacting time is sufficient or the interfacial mass transfer rate is very high. If the equilibrium cannot be maintained, the interfacial mass transfer rate is controlled by the diffusion within each phase.

Parameters

Several parameters are used in the description of the VOC movement and therefore are needed to obtain solutions of the air flow and VOC transport equations. Properties of soil and VOCs should be measured for the accurate design of the SVE operation on the specific site. Most thermodynamic and transport properties of VOC components in air can be obtained from reported data. These properties may change depending on the operating conditions of the SVE system. The property changes by operating conditions sometimes cause considerable variations in the efficiency of SVE. Thermodynamic and transport properties of VOCs in various conditions can be estimated from theoretical and empirical relationships.

Soil Air Permeability

The permeability of soil air with multiphase fluids, i.e. air, water and non-aqueous liquid, in soil pores is expressed by two terms, κ_{ra}, the relative permeability of air, and κ_i, the intrinsic permeability of soil.

$$\kappa_a = \kappa_{ra} \kappa_i \qquad (4\text{-}8)$$

The intrinsic permeability of soil is obtained from hydrogeological data during site characterization process. The relative permeability of air, κ_{ra}, is a function of the air saturation in soil pores (Parker $et\ al.$, 1987).

$$\kappa_{ra} = c\, s_a^{1/2} (1 - (1\text{-}s_a^{1/m}))^{2m} \qquad (4\text{-}9)$$

where m is a shape parameter of the soil water characteristic curve (van Genuchten, 1980), c is a correction factor for the gas slippage (Corey, 1986) and s_a is the air saturation, defined as the ratio of air filled porosity to total porosity. If the gas slippage effect is ignored, c = 1, then the relative permeability becomes solely a function of the air saturation, s_a.

Molecular Weight

The average molecular weight of air is 28.8 g/gmol. Considering all the components in soil air, the average molecular weight becomes

$$MW_a = \sum y_A MW_A \qquad (4\text{-}10)$$

where MW_A is the molecular weight of the component A and y_A is the mole fraction of the component A in soil air. In the conventional SVE application, concentrations of VOCs in soil air even in the saturated condition are so low that the average molecular weight of air can be used.

Viscosity of Gas Mixture

The viscosity of a gas mixture can be obtained from (Reid *et al*, 1977)

$$\mu = \sum \frac{y_A \, \mu_A}{\sum y_A \, \delta_{AB}} \qquad (4\text{-}11)$$

where

$$\delta_{AB} = \frac{[\, 1 + (\mu_A/\mu_B)^{1/2} (MW_A/MW_B)^{1/4}\,]^2}{[\, 8(1 + MW_A/MW_B)\,]^{1/2}}$$

Like the molecular weight of air, the average viscosity of air can be used for the SVE application.

Diffusivity in Gas Mixture

The molecular diffusion coefficient of a single component in a gas mixture can be obtained from the Stefan-Maxwell equation (Hirschfelder *et al.*, 1954). The diffusivity of component A in soil can be obtained from the tortuosity for wet soil (Bruell and Hoag, 1986). The tortuosity, τ, is defined as the ratio of $D/(D_A \phi_a)$, where D_A is the molecular diffusion coefficient in air, and has the relationship with porosities as follows:

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$$\tau = \phi_a^{2.34} / \phi^{2.0} \qquad \qquad (4\text{-}12)$$

where ϕ_a is the air-filled porosity and ϕ is the total porosity (Millington and Quirk, 1961).

Vapor Pressure and Aqueous Solubility

The vapor pressure of a pure component A at the given temperature can be obtained from Antoine's equation (Reid et al, 1977).

$$\ln (p_A^*) = \alpha - \frac{\beta}{\gamma + T} \qquad \qquad (4\text{-}13)$$

where p_A^* is the vapor pressure, T is the absolute temperature, and α, β, γ are constants for the VOC component A. The vapor pressure is very sensitive to the temperature.

The partial pressure of the component A in a gas mixture which is at equilibrium with a liquid mixture can be obtained from Raoult's law.

$$p_A = x_A p_A^* \qquad \qquad (4\text{-}14)$$

where the p_A^* is the vapor pressure of the pure component A at a given temperature and x_A is the mole fraction in liquid phase. Henry's law expresses the relation between the partial pressure and the aqueous phase concentration of a component which has a low solubility, like TCE and hydrocarbons in petroleum products. The Henry's law constant can be obtained from Gossett (1987).

$$H = \exp (\omega - \xi/T) \qquad \qquad (4\text{-}15)$$

where T is the absolute temperature, and ω and ξ are constants.

When immiscible liquid phases of mixed components exist, aqueous solubilities are complicated functions of compositions in immiscible phases and should be estimated from the thermodynamic correlations (i.e., UNIFAC, Reid et al.,1977).

Interfacial Mass Transfer

Two basic theories about interfacial mass transfer, the film theory and the penetration theory, have been widely accepted. The film theory assumes instant equilibrium between the contacting phases and concludes that the mass transfer coefficient is proportional to the diffusivity (Skelland, 1974). The penetration theory assumes a finite contacting time between two phases and shows that the mass transfer coefficient is proportional to the square root of the diffusivity (Skelland, 1974). Estimated values of interfacial mass transfer coefficients from both theories showes little difference (Skelland, 1974).

One of the empirical correlations for the interfacial mass transfer between immiscible phases is the first order kinetics expression. In this model, the rate of mass exchange between immiscible phases is expressed by the mass transfer potential and the mass transfer coefficient. The difference of the concentration at equilibrium and the actual concentration in the main body is defined as the mass transfer potential. The mass transfer rate is expressed as

$$n_A = K_G(c_A^* - c_A) \qquad (4\text{-}16)$$

where c_A^* is the concentration of A at equilibrium, c_A is the actual concentration in the main body of fluid, and K_G is the mass transfer coefficient (Bird et al., 1960). The mass transfer coefficient, K_G, is expected to be a function of Reynolds' number, Schmidt's number, and the air saturation, θ_a, which is the ratio of the air filled porosity to the total porosity of soil.

$$K_G = K_G(Re, Sc, \theta_a) \qquad (4\text{-}17)$$

Reynolds' number of soil air, Re, is given by

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$$Re = \frac{V \rho_a \, d_p}{\mu_a} \qquad\qquad (4\text{-}18)$$

where V is the air flow velocity and d_p is a characteristic length (i.e. particle diameter, diameter of residual blobs). Schmidt's number, Sc, is another dimensionless term, which is

$$Sc = \frac{\mu_a}{\rho_a \, D_A} \qquad\qquad (4\text{-}19)$$

where D_A is the diffusion coefficient of the component A in soil air.

SECTION 5

EFFECT OF PARAMETERS `

Analytical solutions in one-dimensional systems have been obtained for the soil air flow and contaminant transport equations under simplifying assumptions and were applied for the analysis of soil column operations. Effects of parameters on the VOC movement were studied through simulations and comparisons with soil column experiments.

One-Dimensional Solutions

Air Flow

At steady state with a constant permeability and viscosity of soil air, the mass balance equation of soil air, equation (4-4), becomes

$$\nabla(\rho_a \nabla p) = 0 \qquad\qquad (5\text{-}1)$$

Substitution of the density with an averaged value made the above equation a linearized Laplace equation.

$$\nabla^2 p = 0 \qquad\qquad (5\text{-}2)$$

When the ideal gas law is used in place of density, the equation becomes a nonlinear partial differential equation.

$$\nabla (p \nabla p) = 0 \qquad\qquad (5\text{-}3)$$

In the one-dimensional coordinate system, these equations become

$$\frac{\partial^2 p}{\partial x^2} = 0 \qquad (5\text{-}4)$$

for the linearized equation and

$$\frac{\partial^2 (p^2)}{\partial x^2} = 0 \qquad (5\text{-}5)$$

for the nonlinear equation. Applicable boundary conditions are as follows;

$$p = p_{in} \text{ at } x=0 \qquad (5\text{-}6a)$$

$$p = p_{out} \text{ at } x=L \qquad (5\text{-}6b)$$

The pressure distribution obtained from the linearized equation is

$$p = p_{in} + (p_{in} - p_{out}) \frac{x}{L} \qquad (5\text{-}7)$$

and from the nonlinear equation is

$$p = \sqrt{p_{in}^2 + (p_{out}^2 - p_{in}^2) \frac{x}{L}} \qquad (5\text{-}8)$$

From Darcy's law for the fluid flow in porous media, the air flow velocity obtained from equation (5-7) is

$$V_x = \frac{\kappa_a}{\mu_a} \frac{p_{in} - p_{out}}{L} \qquad (5\text{-}9)$$

and from the nonlinear equation, it is

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$$V_x = \frac{\kappa_a}{2\mu_a L} \frac{(p_{in}^2 - p_{out}^2)}{\sqrt{p_{in}^2 + (p_{out}^2 - p_{in}^2)\frac{x}{L}}}$$

(5-10)

The air flow velocity is a function of location when the nonlinear equation is used. It has a constant value when the linearized equation is used.

Transport of Component

The mass balance equation of the component A in soil air without any transformations due to biochemical/chemical reactions in one-dimensional coordinate system becomes

$$\phi_a \frac{\partial c_A}{\partial t} = -V_x \frac{\partial c_A}{\partial x} + \phi_a D \frac{\partial^2 c_A}{\partial x^2} + K_G(c_A^* - c_A)$$

(5-11)

with the initial condition

$$c_A = c_{Ao} \text{ at } t=t_o$$

(5-12a)

and boundary conditions

$$c_A = 0 \text{ for } x=0, \text{ clean air entrance}$$

(5-12b)

$$\frac{\partial c_A}{\partial x} = 0 \text{ for } x = L, \text{ no concentration gradient}$$

(5-12c)

The following conditions are assumed to obtain the one-dimensional solution. A constant tortuosity and air saturation values are assumed, neglecting the fact that VOCs and water are continuously evaporated as air flows through soil pores. The pressure drop through the soil column is negligible and the air flow velocity is assumed to be constant through the column, as equation (5-9), and remains unchanged through the experiment. The vapor pressures of VOCs remain constant through the

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experimental period until all the separate phase liquid evaporates. The temperature is constant, neglecting the heat of evaporation. Then the transport equation of component A in gas phase can be rewritten as follows.

$$\frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2} - V \frac{\partial c_A}{\partial x} + \alpha - \beta c_A \qquad (5\text{-}13)$$

where $V = V_x/\phi_a$, $\alpha = \dfrac{K_G \, c_A^*}{\phi_a}$, and $\beta = \dfrac{K_G}{\phi_a}$. The analytical solution of this equation can be obtained from the dispersion-convection equation with zeroth-order production and first-order decay terms. The analytical solution is (van Genuchten and Alves, 1982)

$$c_A(x,t) = \frac{\alpha}{\beta} + (c_{Ao} - \frac{\alpha}{\beta}) A(x,t) - \frac{\alpha}{\beta} B(x,t) \qquad (5\text{-}14)$$

where

$$A(x,t) = \exp(-\beta t)\{1 - 1/2 \, \text{erfc}(\frac{x - Vt}{2(Dt)^{0.5}})$$

$$-1/2 \exp(Vx/D) \, \text{erfc}(\frac{x + Vt}{2(Dt)^{0.5}})$$

$$-1/2 \, [2 + \frac{V(2L - x)}{D} + \frac{V^2 t}{D}] \exp(VL/D) \, \text{erfc}(\frac{2L - x + Vt}{2(Dt)^{0.5}})$$

$$+ (\frac{V^2 t}{\pi \, D})^{0.5} \exp(\frac{VL}{D} - \frac{1}{4Dt}(2L - x + Vt)^2)\}$$

$$B(x,t) = B_3(x,t) \, / \, B_4(x)$$

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$$B_3(x,t) = \frac{1}{2} \exp(\frac{(V-U)x}{2D}) \operatorname{erfc}(\frac{x - Ut}{2(Dt)^{0.5}})$$

$$+ \frac{1}{2} \exp(\frac{(V+U)x}{2D}) \operatorname{erfc}(\frac{x + Ut}{2(Dt)^{0.5}})$$

$$+ \frac{(U-V)}{2(U+V)} \exp(\frac{(V+U)x - 2UL}{2D}) \operatorname{erfc}(\frac{2L - x - Ut}{2(Dt)^{0.5}})$$

$$+ \frac{(U-V)}{2(U+V)} \exp(\frac{(V-U)x - 2UL}{2D}) \operatorname{erfc}(\frac{2L - x + Ut}{2(Dt)^{0.5}})$$

$$- \frac{V^2}{2\beta t} \exp(\frac{VL}{D} - \beta t) \operatorname{erfc}(\frac{2L - x + Ut}{2(Dt)^{0.5}})$$

$$B_4(x) = 1 + (\frac{U-V}{U+V}) \exp(-UL/D)$$

and

$$U = V (1 + \frac{4\beta D}{V^2})^{1/2}$$

The mass balance of component A in the immobile phase is

$$\phi_I \frac{\partial C_A}{\partial t} = - K_G (c_A^* - c_A) \tag{5-15}$$

with the initial condition

$$C_A = C_{Ao} \text{ at } t = t_o, \quad 0 \le x \le L \tag{5-16}$$

The analytical solution for this equation can be obtained by the integration of the right hand side from $t=t_0$ to the time t at the location x.

$$C_A(x,t) = C_{Ao} - \frac{K_G}{\phi_l} \int_{t_o}^{t} (\dot{c}_A - c_A)\, dt \qquad (5\text{-}17)$$

where c_A is from equation (5-14).

Analysis of SVE Processes

Density Effects

The pressure distribution varies with location inside soil columns, but is not a function of the air permeability at steady state. The pressure and corresponding velocity distributions obtained from the linearized and nonlinear equations are in Figures 5-1 and 5-2. Figure 5-1 shows a small difference between calculated pressures from the linearized and nonlinear equations. The maximum difference is about 20% when the ratio of the inlet pressure, p_{in}, and the outlet pressure, p_{out}, is 0.6. But the corresponding air flow velocity in Figure 5-2 shows a large difference between calculated values from the linearized and nonlinear equations. When the pressure ratio is 0.9, the maximum difference is about 10 %, and it is about 70 % at the location of the lowest pressure when the pressure ratio is 0.6. The error in the air flow velocity calculated from two equations generates errors in the estimation of the convective movement term in the transport equation. Therefore, one should be very careful when the linearized equation is used.

Air Porosity

The air porosity has significant effects on air flow and VOC transport. The relative permeability of soil air is a function of the air saturation as shown in equation (4-5). If the liquid saturation, including the water and immiscible nonaqueous phases, is high, then the relative permeability becomes so small that a large pressure drop is expected. The relative permeability with respect to water saturation in clay soil is plotted in Figure 5-3. The effect of air porosity on VOC transport impacts the diffusivity

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through equation (4-12), so does the interfacial mass transfer from the immobile phase to the air flow through equation (4-17). The liquid saturation also is considered to determine the effective interfacial area for the mass transfer. As the liquid saturation increases above the residual saturation, the mass transfer coefficient is expected to increase due to the increased interfacial area between contacting phases. After passing the maximum point, the interfacial area decreases, and so does the mass transfer coefficient. The change of contacting area is considered to be a complicated function of the hydrogeometry inside soil pores (Hunt et al., 1988), and is expected to vary continuously as the removal process of VOCs and soil water continues. Additional efforts should be made in this area of research. Systematic studies in the laboratory and field should be conducted to gain better knowledge of the process.

Soil Column Experiments

Soil column experiments reported by AWARE, Inc. (1987) were used for additional analyses of the SVE process with the mathematical model. Trichloroethylene (TCE) was used in column experiments of four separate runs with two different types of soil, the New Jersey Cohansey sand and the Tennessee Loess soil. New Jersey sand was used in experiments 1 and 2, and Tennessee soil was used in experiments 3 and 4. Each experiment was spiked with a different amount of TCE. Experimental conditions and properties of soil and chemicals are listed in Tables 5-1 and 5-2.

In experiment 1, TCE amounting to 8 times more than the solubility limit of the water content inside the column was applied. The existence of free pure TCE could be assumed. The flow rate at the outlet was 0.14 cm/min, which was the average value maintained during the experiment. At this flow rate, the pressure drop was negligible because of the low moisture content inside soil. The mass transfer coefficients were assigned to fit the experimental observations by means of the least square optimization method. Plots of calculated removal rates and measured values are in Figure 5-4. After the high initial removal rate because of the saturated condition in soil air, the removal rate reached a steady state in a short time. This steady state was maintained for about 400 days, then the removal rate dropped sharply when the TCE concentration fell below its solubility in water. The effluent concentration and removal rate continuously decreased until all TCE disappeared from the soil column. One check on the numerical technique is the calculation of the conservation of mass. Normally, a small amount of mass is either generated or destroyed due to numerical truncation in the mathematical algorithms. To check these

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calculations, mass balance was calculated at day 400. The total amount removed was calculated to be 98 % and the calculated remaining in the soil column was 4 % of initial mass which suggests a 2 % error in mass balance. In the AWARE, Inc.'s report, a large mass balance error could be found, which is suspected to be caused by poorly maintained analytical procedures.

The operating condition of experiment 2 was the same as that of experiment 1, except for the different applied concentration of TCE. TCE saturated water solution was spiked on the soil column in experiment 2. Therefore, the driving potential for the interfacial mass transfer continuously decreased as the operation continued because the concentration in the water solution continuously decreased. The removal rate never reached the steady state, but decreased continuously until all of the TCE in soil disappeared (Figure 5-5). The maintained air flow rate in the column was 0.155 cm/min. With this air flow rate, the pressure drop through the soil column was negligible.

Soil columns for experiments 3 and 4 had a different soil type which had less permeability than that used in experiments 1 and 2. The initial water contents were greater than in previous runs. The initial amount of TCE in column of experiment 3 was above the solubility limit and TCE existed in a pure product form. The removal rate reached a steady state in a short time after air started to flow (Figure 5-6). The total clean-up time was shorter than that of experiment 1 due to the small initial TCE amount. In 150 days, the removed mass of TCE reached 97% of the initial mass. The mass balance error was 3%.

The column in experiment 4 was almost saturated by water and the required pressure drop was calculated as almost 0.5 atm. over a one foot column to maintain the air flow rate at 0.177 cm/min. This large pressure drop is impractical in a field operation. The initial TCE was in a saturated water solution, and the operation never reached the steady state (Figure 5-7).

All of the mass transfer coefficients were adjusted to fit the experimental data. The values of the mass transfer coefficients for experiments 3 and 4 were different from those of experiments 1 and 2, where different types of soil have been used. Even though some difference existed among the adjusted values, the empirical relationships like the ones in the chemical engineering literature could not be derived mainly due to the lack of experimental data.

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Temperature Effect on the Removal Efficiency

To investigate the temperature effect on the performance of the SVE process, soil column experiment 1 reported by Aware, Inc.(1987) was simulated at different temperatures. Thermodynamic and transport properties of TCE at several temperatures are enlisted in Table 5-3. The mass transfer coefficients were calculated from the penetration theory of the interfacial mass transfer.

In comparing property changes at different temperatures in Table 5-3, the largest differences are found in vapor pressures. At a 15 $^\circ$C increase of temperature in ambient condition, the vapor pressure becomes doubled. The major contributing factor on the performance of the SVE process is the vapor pressure. Figure 5-8 shows that the removal rate can be doubled when the operating temperature increases 15°C. It may be worthwhile to consider increased temperature operation.

TABLE 5-1. Characteristics of Soil Columns

Properties	Run1	Run2	Run3	Run4
[a]Intrinsic Permeability($cm^2 \times 10^7$)	4.34	4.34	1.09	1.09
[a]Soil Particle Density (g/cm^3)	2.68	2.68	2.66	2.66
[a]Soil Bulk Density (g/cm^3)	1.46	1.45	1.43	1.43
[b]Initial Water Content (%)	4.1	17.4	10.2	24.4
[b]Initial VOC Content ($\mu g/g$ soil)	8850	15	4010	4.2
[b]Initial Amount of Soil (g)	2600	2680	2600	2470
[b]Diameter of Soil Column (cm)	6.35	6.35	6.35	6.35
[c]Pressure at Exit (Kpa)	101	101	101	63
[c]Mass Trans. Co. K_G($sec^{-1} \times 10^7$)	8.9	8.75	1.27	1.75

a: estimated values

b: Aware, Inc. (1987)

c: adjusted values to fit the experimental result

TABLE 5-2. Chemical Properties and Operating Conditions

[a]Molecular Weight of TCE	131.4
[a]TCE Liquid Density(g/cm^3)	1.46
[a]Diffusivity (cm^2/sec)	8.0x10^{-2}
[a]Vapor Pressure (Kpa)	7.73
[a]Aqueous Solubility(g/cm^3)	1.1x10^{-3}
[a]Henry's Law Constant (Kpa/(gmol/cm^3))	7.14x10^3
[a]Viscosity of Air at 20°C (cp)	0.01846
[b]Initial Pressure inside column (Kpa)	101.3
[b]Entering Air Pressure (Kpa)	101.3
[b]Mole Fraction of TCE in Entering Air	0.0
[b]Temperature ($^\circ$K)	293

a: Chemical Engineers' Handbook (1973)

b: Aware Inc. (1987)

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TABLE 5-3. Properties of TCE at Various Temperatures

Temperature	Diffusivity[a]	Viscosity[b]	Vapor Pres.[c]	Henry's Law[d]	K_G[e]
^oK	(cm^2/sec)	cp	Kpa	$Kpa/(g/cm^3)$	(cm/sec)
278	7.30×10^{-2}	1.75×10^{-2}	3.57	2.98×10^3	8.12×10^{-7}
293	8.00×10^{-2}	1.85×10^{-2}	7.75	7.22×10^3	8.90×10^{-7}
308	8.73×10^{-2}	1.92×10^{-2}	1.54	1.60×10^4	9.70×10^{-7}

a: Reid et al. (1977)

b: Reid et al. (1977)

c: equation (4-13)
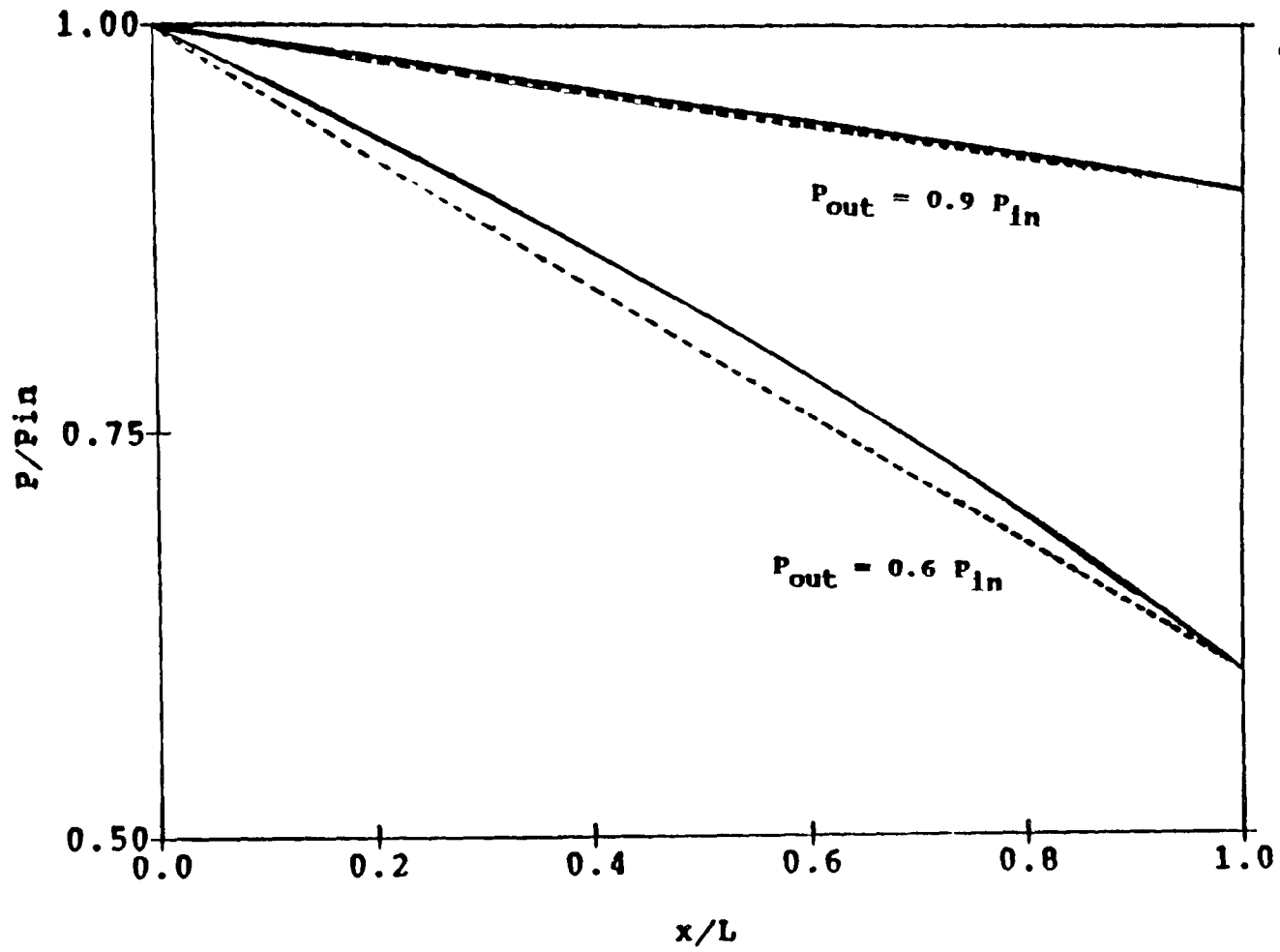
d: equation (4-15)

e: $K_G \propto D^{1/2}$

Figure 5-1. Pressure distribution inside soil column
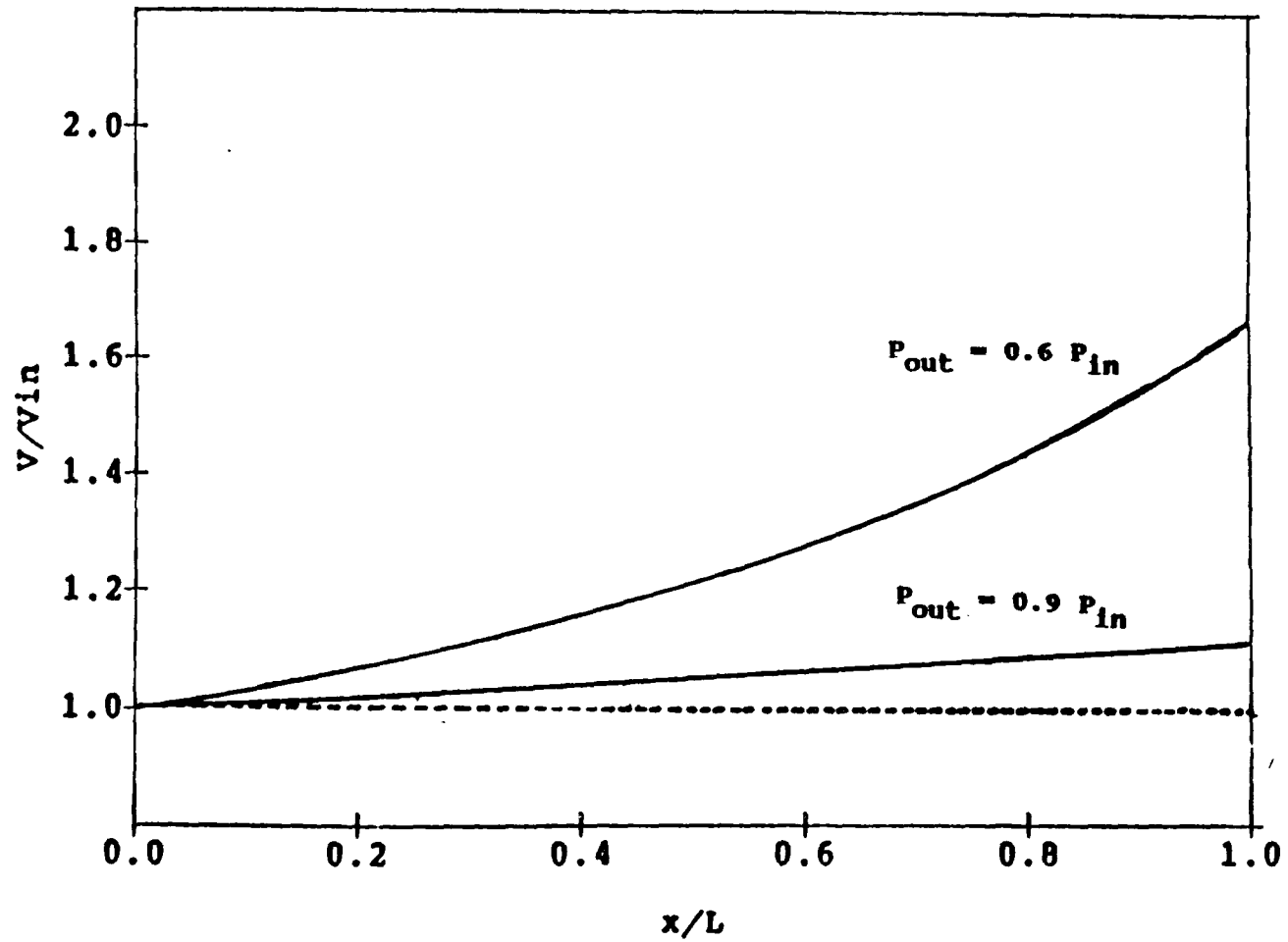—— Calculated from nonlinear equation
--- Calculated from linear equation

Figure 5-2. Air velocity distribution inside soil column
—— Calculated from nonlinear equation
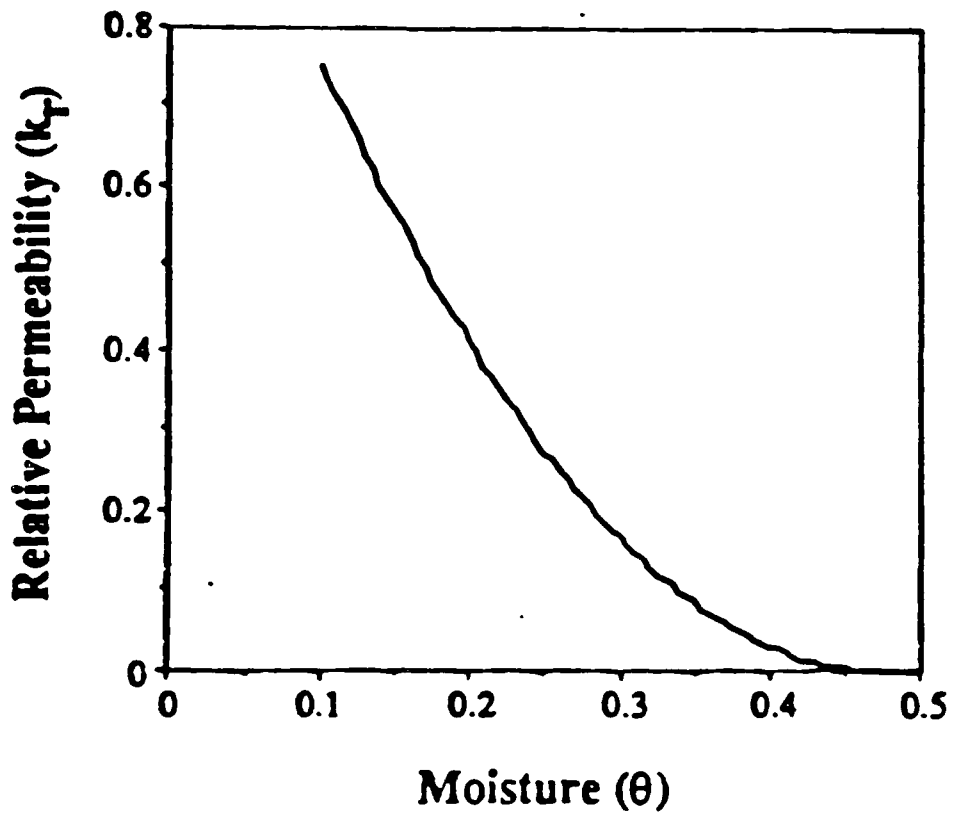— Calculated from linear equation

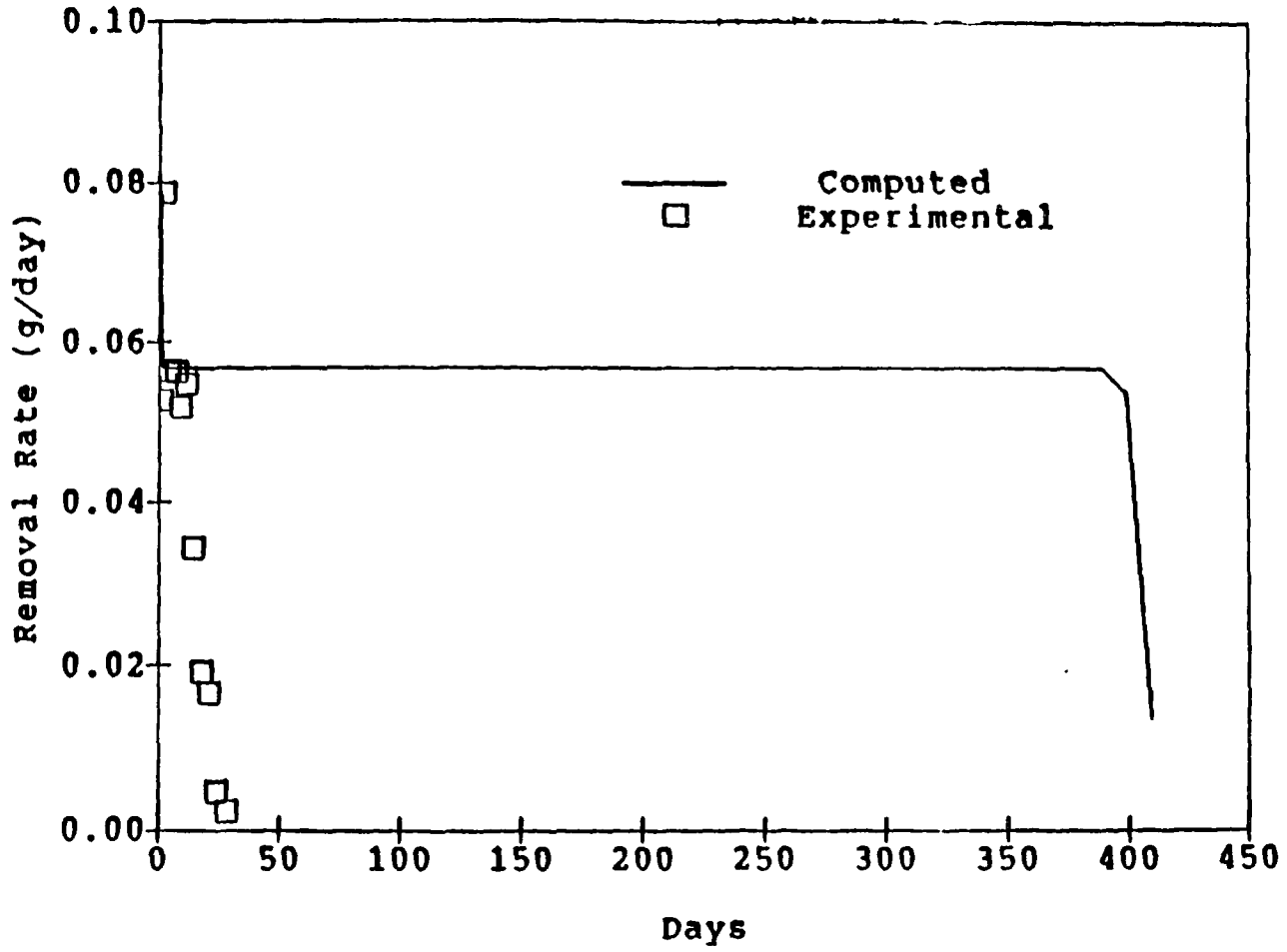Figure 5-3. Relative permeability of soil air with moisture content inside clay soil

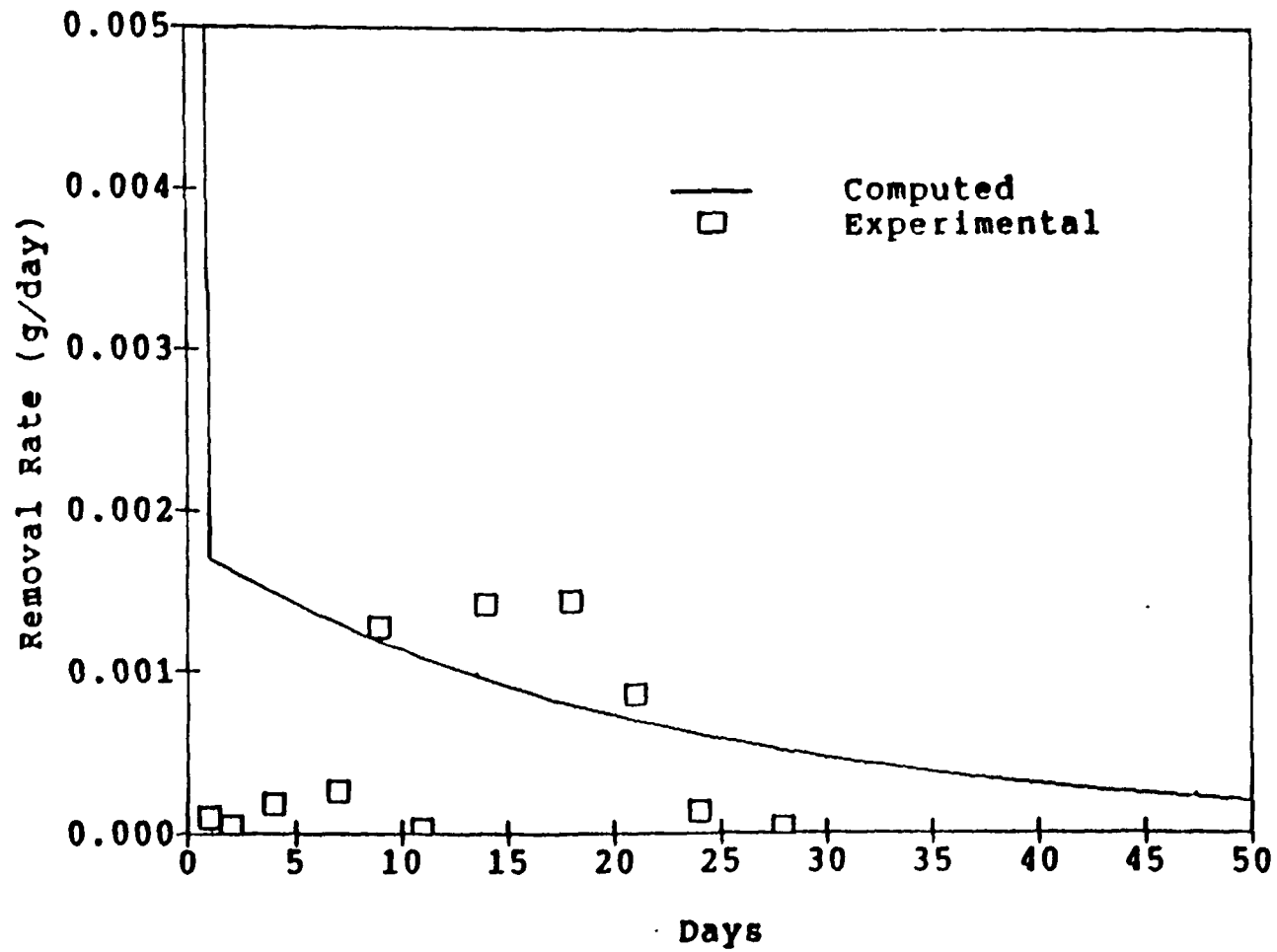Figure 5-4. Removal rate from soil column, experiment 1
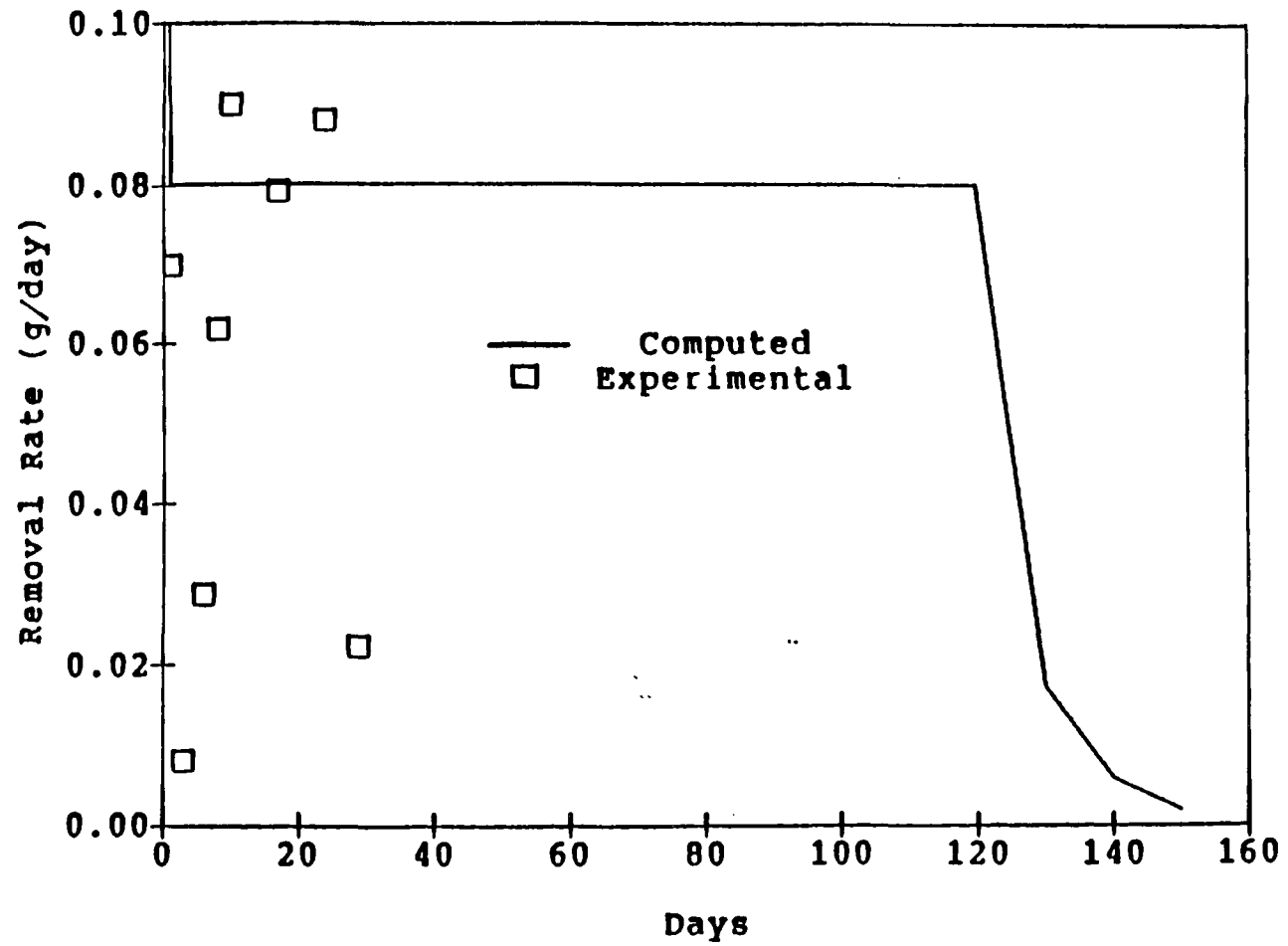
Figure 5-5. Removal rate from soil column, experiment 2
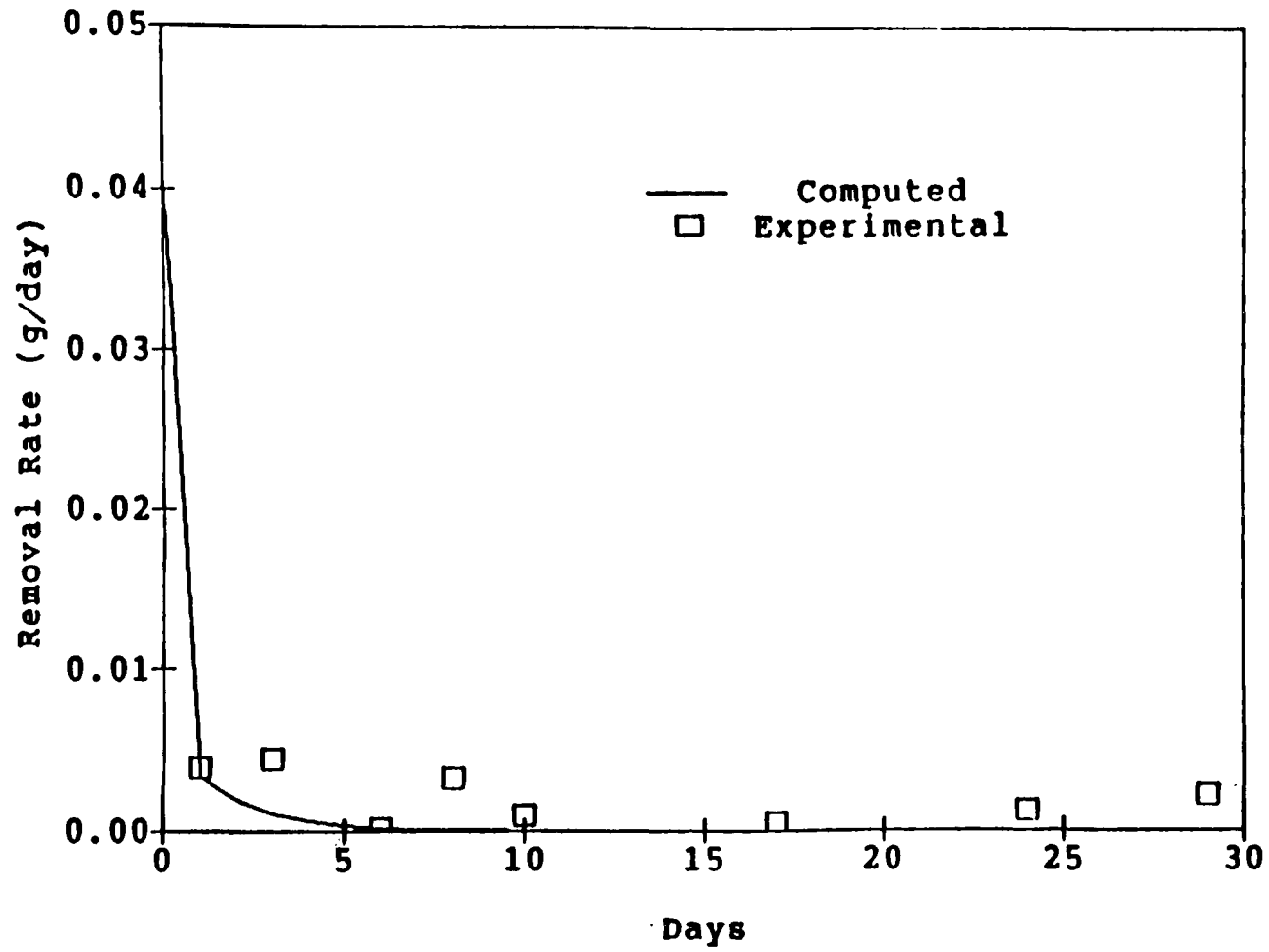
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Figure 5-6.   Removal rate from soil column, experiment 3

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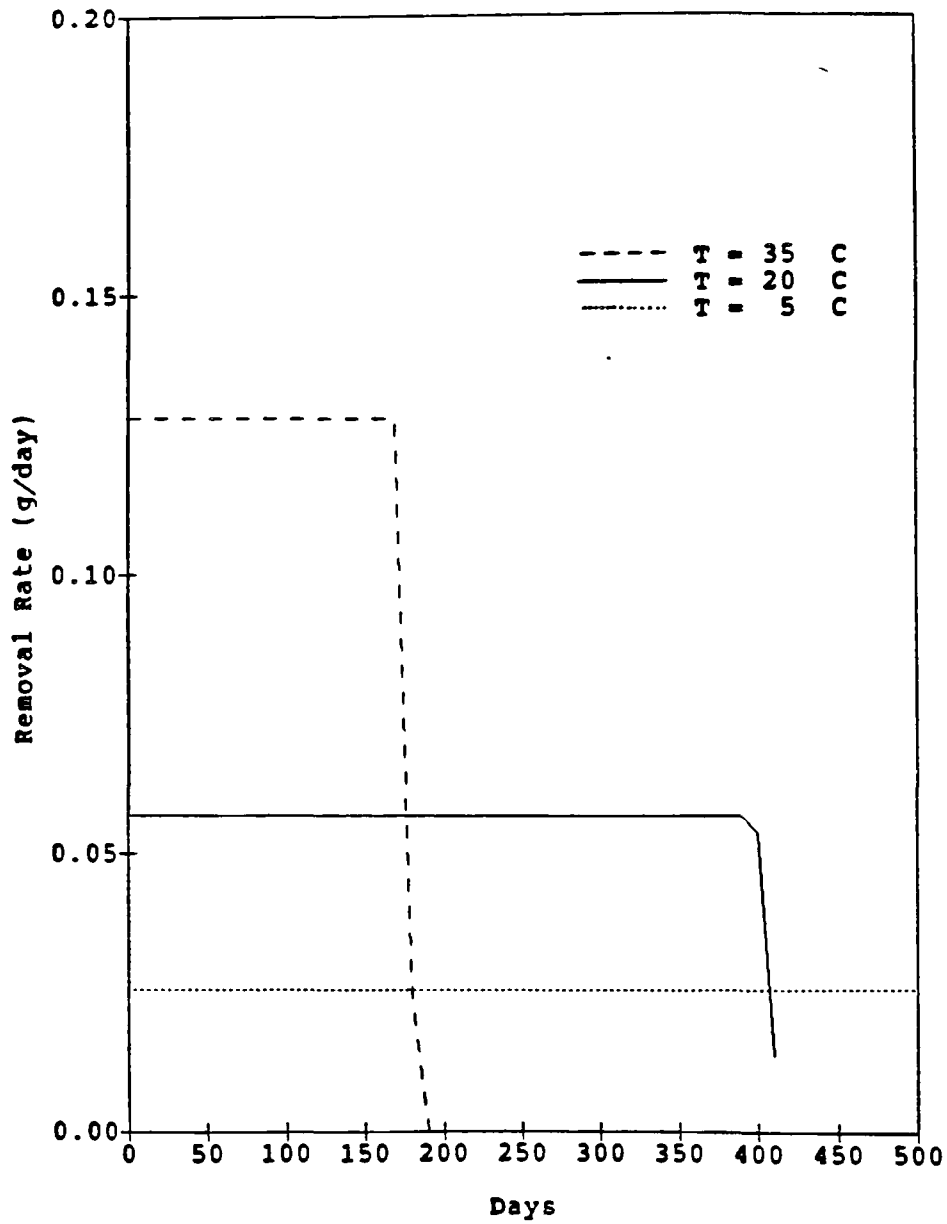Figure 5-7. Removal rate from soil column, experiment 4

Figure 5-8. Removal rates at different operating temperatures

SECTION 6
VOC REMOVAL RATE MEASUREMENTS

One of the major controlling processes in SVE is the partitioning among gas, liquid and solid soil phases. Usually, local equilibrium is assumed between flowing air and less mobile liquid /solid phases (Pfannkuch, 1984). When convective movement dominates the transport of contaminant and its rate is fast, the local equilibrium assumption is not accurate and a kinetics model seems to be more proper in description of sorption processes (Cho and Jaffe, 1988). Several physical and chemical properties of soil and contaminants will affect the interfacial mass transfer rate. Experimental investigations of two parameters, the air flow rate and the liquid distribution including the nonaqueous phase liquid and water, on the removal rate of VOCs from soil pores are presented.

Soil Column Experiments

Nine soil columns made of 2 inch, Schedule 80, PVC pipe were used. Each column had a soil packed section 28 to 30 cm long and two additional empty sections with a cap on each end. Brass fittings were attached on the top and bottom sections of the columns. Both 1/4 inch I.D. plastic and copper tubings were used. Plastic tubings were used in the place where VOCs did not come in contact. The Oil-Creek sand was packed in the columns. The sand was white-colored, and uniformly sized with a very small amount of organic content on surface. These columns were set up in a constant temperature room.

Pure toluene was used as the VOC in the vacuum extraction experiment in soil columns. The properties of pure toluene are listed in Tables 5-2 and 5-3. Pure toluene was applied on the top of the soil packed section of the column drop by drop through a hypodermic syringe to minimize the disturbance of soil packing. The same method was used for water application for the control of water content. After application of each liquid, a 24 hour equilibrium period was set to achieve uniform distributions of each liquid.

The air flow rate was monitored with a rotameter and adjusted as necessary with two needle valves. The vacuum pressure and the pressure drop through the column were measured with manometers. An in-house vacuum line was attached to the column for the vacuum source. The vacuum pressure and corresponding air flow rate fluctuated about 10 % from the set point. Air was saturated with moisture by passing through water baths before entering columns to minimize the water content change in the soil. A schematic diagram of the column is in Figure 6-1.

Samples of effluent air from each column were taken directly by a gas-tight chromatograph syringe and injected into an HP 5840A gas chromatograph equipped with an FID. A 6 ft, 1/4 inch O.D. custom packed stainless steel column (Supelco, EPA method 602) was used for analysis of toluene concentration in air. Nitrogen served as the carrier gas at a flow rate of 36 ml/min. The injector and FID temperatures were set at $110^{\circ}C$ and $150^{\circ}C$, respectively. The column oven temperature was fixed at $90^{\circ}C$. A specialty gas mixture (blend 3, Scott Specialty Gas) was used as a standard for calibration.

Results and Discussions

Two major parameters investigated in this experiment were the air flow rate and liquid phase contents of the immiscible nonaqueous VOCs and water in soil. In Figures 6-2 to 6-5, toluene concentrations in the effluent air from columns are plotted. The effluent concentration decreased as the time passed even in the case where only pure toluene was applied (Figure 6-2). This decrease of effluent concentration suggests that the interfacial mass transfer is a function of residual liquid contents inside soil pores. Also these decreasing rates of effluent concentrations varied with respect to the air flow rate. At a lower flow rate, the effluent concentration change was slower than at the higher air flow rate. These trends were maintained through different water content and distributions inside the soil columns (Figures 6-2 through 6-5). To verify the effect of VOCs and water distribution effects on the removal, the effluent concentration changes at different initial liquid conditions are plotted in Figures 6-6 through 6-8. Through the entire experiments, the amount of toluene in each column was far above the water solubility limit and therefore toluene existed as an immiscible nonaqueous liquid. The vapor pressure was expected to be that of pure toluene. Even with those facts, the effluent rate was affected seriously by the water content in the soil. In Figures 6-6 and 6-7, the increased water content shows a serious reduction of removal rate at the same air flow. This phenomenon indicates decreased effects of water contents at the higher air flow rate and this may be due to the entrapment of residual VOCs inside soil pores by water and thereby

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reducing the contacting area between the air and immiscible liquid phase. However, this could not be verified (Figure 6-8).

Even though the air flow rate and the liquid distribution of VOCs and water were distinctive parameters verified through these experiments, it was not possible to obtain quantitative correlations among them. The main reason was that throughout these experiments, mass balance checks of VOCs and water could not be performed. Another problem found during the experiments was redistribution of VOCs and water inside soil columns. It was detected that liquids, including toluene and water moved upward as air flowed up from the bottom of the column and accumulated in the upper part of the soil packed section of column. Redistribution of liquids and experimental results suggest the necessity for a new design of soil column and experimental procedures which include the control and measurement of liquid content changes.

Removal Rate Model

A similarity of physics involved in the moisture removal from wet solid by dry air and the VOC removal from soil pores by uncontaminated air suggests the same conceptual model for mass removal. A two-period model was developed for the moisture removal from wet solid (Chemical Engineers' Handbook, 1973). The model consists of the constant rate period and the falling period. The constant rate period is at the first stage of the drying process in which the moisture removal rate remains constant and is mainly controlled by external factors like air flow, temperature, and the moisture content in the air (line BC in Figure 6-9).

The falling rate period represents the second stage of the removal process in which the removal rate decreases as the moisture content reduces after a critical point (line CD in Figure 6-9). In this stage, the moisture removal rate is controlled by internal factors such as the liquid diffusion, the capillary flow of liquid, or the flow by shrinkage of solid. The capillary movement of liquid water due to the change of the suction potential by evaporation of moisture inside pores is expected to control the drying rate of sand soil or granular materials by air flowing through pores. The moisture removal rate is approximated by first order kinetics.

The removal rate of VOCs can be expressed with the same concepts of physical process. During the first stage after air flow begins, the removal rate of VOCs from soil pores remains constant until the VOC content is reduced to a critical value.

$$\phi_l \frac{\partial C_A}{\partial t} = -S_1 \text{ when } C_A \le C_c \text{(critical amount)} \qquad (6\text{-}1)$$

At the second stage, after the critical point of the VOC content has been reached, the removal rate decreases as the VOC content decreases. It is expressed by a first order kinetics model.

$$\phi_l \frac{\partial C_A}{\partial t} = K_1 (C_A - C_{A,e}) \text{ when } C_c \le C_A \le C_e \qquad (6\text{-}2)$$

where $K_1 = \dfrac{-S_1}{(C_{A,c} - C_{A,e})}$, and $C_{A,e}$ = obtainable lowest amount of the VOC content under the given operating conditions.

The solution of equation (6-2) for the falling rate period can be obtained.

$$t = \frac{(C_{A,c} - C_{A,e})}{-S_1} \ln \frac{(C_{A,c} - C_{A,e})}{(C_A - C_{A,e})} \qquad (6\text{-}3)$$

The semilogarithmic plot of $\dfrac{(C_{A,c} - C_{A,e})}{(C_A - C_{A,e})}$ vs. t should give a straight line and the slope of the curve is related to the constant rate. The constant rate S_1, and the coefficient, K_1, are expected to be complex functions of the liquid saturation, θ_l and various operating conditions.

$$K_1 = K_1 (Re, Sc, \theta_l) \qquad (6\text{-}4)$$

$$\theta_l = 1 - \theta_a \qquad\qquad (6\text{-}5)$$

The mass transfer coefficient in equation (4-17) is a function of K_1 as

$$K_G = K_G (Re, Sc, K_1) \qquad\qquad (6\text{-}6)$$
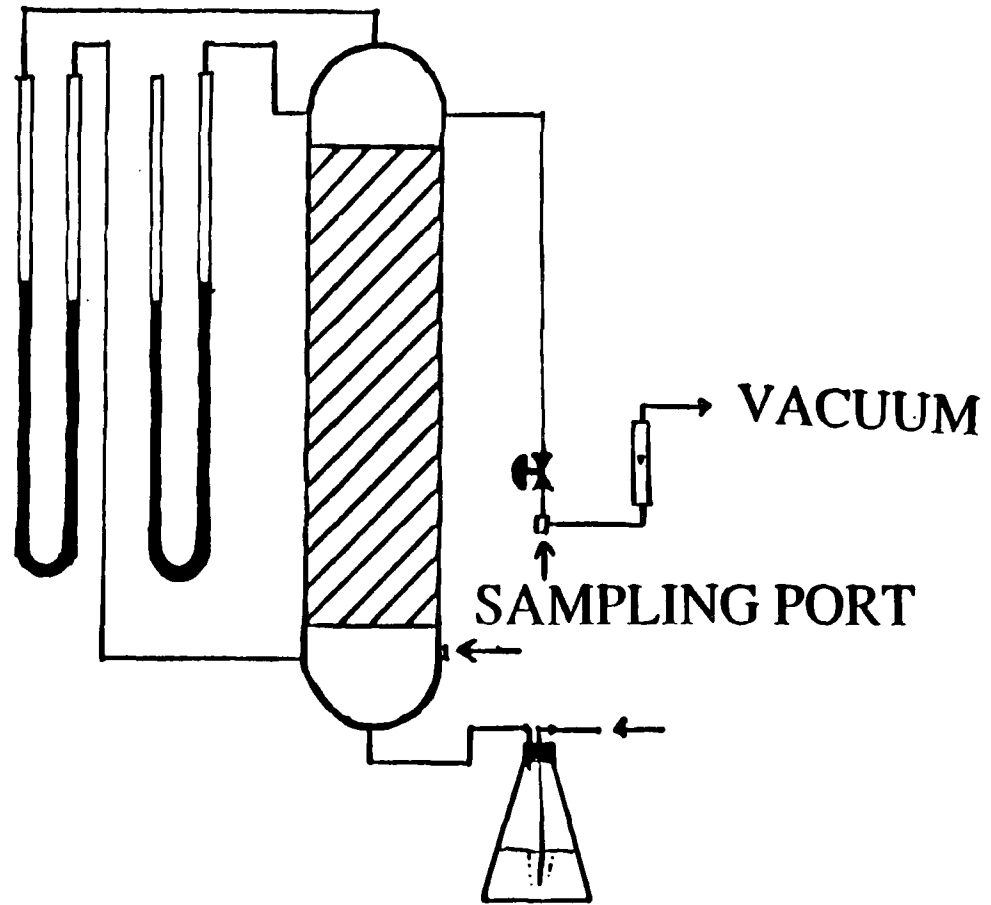
VACUUM

SAMPLING PORT

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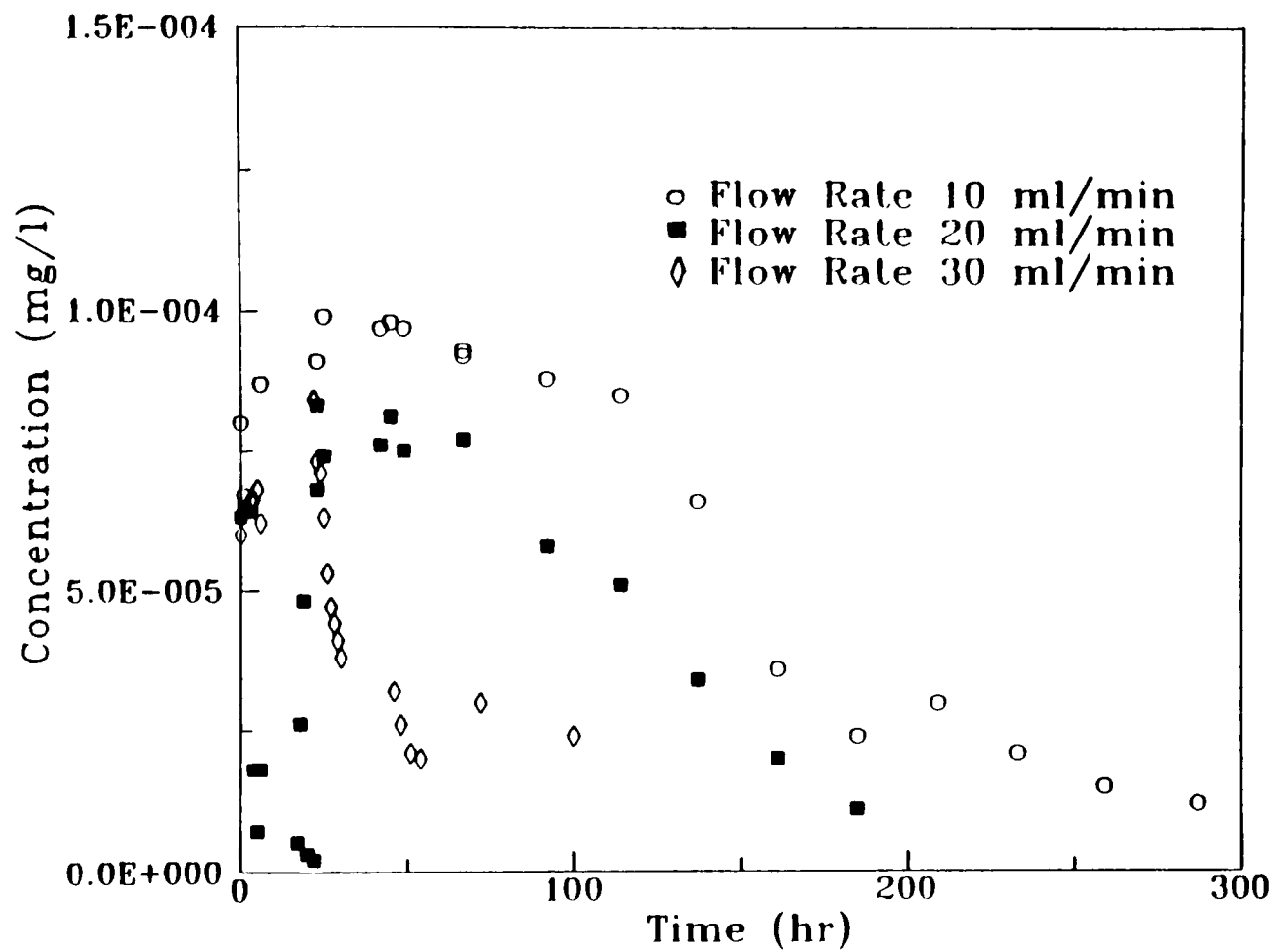Figure 6-1.   Schematic diagram of soil column experiment

Figure 6-2.   Toluene concentration in effluent air from soil column
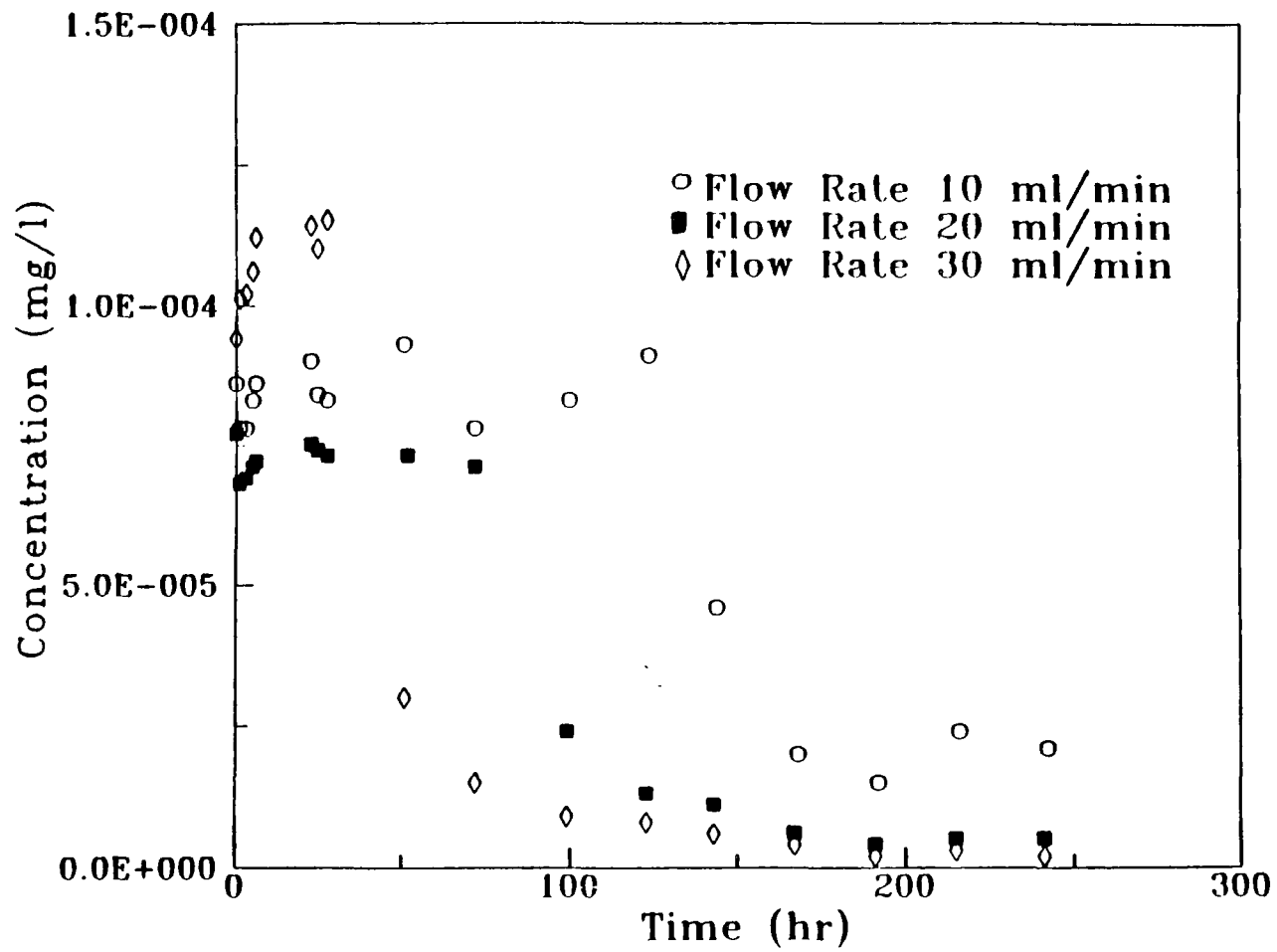20 ml of pure toluene

Figure 6-3. Toluene concentration in effluent air from soil column
10 ml pure toluene following 10 ml water
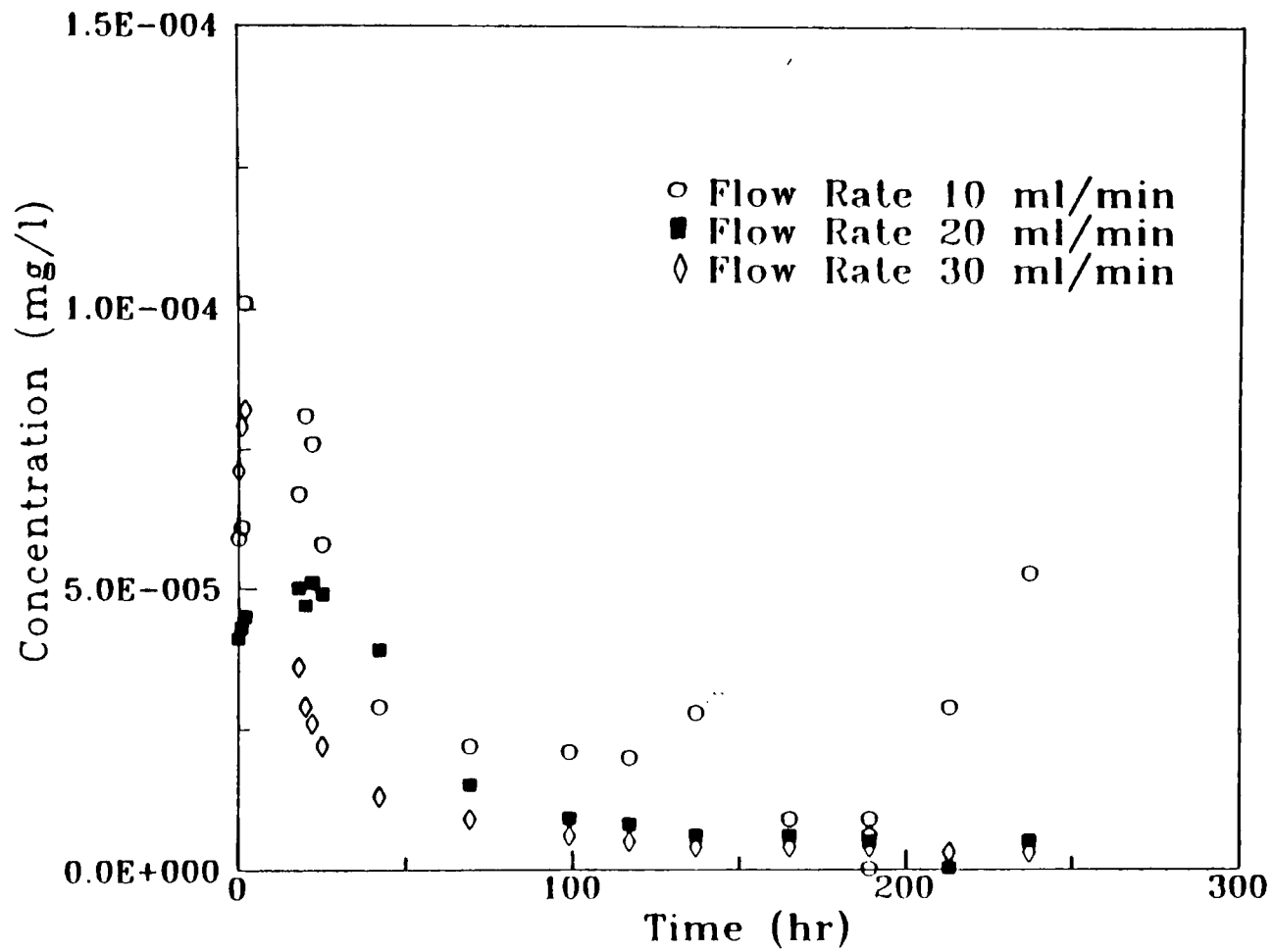
Figure 6-4. Toluene concentration in effluent air from soil column
10 ml water following 10 ml toluene
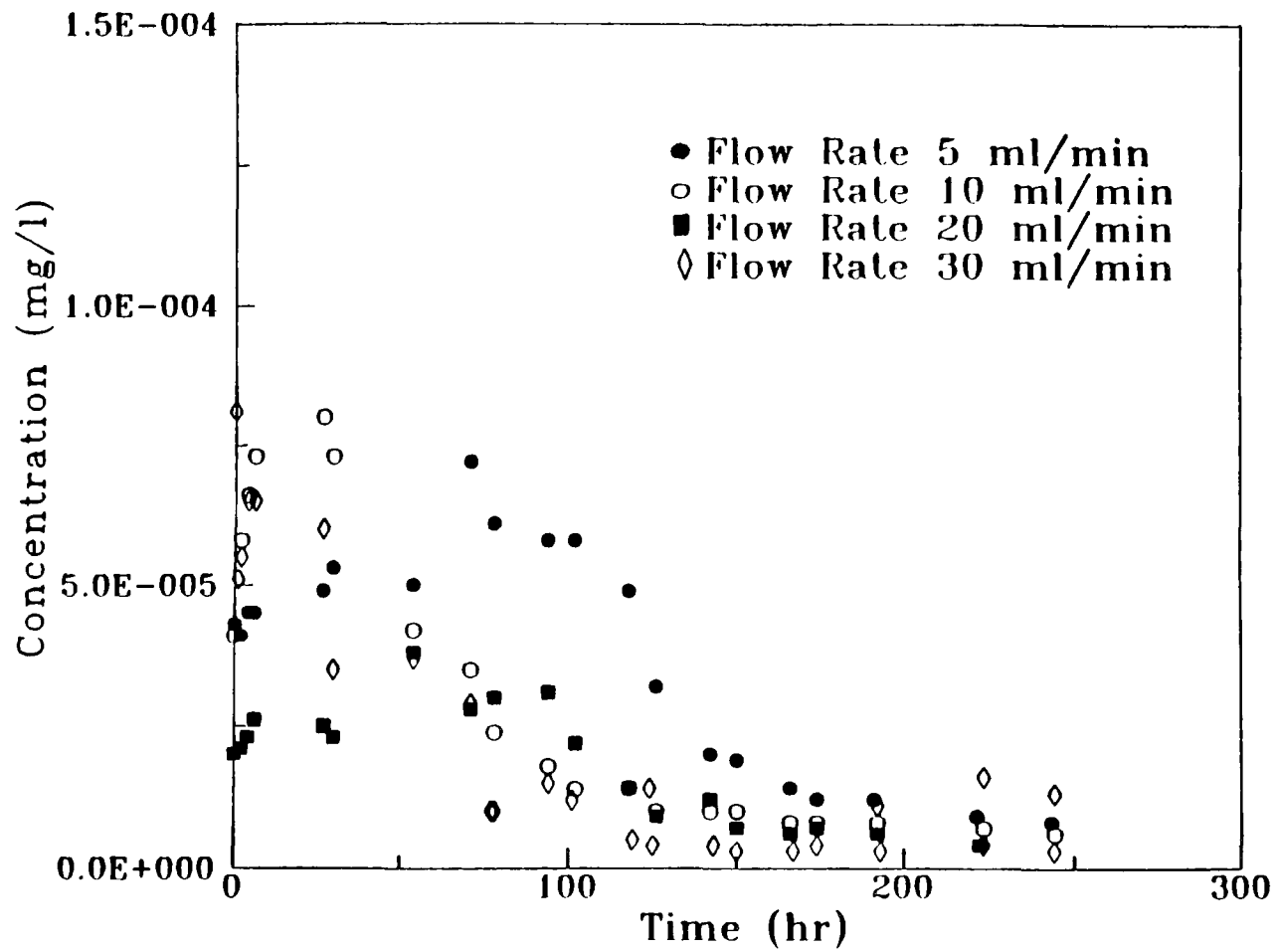
Figure 6-5. Toluene concentration in effluent air from soil column
15 ml water following 5 ml toluene
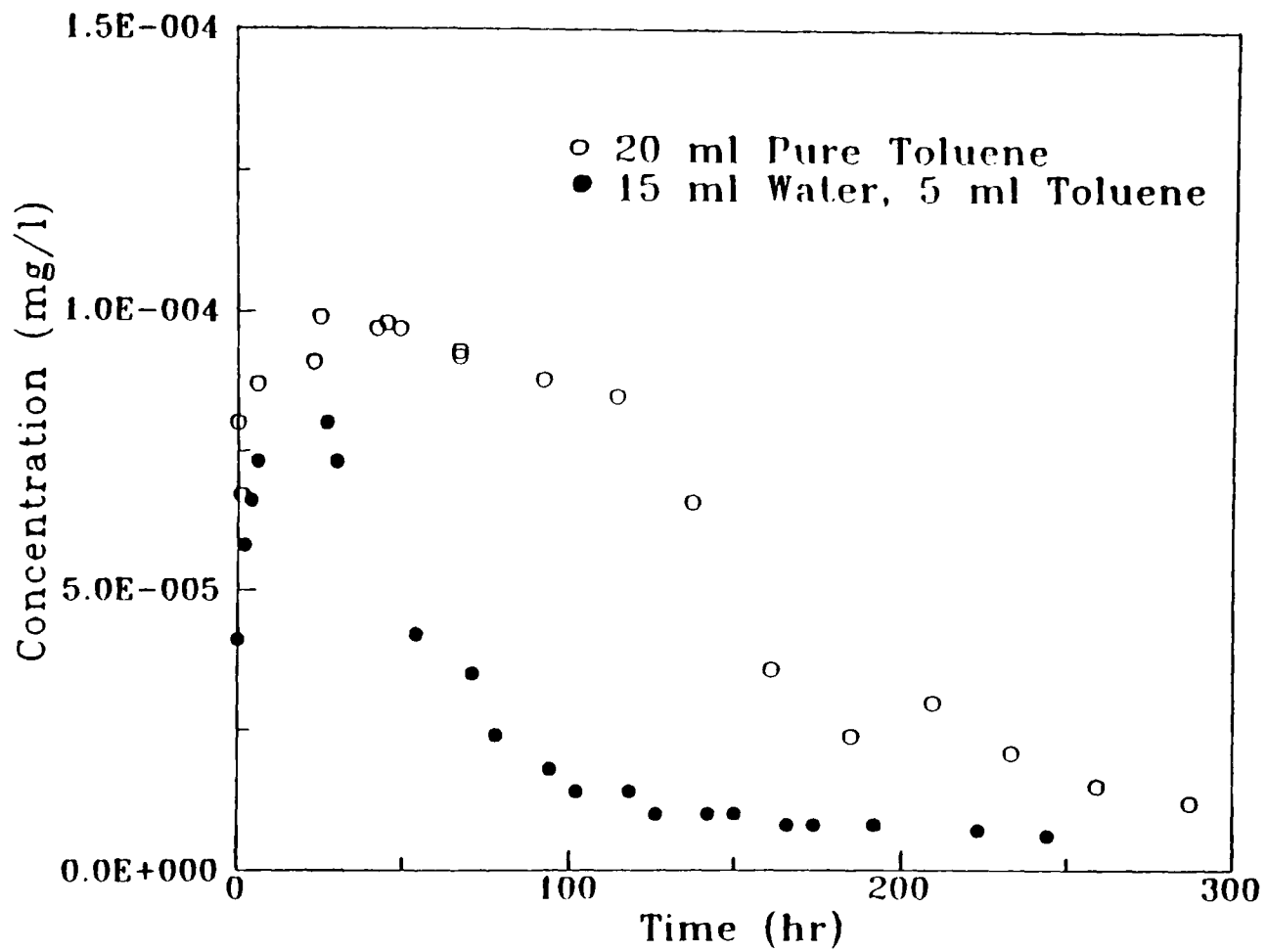
Figure 6-6. Comparison of effluent concentrations from different soil columns
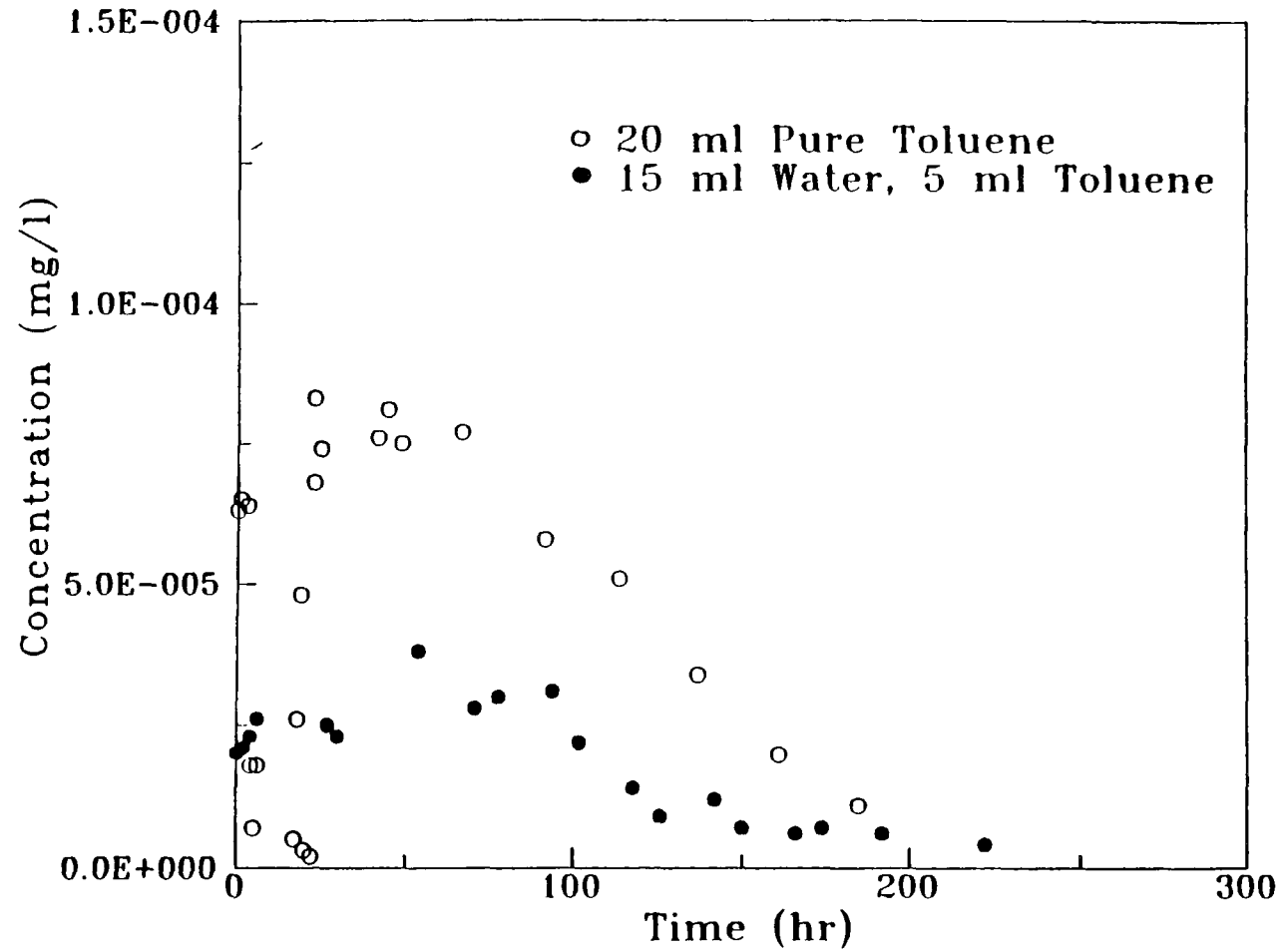Air flow rate   10 ml/min

Figure 6-7. Comparison of effluent concentrations from different soil columns
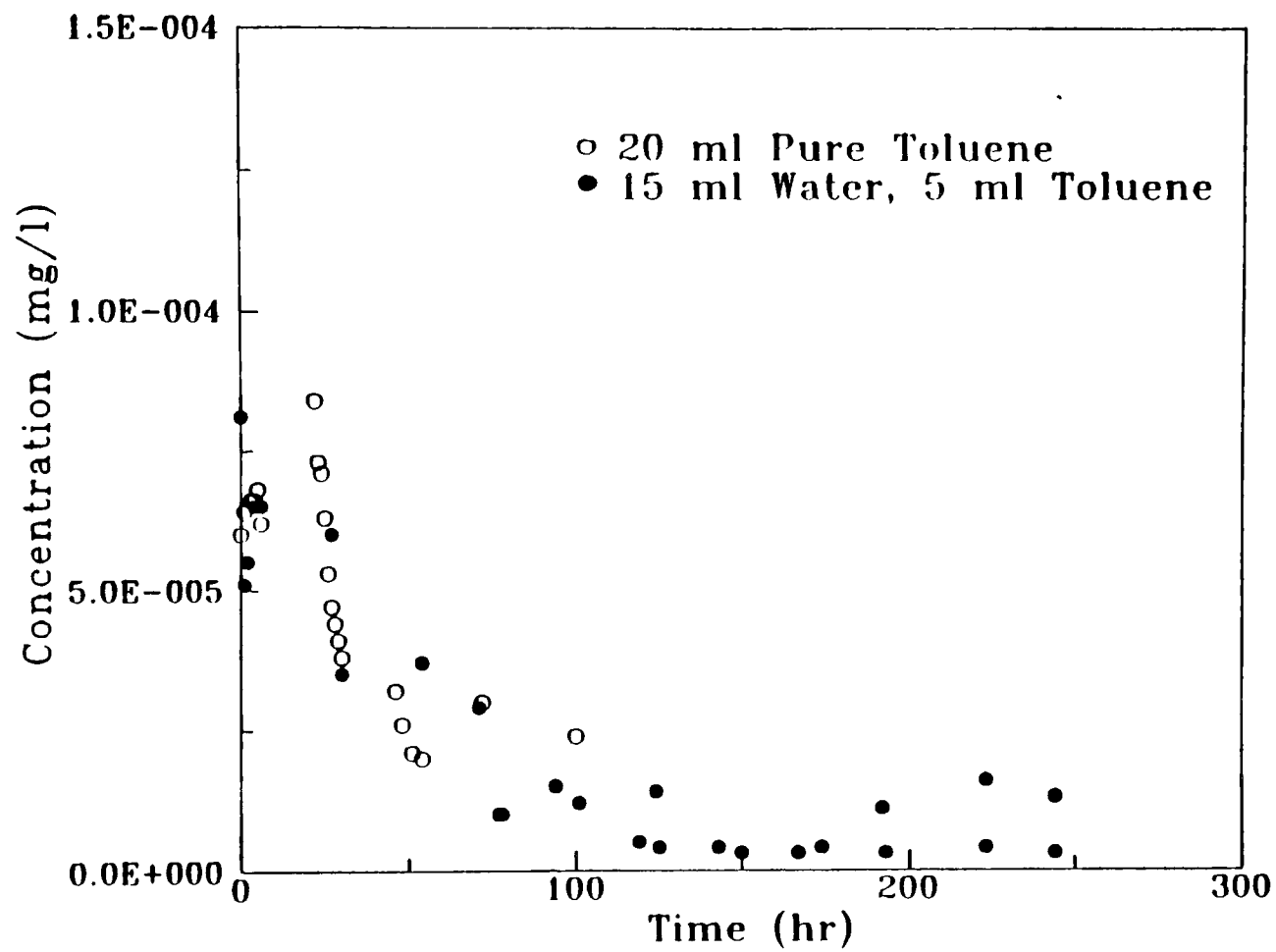Air flow rate   20 ml/min

Figure 6-8. Comparison of effluent concentrations from different soil columns
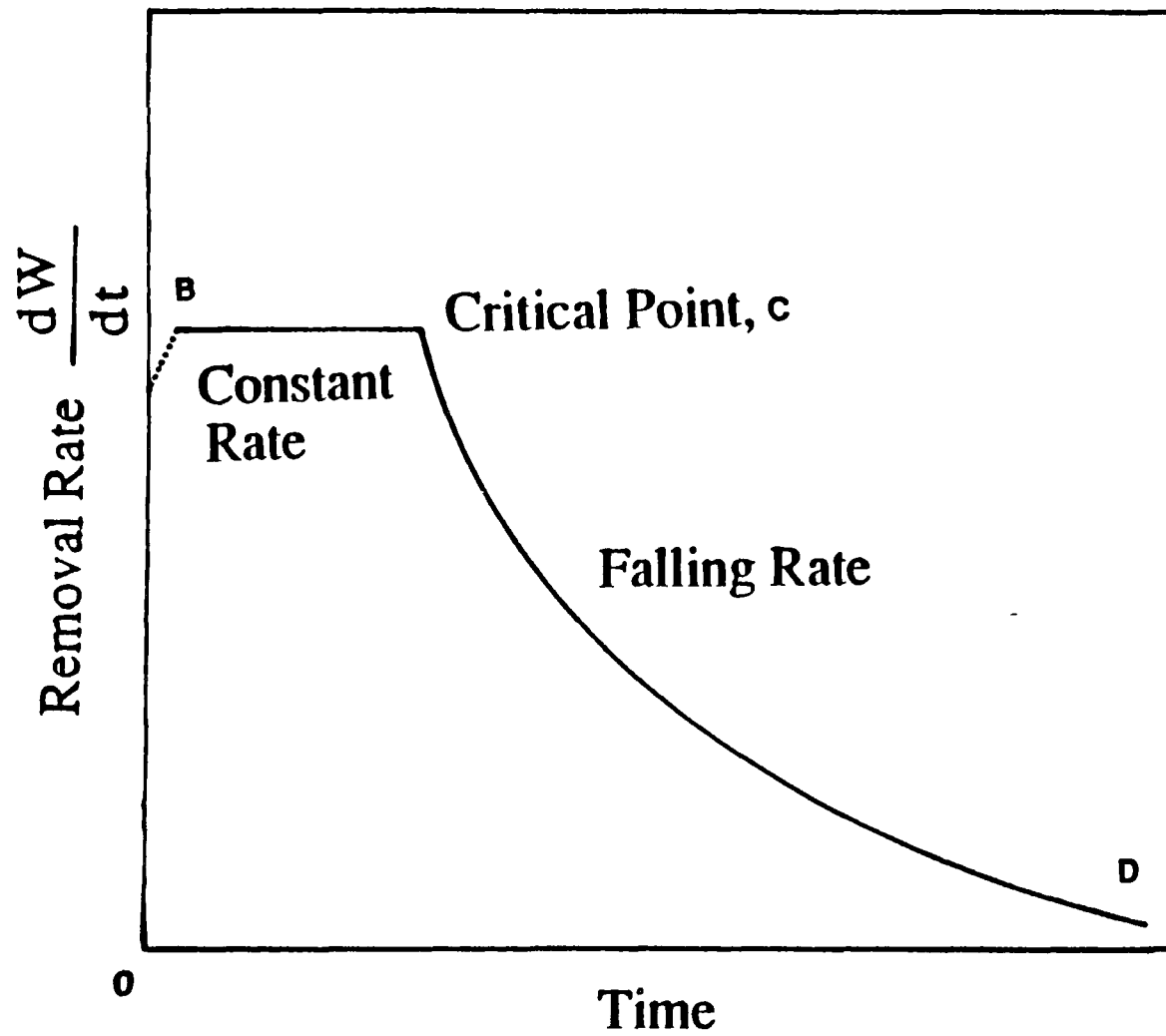Air flow rate   30 ml/min

Figure 6-9. Conceptual model of VOC removal from soil pores

SECTION 7

MODEL WITH SUPERPOSITION OF ANALYTICAL SOLUTIONS

The development of a three-dimensional analytical approximate model to simulate the air flow during the SVE operation and a simple pneumatic pump test conducted on an aviation gasoline contaminated site are presented in this section. This model adopted a superposition method of the analytical solutions from potential theory in a three-dimensional space. This analytical model is only applicable to homogeneous media. Pneumatic pump tests were conducted to obtain soil air flow characterization around an air injection and vacuum extraction well in relation to a field demonstration project of a bioremediation. The operating condition of the test was very favorable to the application of SVE. The information obtained was very valuable and showed the importance of the pneumatic pump test prior to the design of a full scale operation. A part of the test results were used for the validation of the model.

Analytical Solutions

Various solution methods have been developed to solve the partial differential equations including numerical and analytical techniques. In general, there are two methods in numerical techniques. The first one is the total domain discretization method which includes the finite difference and finite element techniques. In this method, the boundary conditions are satisfied and the solutions inside the boundary are obtained by approximation at the grid points. The other methods are to obtain exact solutions satisfying the differential equations inside the domain and to approximate boundary conditions by summation or integration of exact solutions on the boundary. The latter includes the boundary element method and superposition method of exact solutions. The numerical technique of the total domain discretization method has a long history and is well established. A limitation to the large scale application of these methods is the excessive memory and computational time requirements (Frind and Verge, 1978). A major advantage is the ease of handling heterogenous media. The boundary element method and superposition method of exact solutions require less memory and computational time because they need approximations only on the boundaries (Hess, 1973). Another advantage is that computed data

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points are not limited on the grid points, as with the finite difference and finite element methods. A disadvantage is their limited applicability to heterogenous media. Complex heterogenous media requires the discretization of the whole domain to be satisfied by the approximation method, and in this case, the finite difference and finite element methods are superior to the boundary element method.

At the steady state, the equation describing the pressure distribution of soil air is

$$\nabla K_a p \nabla p = 0 \qquad (7\text{-}1)$$

where K_a is the soil-air conductivity tensor which is a function of location and direction due to soil heterogeneity and anisotropy. Along with this pressure equation, proper sets of boundary conditions are needed for the problem domain. The first boundary is the constant pressure condition at the soil surface exposed to the atmosphere.

$$p = p_c \qquad (7\text{-}2)$$

The second one is the zero flux boundary for the impermeable layer.

$$\nabla K_a p = 0 \qquad (7\text{-}3)$$

The last one is the continuous flux condition along the interfaces between layers of different permeabilities.

$$\nabla K_{a1} p = \nabla K_{a2} p \qquad (7\text{-}4)$$

The superposition of exact solutions is only possible only for the linear equations. By applying the Kirchoff transformation on equation (7-1) as follows,

$$\frac{dm}{dp} = K_a P \quad \text{or} \quad m = \frac{K_a}{2} (p^2 - p_r^2) \qquad (7\text{-}5)$$

where p_r is a reference pressure (i.e., atmospheric pressure), the equation becomes a Laplace type equation.

$$\nabla^2 m = 0 \qquad (7\text{-}6)$$

where m can be defined as the discharge potential at location x. Boundary conditions become as follows: Constant pressure boundary,

$$m = \frac{K_a}{2}(p_c^2 - p_r^2) \qquad (7\text{-}7)$$

No flux boundary,

$$\nabla m = 0 \qquad (7\text{-}8)$$

Continuous flux boundary between layers of different permeabilities

$$m_1 - m_2 = \frac{(K_{a1} - K_{a2})}{2}(p^2 - p_r^2) \qquad (7\text{-}9)$$

which means the potential jump at the interface when the location vector, x, crosses the boundary from medium 1 to medium 2.

One of the exact solutions which satisfy the equation (7-6) is the point source

$$m = -\frac{Q}{4\pi}\frac{1}{r} \qquad (7\text{-}10)$$

where Q is the source strength and r is the distance from the source point. A finite length well in the subsurface can be modeled as a line source with finite length. The discharge potential at x due to the line source becomes

$$m = - \int_0^L \frac{Q(z)}{4\pi} \frac{1}{r} \, dz \qquad\qquad (7\text{-}11)$$

where L is the length of the well. When the source strength Q is of zeroth order with respect to well length, the equation (7-11) becomes

$$m = - \frac{Q}{4\pi} \ln \frac{u + v - 2h}{u + v + 2h} \qquad\qquad (7\text{-}12)$$

where u, v, h are lengths of vectors defined in Figure 7-1. Another useful solution for equation (7-6) is the point dipole which is defined as a point potential of combined point source and point sink of same strength at an infinitesimally short distance. The potential at x due to a point dipole is

$$m = \frac{q \, c \, r}{4\pi \, r^3} \qquad\qquad (7\text{-}13)$$

where q is the dipole strength, c, the unit orientation vector of dipole, r, the vector from dipole point to location x, and r, the length of vector r. Potentials due to the line dipole and dipole panel can be obtained by an integration method (Haitjema, 1985).

Boundary conditions can be satisfied by superposition of line and panel dipoles on boundaries. Unknown variables are the strength terms for sources and dipoles. These unknowns can be obtained by solving simultaneous equations satisfying boundary conditions and potential values at selected control points. Selection of control points can be optimized from the numerical analysis (Hess, 1973).

Pneumatic Pump Test

<u>Site Characterization</u>

A series of pneumatic pump tests were conducted on an aviation gasoline contaminated site. The soil type at the site was categorized as a fine sand which had a grain size of 0.35 mm average

and 90% in the range of 0.1 to 1 mm. The intrinsic permeability of this sand was reported as 5.2×10^{-10} ft^2 (Ostendorf, et al., 1989). The thickness of this sand layer was about 47 ft and a thick clay layer was located underneath. The water table was 17 ± 2 ft from the soil surface and the ground-water flow direction was northeast.

Test Design

An injection well and an extraction well were installed 20 ft apart. Both wells were made of 5 inch schedule 40 PVC pipe and had a 1 ft screened section 15 ft from the soil surface. Each well was connected to a separate blower pump. To control the pressure and air flow into/out of the well, a by-pass line, which had a opening to the atmosphere with a ball valve, was attached to each connecting pipe. Several different pressures and air flow rates could be applied to each well by controlling valve openings. The pressure inside the well was measured by a pressure gauge installed on the top of each well. The volumetric flow of air inside the well was measured with pitot tubes installed on 4 inch schedule 40 PVC pipe that connected the well and the blower pump. The maximum capacity of blower pumps was 176 scfm at the positive pressure of 52.3 inch water inside the injection well. The pressure distribution in the subsurface around the well was measured with Magnahelic pressure gauges. Gauges were connected through quick release connectors on probe clusters located 5, 10, 12.5, 15, and 30 ft away from the injection well along the straight line between injection and extraction wells. Each cluster had three probes. Each probe had a screened opening at the bottom of 1/4 inch O.D. copper tubing and a quick release connector at the top. The length of probes was 3, 10, and 15 ft. The schematic diagram of the test system is shown in Figure 7-2.

Test Results

A series of tests of air injection, extraction, or combined operations were conducted. The same procedure was applied to each set of tests. The blower pump connected to the well was powered on and the pressure and air flow were controlled by the control valve. Due to the high permeability and low moisture content in the soil, the transient pressure change around the well reached the steady state very rapidly. Only the pressure distribution at the steady state could be obtained.

In Figure 7-3, pressure distributions at a depth of 15 ft are plotted against distances from the injection well with various well pressures. As we expect, the pressure change is large within 15 ft from the well; beyond this distance, the pressure gradient is small. Because the air flow is proportional to the pressure gradient, the horizontal air flow velocity decreases sharply as the distance from the well increases. The vertical pressure gradient and air flow in that direction also decreases as the distance from the well increase. In Figure 7-4, the pressure distribution of the soil in the case of 42 inch water injection well pressure is shown.

In Figure 7-5, vacuum pressure distributions at a depth of 15 ft are shown for various vacuum pressures applied. The same trend of pressure changes and air flow velocity changes can be seen from the figure. Conventionally, field engineers set up a pilot scale test of a single extraction well and measure the pressure distribution and estimate the zone of influence from the measured pressure distribution. The most important factor in determining the zone of influence and the well interval should be the pressure gradient and the air flow velocity. For our study case, the wells should be spaced less than 30 ft apart to induce sufficient air flow in the contaminated zone.

The pressure distribution at a depth of 15 ft for the combined operation of injection and extraction wells with various combinations of positive and negative pressures inside the wells is shown in Figure 7-6. The maximum injection pressure was 52 inch water with the volumetric air flow of 176 scfm. The pressure at the extraction well was -48 inch water and the volumetric flow was 140 scfm. A small horizontal pressure gradient at a depth of 15 ft exists, and horizontal air flow can be expected. But the pressure gradient is very small compared to the total pressure difference between two wells (100 inch water). The horizontal air flow and the removal rate of VOCs in that direction are expected to be low. Figure 7-7 shows the pressure distribution at different depths at maximum capacity operation. Large vertical pressure gradients in the vicinities of the wells (within 5 ft) are seen and large volumes of air flow in vertical direction around the wells can be expected. At the midpoint, a very small vertical gradient and air flow exist. Therefore, it is not efficient to induce horizontal air flow with distantly located wells and large pressure differences.

Very important information could be obtained from pneumatic pump tests. Design parameters in the SVE system should include the zone of influence in which the pumps can produce sufficient air flow. The conventional method of measuring the zone of influence with soil vacuum pressure

with one well can overestimate the size of effective area of SVE. Major factors in determining the zone of influence should be the pressure gradient and corresponding air flow.

The pumping efficiency could be measured from the tests. A single high vacuum pumping well does not have a larger zone of influence than the low vacuum pumping well because a large air flow exists only in the vicinity of the well. Therefore, operating multiple low vacuum wells may be more efficient than operating a single high vacuum well.

Combined operation of extraction and injection wells could induce horizontal air flow, but still a large vertical flow is expected in the vicinity of the wells. Therefore, the system should be carefully engineered to obtain reasonable efficiency. A tightly covered soil surface may help inducing more horizontal flow.

Additional field tests are suggested to measure the pressure distribution of the operation with a tightly covered soil surface and also with various lengths and locations of well screens.

Simulation of Pneumatic Pump Test

The pneumatic pump test conducted could be simulated by the model using the superposition of line sources representing wells. Applicable boundary conditions were the constant pressure at the soil surface and the impermeable boundary on water table. With the atmospheric pressure as the reference pressure, the first boundary condition became

$$m = 0 \text{ at } z = z_{surface} \tag{7-14}$$

and the second boundary condition became

$$\frac{\partial m}{\partial z} = 0 \text{ at } z = z_{water} \tag{7-15}$$

These two boundary conditions could be easily satisfied by the method of images. By locating mirror images of sources with opposite strength, the first boundary condition could be satisfied at the soil

surface. Mirror imaged wells with the same strength could satisfy the boundary condition at the water table. Source strengths could be obtained by solving simultaneous equations yielding the desired well pressure at selected control points on well surface. The zeroth order well strength expression was used for this simulation.

Figure 7-8 shows the simulated pressure distribution with measured point values for injection well operation. Figure 7-9 shows the combined operation of injection/extraction wells operation. The model simulation seems reasonably good. Calculated air flows were within ± 20 % of measured values. The calculated value of the intrinsic permeability from the pneumatic pump test was 7.0×10^{-10} ft^2 which was comparable with the reported value, 5.2×10^{-10} ft^2 (Ostendorf et al, 1989).
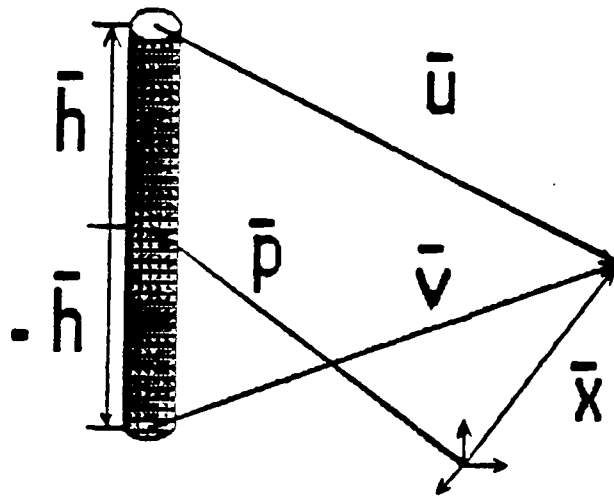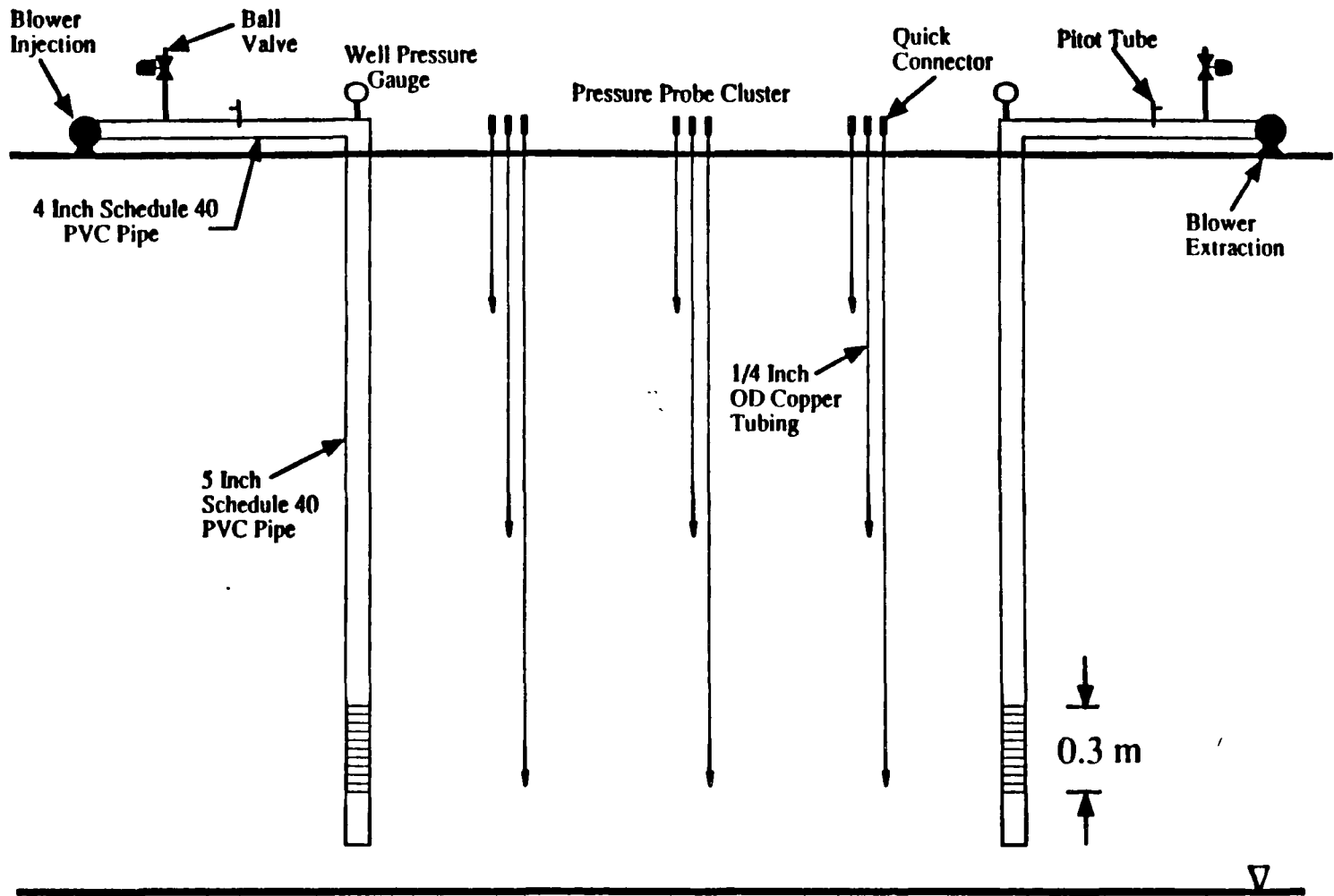
Figure 7-1. Vector presentation of well screened section in three-dimensional space

Figure 7-2. Schematic diagram of pneumatic pump test

Blower Injection

Ball Valve

Well Pressure Gauge

Pressure Probe Cluster

Quick Connector

Pitot Tube

4 Inch Schedule 40 PVC Pipe

Blower Extraction

1/4 Inch OD Copper Tubing

5 Inch Schedule 40 PVC Pipe

0.3 m

∇

Figure 7-3. Measured pressure distribution at 15 ft depth for air injection well test

The figure shows pressure (inch H₂O) on the y-axis versus distance from well (ft) on the x-axis, with five curves labeled a through e:

a: Well Pressure -50 inch H_2O

b: Well Pressure -42 inch H_2O

c: Well Pressure -36 inch H_2O

d: Well Pressure -24 inch H_2O

e: Well Pressure -16 inch H_2O
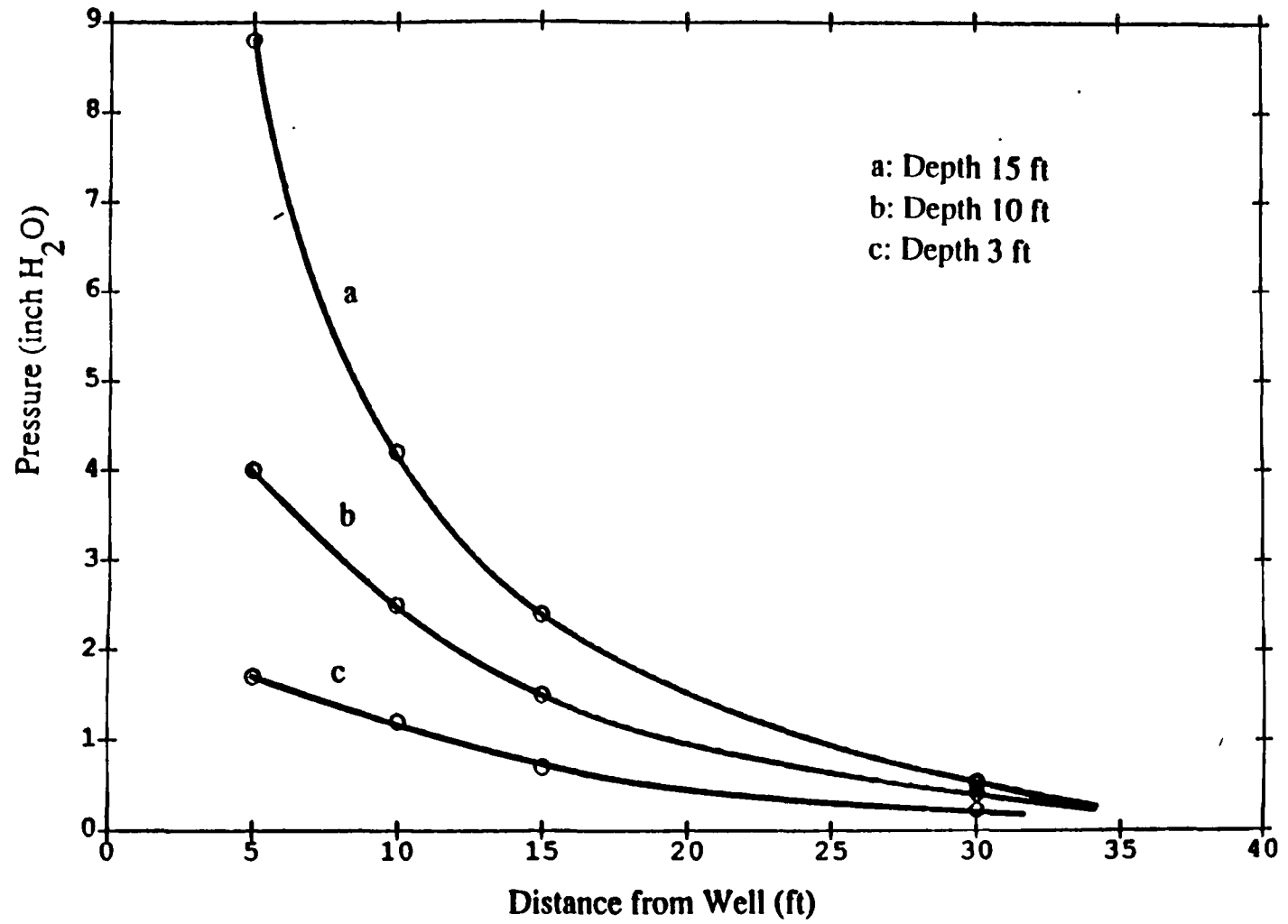
Figure 7-4.   Measured pressure distribution at various depths
Air injection well pressure 50 inch water

a: Well Pressure 44 inch H_2O

b: WEll Pressure 36 inch H_2O

c: Well Pressure 24 inch H_2O

d: Well Pressure 16 inch H_2O

e: Well Pressure 4 inch H_2O

Figure 7-5. Measured pressure distribution at 15 ft depth for vacuum extraction well test
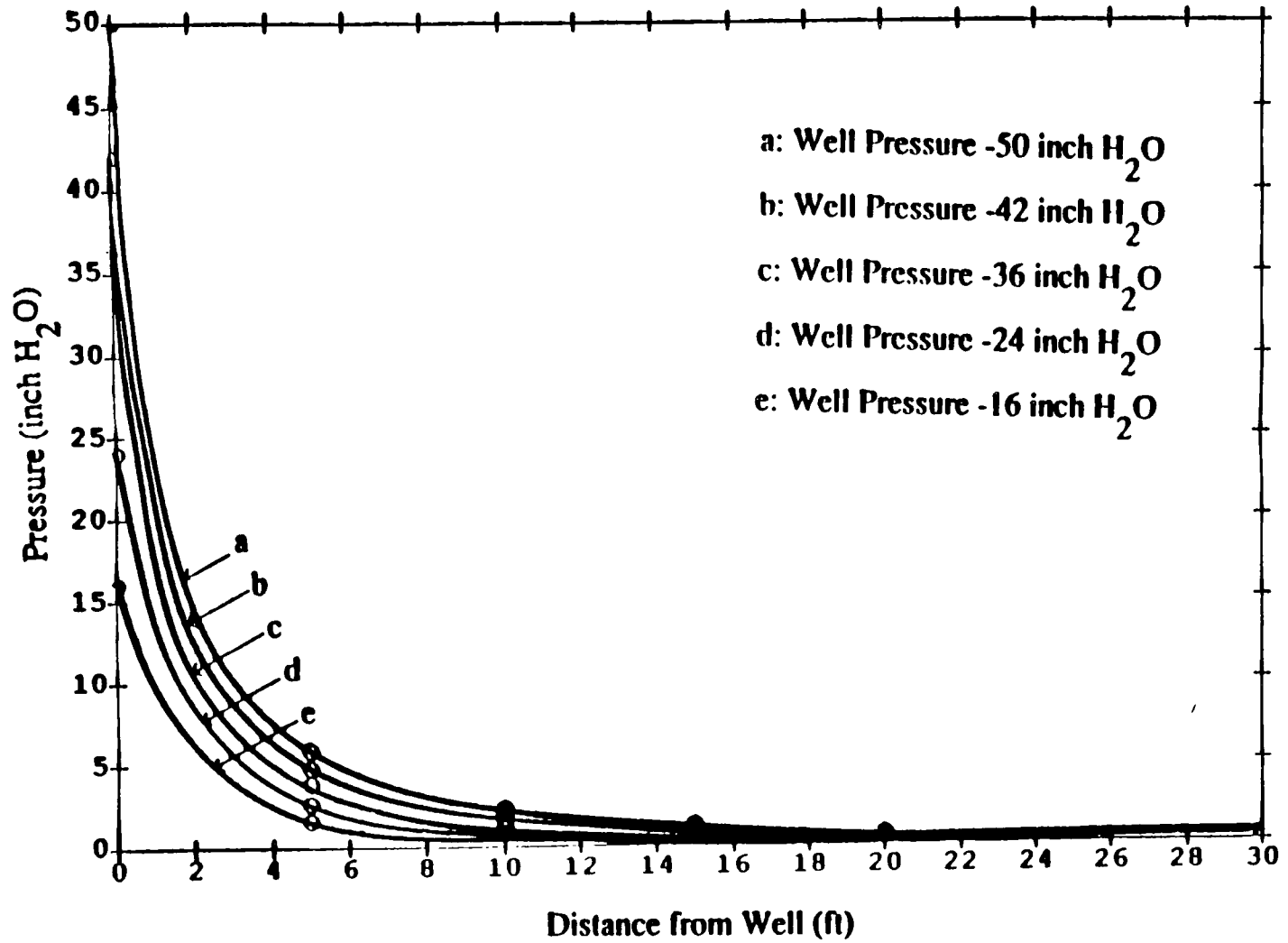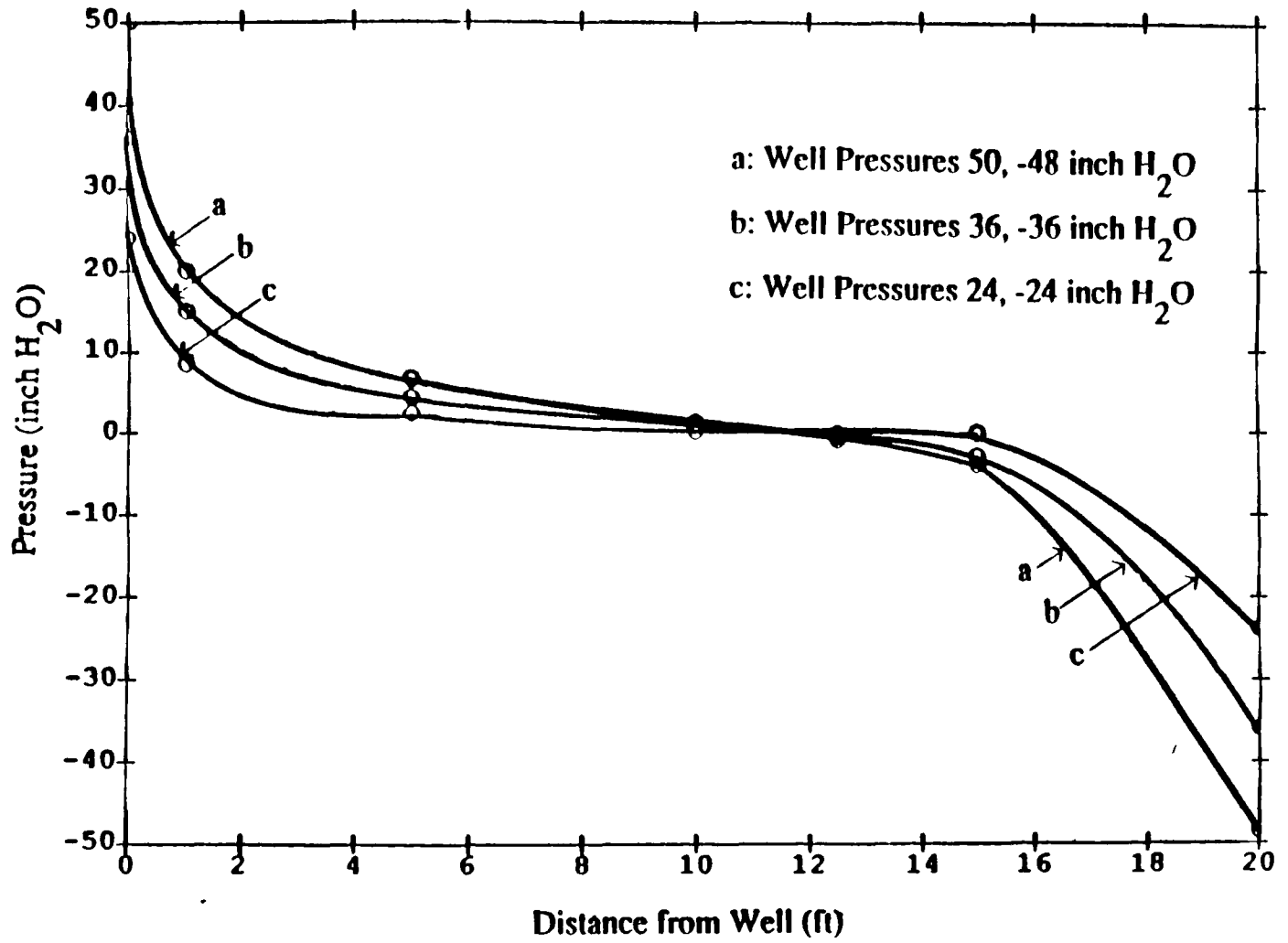
Figure 7-6. Measured pressure distribution at 15 ft depth for injection/extraction wells test

Figure 7-7.   Measured pressure distribution at various depths
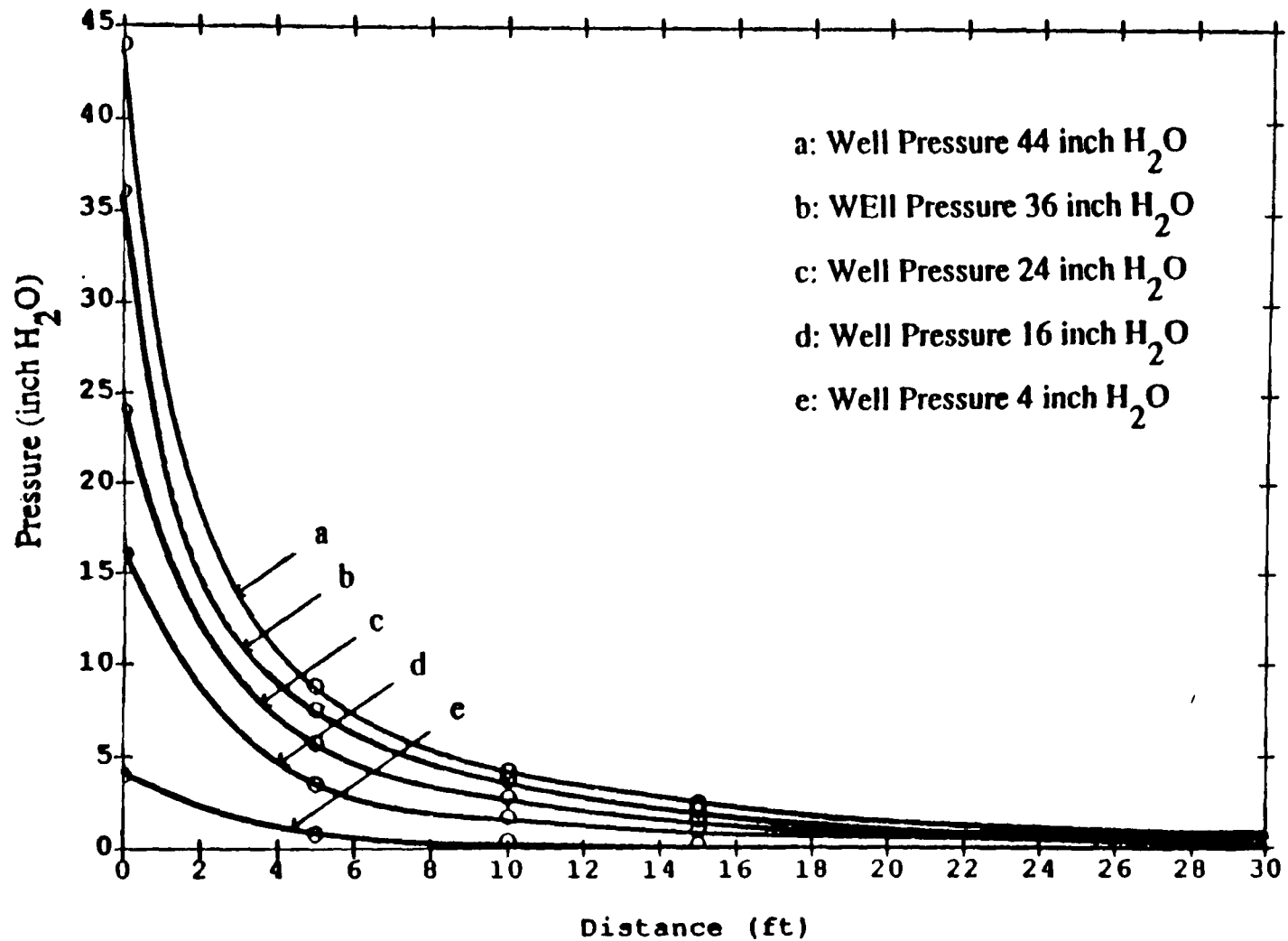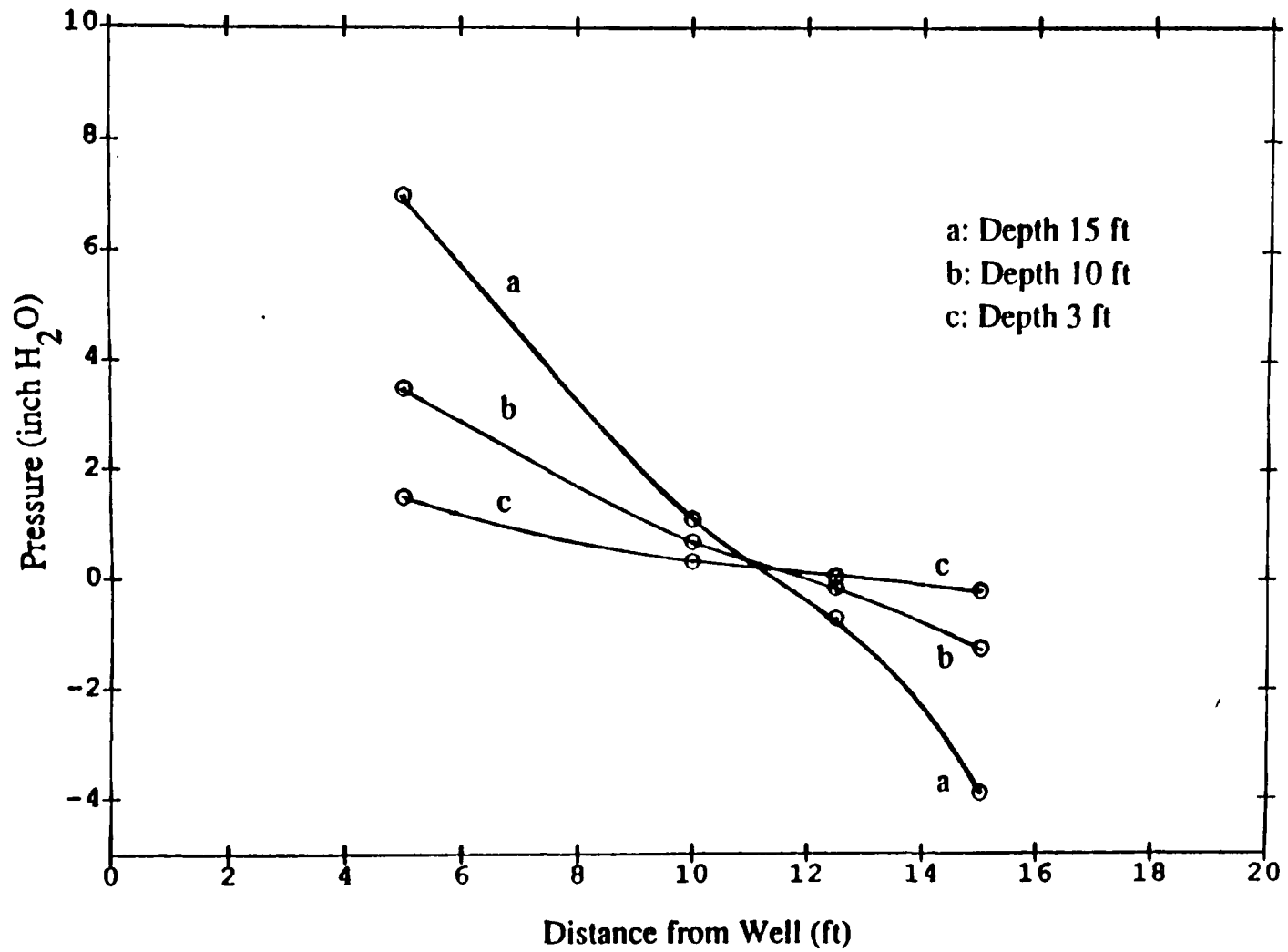Air injection well pressure 50 inch water
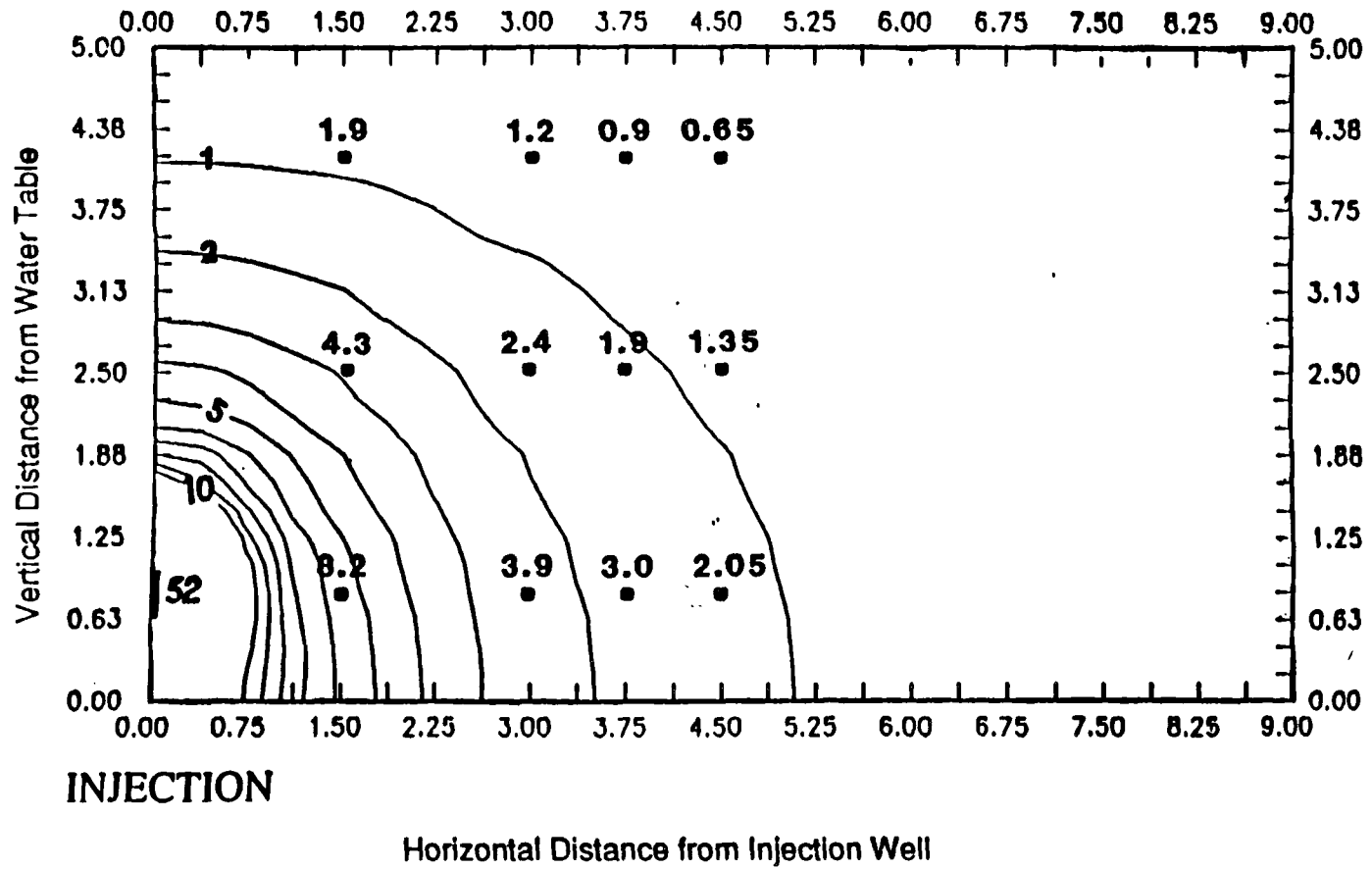Vacuum extraction well pressure -48 inch water

Figure 7-8. Isobaric contour plots of computed pressure distribution
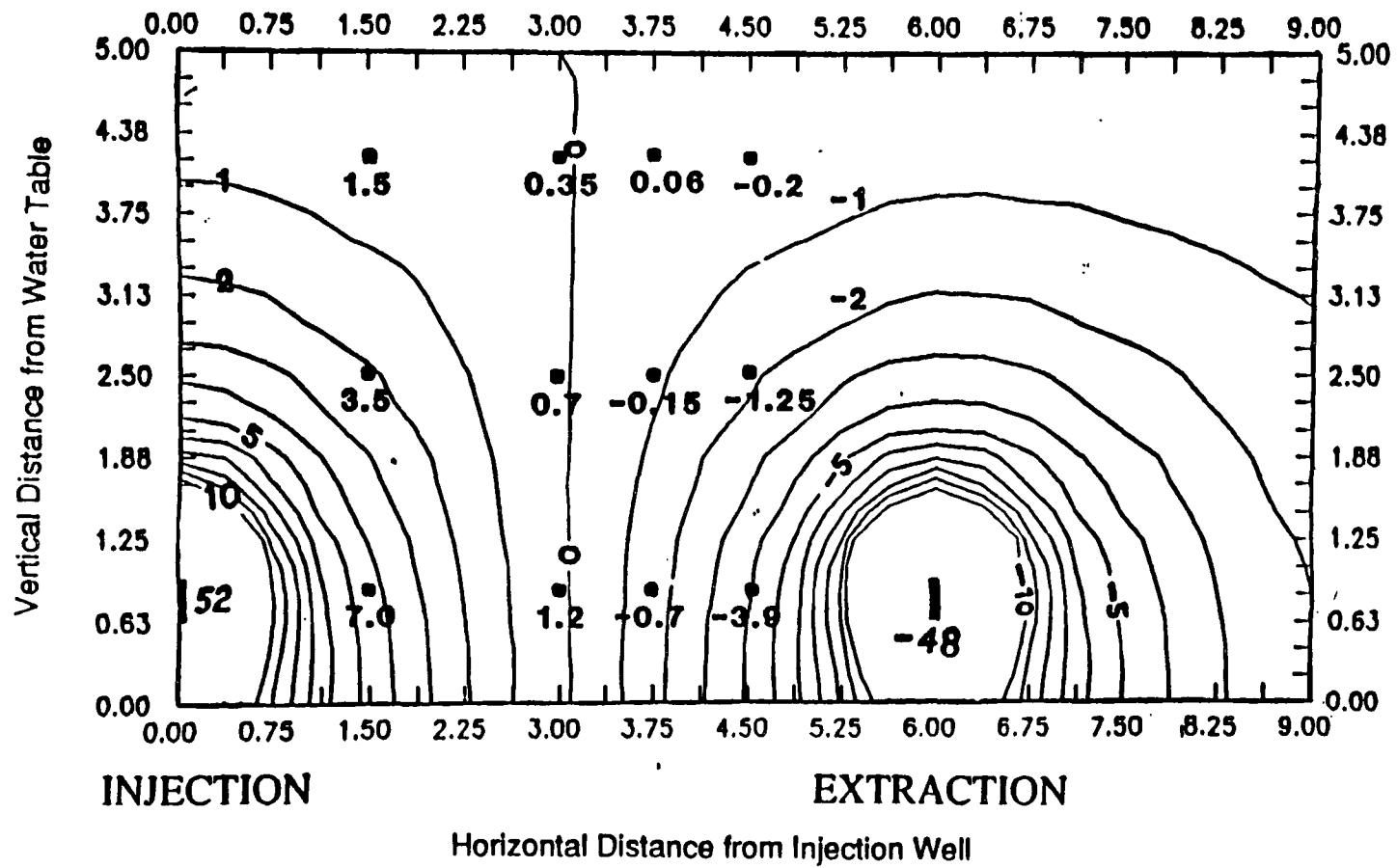
● Measured pressure (inch water)

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Figure 7-9. Isobaric contour plots of computed pressure distribution
● Measured pressure (inch water)

SECTION 8

THREE-DIMENSIONAL FINITE DIFFERENCE MODEL

A computational model has been developed to simulate the soil vacuum extraction process in field scale. This model consisted of a soil air flow equation, the contaminant transport equation and the mass balance equation of residual hydrocarbon inside soil matrices. The general air flow equation was transformed to a Laplace type equation to obtain the soil air pressure distribution and the air flow rate. The calculated air flow velocity was used in the transport equation to describe the convective movement of contaminant along with the bulk air flow. In addition to the convective movement, the transport equation included the diffusive movement and the interfacial mass transfer between the air and the residual hydrocarbon contacting the flowing air. The mass balance equation for the residual hydrocarbon was also used. The numerical method to solve these differential equations with boundary conditions was the finite difference method in a three-dimensional space domain and the unsteady state time process.

Finite Difference Solutions

Soil Air Flow

The soil air flow arrives at steady state quite rapidly after the SVE system is initiated by pumping the air into/out of the subsurface. The contaminant movement usually is a non-steady state problem until all the contaminant mass is removed from the system. Therefore it is a reasonable to assume that the air flow is at steady state during the operating period. The mass balance equation of soil air at steady state may be expressed from equation (4-4)

$$\nabla \left(\frac{\rho_a \kappa_a}{\mu_a} \nabla p \right) = 0 \tag{8-1}$$

This equation is non-linear due to the dependence of the density of air on the pressure. The equation becomes linear when the viscosity and density terms are replaced by constant values. In this case, the equation becomes

$$\nabla (\kappa_a \nabla p) = 0 \qquad (8\text{-}2)$$

If the pressure dependence of density should be included, the equation becomes

$$\nabla (\kappa_a \, p \, \nabla p) = 0 \qquad (8\text{-}3)$$

By applying a Kirchoff type transformation like

$$\frac{dm}{dp} = \kappa_a \text{ or } m = \kappa_a (p - p_r) \text{ for the equation (8-2)} \qquad (8\text{-}4a)$$

and

$$\frac{dm}{dp} = \kappa_a p \text{ or } m = \frac{\kappa_a}{2} (p^2 - p_r^2) \text{ for the equation(8-3)} \qquad (8\text{-}4b)$$

where p_r is a reference pressure, the soil air flow equations become

$$\nabla^2 m = 0 \qquad (8\text{-}5)$$

which is a Laplace equation. The air flow velocity becomes

$$V = \kappa_a \nabla p = \nabla m \text{ for the linear equation} \qquad (8\text{-}6a)$$

$$V = \frac{1}{p} \nabla m \text{ for the nonlinear equation} \qquad (8\text{-}6b)$$

The proper boundary conditions are

1. constant pressure boundary

$$p = p_a \qquad\qquad (8\text{-}7a)$$

which is

$$m = m_a \qquad\qquad (8\text{-}7b)$$

2. no air flow boundary or no pressure gradient

$$\frac{\partial p}{\partial x_i} = 0 \qquad\qquad (8\text{-}8a)$$

which is

$$\frac{\partial m}{\partial x_i} = \frac{\partial m}{\partial p} \frac{\partial p}{\partial x_i} = 0 \qquad\qquad (8\text{-}8b)$$

The equation (8-5) with boundary conditions (8-7) and (8-8) is a linear Laplace equation and can be solved by a standard numerical technique.

The finite difference method with central spatial difference scheme was adopted to solve this air flow equation. Replacing equation(8-4) with the difference operator results in the following difference equation,

$$\nabla^2 m = \frac{m_{i+1,j,k} - 2 m_{i,j,k} + m_{i-1,j,k}}{(\Delta x)^2}$$

$$+ \frac{m_{i,j+1,k} - 2 m_{i,j,k} + m_{i,j-1,k}}{(\Delta y)^2}$$

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$$+ \frac{m_{i,j,k+1} - 2 \, m_{i,j,k} + m_{i,j,k-1}}{(\Delta z)^2} = 0 \qquad (8\text{-}9)$$

Let M+1, N+1, and L+1 be the numbers of nodes in x, y, and z directions, respectively. By applying the above finite difference operator on all the interior nodal points, excluding the boundary points, w, where specific conditions are assigned, total number of linear algebraic equations becomes (M-1) x (N-1) x (L-1)-w. The number of equations increases rapidly as the nodal points increases. For example, 100x100x100 system generates 100,000 simultaneous algebraic equations which need a tremendous amount of computational time. In this project, the point Jacob iterative method was selected to solve the equations because it uses considerably less CPU memory than the direct solution method, allowing the large physical problems to be simulated. Additional refinement adopting various preconditioner and accelerator schemes is needed to make the program more stable and faster.

Transport Equation

The contaminant transport in soil air is assumed due to diffusion, convection/, and the interfacial mass transfer between the gas and the residual hydrocarbon inside the soil matrix. Mathematical expressions that represents these are equations (4-6) and (4-7) for mass balances of VOCs and equation (4-8) for interfacial mass transfer. Without considering the biological or chemical transformation of hydrocarbon in the gas and the residual hydrocarbon phase, these equations become

$$\phi_a \frac{\partial c_A}{\partial t} = - \nabla c_A V + \nabla \phi_a D \nabla c_A + K_G (c_A^* - c_A) \qquad (8\text{-}10)$$

$$\phi_l \frac{\partial C_A}{\partial t} = - K_G (c_A^* - c_A) \qquad (8\text{-}11)$$

Several finite difference schemes have been developed to solve these convective diffusion equations. In this project period, two simple schemes have been tested, the explicit method and the alternating direction implicit schemes. Only the explicit scheme was implemented in the program. With the explicit scheme, the equations above become

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$$\phi_a \frac{c_A^{n+1} - c_A^n}{\Delta t} = (-\nabla c_A V)^n + (\nabla \phi_a D \nabla c_A)^n + (K_G (c_A^* - c_A))^n \qquad (8\text{-}12)$$

and

$$\phi_l \frac{C_A^{n+1} - C_A^n}{\Delta t} = (-K_G (c_A^* - c_A))^n \qquad (8\text{-}13)$$

which allows computing the concentration c_A and C_A for all nodes at the future time step $t+\Delta t$ explicitly.

The advantage of the explicit scheme over the implicit scheme is that each node is computed explicitly and the computations need less memory and processor time. The disadvantage is that the selection of time step increment is severely dictated by the stability conditions. Usually, the ADI scheme is unconditionally stable and has second-order convergence error. When using the ADI scheme, one would have to invert a set of three tridiagonal matrices for each time step.

Computer Implementation

Very often the modeling of fluid flow and contaminant transport in the subsurface is dictated by availability of computer resources. Because of limited computational resources at Kerr Laboratory, the point Jacobi method for the air flow equation and the explicit scheme for the VOC transport equation were selected. Both methods require less memory and computational time; but because of the limited time step allowed for stability, they may not be suitable for the long period of simulation.

Currently, the algorithms and controlling program discussed above are implemented in FORTRAN 77 on an Apollo DN4500 using Unix system V as the primary operating system. The sampling array used by this model is 101x101x51 which calculates to 520,251 physical nodes. Given this amount of nodes, the program requires approximately 10 Megabytes (MB) of memory which is not suitable for personal computers. Through implication, a larger model would require even greater memory to function.

Provided with the main program is a postprocessor program which is for the graphical display of data generated by the main program. It is specifically designed with an XWindows interface, and will require an XWindows server be available to run the postprocessor.

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