



Proceedings of the Symposium on Soil Venting

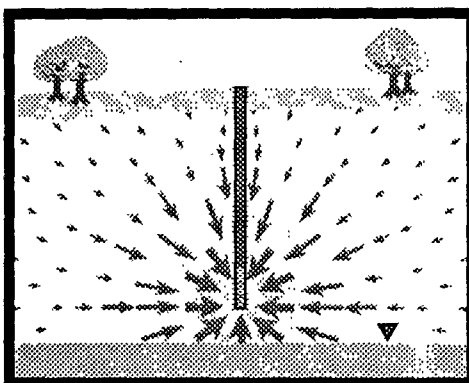
April 29 - May 1, 1991
Houston, Texas



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PROCEEDINGS OF THE SYMPOSIUM ON SOIL VENTING

April 29 - May 1, 1991
Houston, Texas



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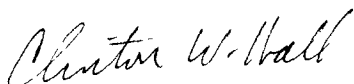
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FOREWORD

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 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 symposium proceedings provides information which can be used to improve the performance of soil venting systems. The emphasis of the symposium was to describe subsurface physical, chemical, and biological processes affecting soil venting performance and to introduce recently developed enhancements to conventional soil venting application.



Clinton W. Hall

Director

Robert S. Kerr Environmental
Research Laboratory

PREFACE

Soil venting has been used to remediate soils in the United States since the early 1980's. It is a recognized standard technology in Germany and is widely utilized in the Netherlands. While its application can sometimes be complex, the basic principle behind soil venting is simple. Air extraction or injection wells are used to create a pressure differential which causes air circulation through contaminated soils or consolidated geologic media.

Soil venting has many advantages over remediation techniques requiring excavation and above ground or offsite treatment. Advantages of venting over excavation include the following.

- Venting can be implemented at actively operating facilities with minimal site disturbance and interruption of business activities.
- Venting systems can be placed near existing buildings with little concern over structural stability. Capture zones of vertical wells and angle and horizontal drilling technologies enable remediation of soils under existing structures.
- Venting can be applied at depths limited only by drilling technology.
- Venting can be applied to consolidated geologic media.
- Venting offgas treatment eliminates uncontrolled release of vapors during operation.

Soil venting is often preferable to above ground onsite and offsite treatment of soils because of lower cost. Venting involves the use of standard and readily obtainable commercial and industrial equipment (e.g., positive displacement blowers, liquid ring vacuum pumps, PVC or stainless steel pipe). Capital expenditures and energy consumption are often far less than other remedial technologies such as thermal desorption.

Another distinct advantage of venting is that air is introduced into soils which are often deficient in oxygen causing concomitant removal of VOCs and semivolatile organic compounds through biodegradation.

Given all of these advantages, it is easy to understand why venting is receiving such great interest from industry, environmental consulting firms, and regulators. Because of this increased interest, a symposium dedicated solely to this technology was organized to provide information in optimizing venting design and operation.

The symposium was organized in a way in that would enable attendees to go through many of the steps commonly followed in designing a soil venting system. The first session entitled "Subsurface Physicochemical and Microbial Processes" provided necessary background in better understanding complex subsurface physical, chemical, and biological processes which often dictate the ultimate effectiveness of soil venting application. Mistakes are sometimes made in venting design because of lack of appreciation of subsurface processes.

The second session was entitled "Mathematical Modeling". Modeling is often utilized as an interpretation tool after collection of data. While this utilization of models is appropriate, papers presented in the symposium illustrate how models can be used to help plan field studies and remedial design prior to entering the field. Discussion in this session also shows how modeling can be used to help understand or conceptualize the subsurface system when preliminary information from previous investigations is available.

The third session entitled "Site Characterization" described actual data collection techniques such as pneumatic testing, soil sampling, and soil gas surveying. A rigorous method to determine radial and vertical pneumatic permeability of soils was described in this session. Determination of pneumatic permeability is necessary to evaluate air exchange rates and to space air extraction and injection wells. Presentations were also given during this session on how soil gas surveying and sampling techniques can improve delineation of areal and vertical gradients in contaminant concentration.

The fourth session entitled "Field Studies: Conventional Venting/Vapor Treatment" contained presentations on actual venting application. Factors affecting remediation time and methods to optimize venting design were discussed. Separate presentations were given on methods to enhance venting application such as hot air injection, ground water sparging, and an in-situ air stripping remediation method utilized in Germany. Vapor treatment methods were also presented in this session including discussion on development of a new catalyst capable of thermally oxidizing chlorinated hydrocarbons.

The fifth and last session was entitled "bioventing". With the exception of a few field research projects, soil vacuum extraction has been applied primarily for removal of volatile organic compounds from the vadose zone. However, circulation of air in soils often enhances the aerobic biodegradation of both volatile and semivolatile organic compounds. Presentations in this session describe how subsurface oxygen levels and air flow rates can be manipulated to maximize in-situ biodegradation. Presenters also discuss how bioventing can reduce vapor treatment costs and result in the remediation of semivolatile organic compounds which cannot be removed by physical stripping alone.

The primary purpose of this symposium and the proceedings which follow are to provide information to improve remedial design of venting systems. Optimization of soil venting application results in greater utilization of the technology and decreased remedial costs. Minimizing the financial burden of subsurface remediation is a goal shared by both industry and government.

TABLE OF CONTENTS

SYMPOSIUM ON SOIL VENTING

Foreword	iii
Preface	v
Venting Overview/Subsurface Physiochemical and Microbial Processes	
Soil Vapor Extraction Technology Development Status and Trends	1
Tom A. Pederson, Camp Dresser & McKee Inc. and Chi-Yuan Fan, U.S. EPA RREL-Edison, NJ	
Soil, Site and Waste Characteristics Controlling the Volatilization of Organic Contaminants in the Vadose Zone..... <i>abstract only</i>	11
R. Ryan Dupont, Utah State University	
The Effect of Moisture on Adsorption of Trichloroethylene Vapor on Natural Soils	13
Karol J. Oja, Salt River Project and David K. Kreamer, University of Nevada, Las Vegas	
Use of In-Situ Ozonation for the Removal of VOCs and PAHs from Soils	29
Susan J. Masten, Michigan State University	
Habitat Conditions Affecting Bioventing Processes	55
Darwin L. Sorensen and Ronald C. Sims, Utah State University	
Opportunities for Biotreatment of Trichloroethylene in the Vadose Zone <i>abstract only</i>	71
John T. Wilson, Don H. Kampbell and Jong Cho, U.S. EPA, Ada, Oklahoma	
Mathematical Modeling	
Soil Venting Design: Models and Decision Analysis <i>abstract only</i>	73
Marian W. Kemblowski and Shyamal Chowdery, Utah State University	
Modeling Transport of Organic Chemicals in Gas and Liquid Phases	75
A. K. Katyal, P. K. Patel and J. C. Parker, Virginia Polytechnic Institute	

Application of Computer Simulation Models to the Design of a Large-Scale Soil Venting Systems and Bioremediation	91
J.C. Walton, R.G. Baca, J. B. Sisson, A.J. Sondrup, and S.O. Magnusen, Idaho National Engineering Laboratory	
Mathematical Modeling of SVE: Effects of Diffusion Kinetics and Variable Permeabilities	103
Jose M. Rodriguez-Maroto, Cesar Gomez-Lahoz and David J. Wilson, Vanderbilt University	
Development and Application of a Three-Dimensional Air Flow Model in the Design of a Vapor Extraction System.....	125
Michael C. Marley, Vapex Environmental Technologies, Inc.	
Modeling In-Situ Biodegradation in Unsaturated and Saturated Soils <i>abstract only</i>	141
Harold W. Bentley, HydroGeoChem, Inc. and Byran Travis, Los Alamos National Laboratory	
Site Characterization	
Characterizing Permeability to Gas in the Vadose Zone <i>abstract only</i>	143
Michael Sully, University of Arizona	
Use of Soil Gas Measurements in the Design of Soil Vapor Extraction Systems ... <i>abstract only</i> ...	145
Gary R. Walter and Harold W. Bentley, HydroGeoChem, Inc.	
Assessing the Performance of In situ Soil Venting Systems by Soil Sampling and Volatile Organic Compound Measurements <i>abstract only</i>	147
Robert L. Siegrist, Oak Ridge National Laboratory	
A Field Technique for Determining Unsaturated Zone Air-Permeability	149
Craig J. Joss, Drexel University, Arthur L. Baehr and Jeffery M. Fischer, U.S. Geological Survey	
Field Studies: Conventional Venting/Vapor Treatment	
Optimization of the Vapor Extraction Process: Large Physical Model Studies..... <i>abstract only</i>	171
Richard L. Johnson, Oregon Graduate Institute	
Field Test of Enhancement of Soil Venting By Heating <i>abstract only</i>	173
David W. DePaoli, Oak Ridge National Laboratory, and Neil J. Hutzler, Michigan Technological University	

Performance Characteristics of Vapor Extraction Systems Operated in Europe	193
Dieter H. Hiller, HPC Harress Pickel Consult GmbH, Germany	
Vacuum-Vaporizer-Wells (UVB) for In Situ Remediation of Volatile and Strippable Contaminants in the Unsaturated and Saturated Zone	203
B. Herrling and J. Stamm, University of Karlsruhe, Germany	
E.J. Alesi, GfS MbH, Kirchheim/Teck, Germany and	
P. Brinnel, Hydrodata GmbH, Oberursel, Germany	
Final Results of a Year-Long USEPA SBIRP/Industry-Funded In Situ Vapor Stripping Pilot Scale Study	229
Ann N. Clarke, Robert D. Mutch, Eckenfelder, Inc., and David J. Wilson, Vanderbilt University	
Air Sparging-Extending Volatilization to Contaminated Aquifers	249
Richard A. Brown and Ricardo Fraxedas, Ground Water Technology, Inc.	
Commercial Vapor Treatment Processes	271
F.A.M. Buck and E.L. Seider, King, Buck, and Associates, Inc.	
Catalytic Destruction of Hazardous Halogenated Organic Chemicals <i>abstract only</i>	281
George R. Lester, Allied Signal, Inc.	
 Field Studies: Bioventing	
Bioventing For In-Situ Remediation of Petroleum Hydrocarbons	283
Robert E. Hinchee, Battelle and Ross N. Miller, U.S. Air Force	
A Field Scale Investigation of Soil Venting Enhanced Petroleum Hydrocarbon Biodegradation in the Vadose-Zone at Tyndall AFB, Florida	293
Ross N. Miller, U.S. Air Force, Robert E. Hinchee, Battelle, Catherine C. Vogel, U.S. Air Force	
Subsurface Remediation at a Gasoline Spill Using a Bioventing Approach	309
Don Kampbell, U.S. EPA, Ada, Oklahoma	
A Demo-Project for In Situ Subsoil and Aquifer Restoration Following Hydrocarbon Spills at a Tankstation	317
J. van Eyk and C. Vreeken, Delft Geotechnics, The Netherlands	

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SOIL VAPOR EXTRACTION TECHNOLOGY DEVELOPMENT STATUS AND TRENDS

TOM A. PEDERSEN

Camp Dresser & McKee Inc.

Ten Cambridge Center

Cambridge, MA 02142

CHI-YUAN FAN

USEPA RREL

2890 Woodbridge Avenue

Edison, NJ 08837

INTRODUCTION

Soil Vapor Extraction (SVE) is the process of removing gaseous contaminants from soil pore spaces by causing air to flow through the subsurface environment. Air flow is usually induced by pumping from a well screened in the unsaturated soil zone. SVE technologies have been widely applied for the treatment of unsaturated soils contaminated with volatile and semivolatile organic compounds and has been shown to provide cost effective and environmentally sound remediation when appropriately designed and operated.

Although extraction of natural gas from geologic deposits and venting of methane from landfills has been practiced for decades, application of gas extraction techniques for the remediation of environmentally impacted soils is a relatively recent development. Scientific and trade publications are replete with reports of SVE experiments and case studies undertaken since 1985, however, only a few published reports pre-date this period; most notably being those by the Texas Research Institute (1980), and Thornton and Wootan (1982).

SVE system components have been outlined in a number of publications (3, 4, 13); leading to the widespread use of this technology at diverse site types. Although these technologies have most frequently been used to treat underground storage tank (UST) petroleum product releases, they are being applied increasingly at chlorinated organic solvent release sites as-well as Superfund sites. SVE has been identified as a remedial technology in 48 of the 749 U.S. Environmental Protection Agency (USEPA) Superfund Records of Decisions (RODs) signed from fiscal year (FY) 1982 through FY 1990 (17). The first ROD to include SVE was signed in FY 1985 whereas 19 FY 1990 RODs included SVE treatment approaches.

This paper provides a brief description of system components and operation, as well as a brief review of soil/contaminant principles important for assessing SVE applicability. SVE system enhancements, such as air sparging, steam injection, and modifications, including bioventing and soil mounds and technology trends are also discussed.

SVE APPROACHES

SVE technologies are relatively simple in design and the equipment that comprises the systems consists of commonly-used and widely available devices such as PVC piping, valves, and pumps. These factors impart an advantage to SVE over other techniques that may require more complex design, or which require single-purpose equipment. Simplicity of system components however, does not imply ease of design. Maximum system efficiency and contaminant removal will occur only through a thorough understanding of site conditions and SVE processes.

The objective of a well-thought out and reasoned design process is to construct a soil vapor extraction system that removes the greatest degree of contamination from the site in the most efficient, timely, and cost-effective manner. The attainment of these objectives requires an understanding of the determinants of system effectiveness which include: the composition and characteristics of the contaminant; the vapor flow path and flow rate; and the location of the contamination with respect to the vapor flow paths (6). Design of an SVE system is basically a process to maximize the intersection of the contaminated zone with the vapor flow paths. Operation of the system should be aimed to maximize the efficiency of the contaminant removal and reduce costs.

The basic equipment for SVE systems consists of: pumps or blowers to provide the motive force for the applied vacuum; piping, valves, and instrumentation to transmit the air from the wells through the system and to measure the contaminant concentration and total air flow; vapor pretreatment to remove soil particles and water from the vapors treat; and an emission control unit to concentrate or destroy the vapor phase contaminants (Figure 1).

Modified SVE approaches included bioventing, soil mounds and air sparging.

Bioventing

Bioventing is a term which has been used to describe the in situ microbial degradation of contaminants mediated by SVE. Many environmental contaminants are subject to degradation by naturally occurring, introduced or engineered organisms. The rate at which degradation proceeds is related to soil/waste characteristics and in many cases is controlled by an adequate oxygen, or other electron acceptor or nutrient source. Bioventing provides a means of introducing added oxygen to the subsurface environment needed for aerobic degradation of organic contaminants. Although SVE applications will invariably result in stimulating biodegradation, bioventing attempts to engineer the vapor flow rates and nutrient balance in soils to maximize microbial activity.

Soil Mounds

Extraction of vapors from stockpiled soil mounds is a modified form of SVE. Vapors are extracted from the stockpiled soil by use of blowers and slotted or perforated extraction piping placed within the soil mound. The mounds are generally covered with geomembranes to provide control of volatile release and moisture content. The air in the mounded soil also provides oxygen needed to mediate bioremediation. The use of mounds to degrade organic compounds has been widely applied for composting of wastewater treatment

plant sludges. However, treatment of petroleum contaminants or xenobiotics does not necessarily require achievement of the thermic temperature regimes needed to destroy pathogenic organisms present in sludge. The key conditions needed for enhancement of biodegradation in soil mound systems are the exchange of air to remove volatile components and provide oxygen required for microbial growth, adequate moisture and nutrients for growth, and mesic temperature regimes.

Biofilters

Soil mounds in the form of biofilters can also be used to treat gases extracted using in situ SVE systems. The extracted contaminant laden vapor are introduced into the soil mound which serves as a growth media for microbial growth. The compounds introduced are sorbed to soil particles and acted upon by microbes in the soil mound. The treated air flows from the soil mound which are uncovered in most biofilter applications.

Air Sparging

Air sparging, also referred to as “in situ air stripping”, is a treatment technology applied to remove volatile organic contaminants from the subsurface saturated soil and groundwater zones. Air sparging is the process of introducing contaminant-free air into the groundwater of an affected aquifer to achieve the transfer of the contaminants from the saturated soil and groundwater to the unsaturated soil pore space, from which they can be removed by soil vapor extraction (8).

Air sparging systems are almost always coupled with SVE systems to allow for the capture of the volatile contaminants stripped from the saturated zone. The use of an air sparging system without an SVE system could result in a net positive pressure in the subsurface which may cause contaminated soil vapor to migrate to previously uncontaminated areas, thus increasing the overall zone of contamination. Additionally, without SVE, uncontrolled contaminated soil vapor flow could enter building structures or utility conduits creating potential explosion or health hazard.

Marley et. al. (1990) suggest that the transport of immiscible contaminants from the saturated zone to the vadose zone requires the dissolution into the aqueous phase followed by diffusion/ dispersion of the dissolved contaminants through the aqueous phase to the air-water interface where they can be removed by SVE. This rate of contaminant transport from the groundwater to soil gas phase has been shown to increase by sparging.

The effectiveness of the air sparging/SVE system can be attributed to two major mechanisms: contaminant mass transport and biodegradation. Depending on the configuration of the system, the operating parameters, and the types of contaminants found at the site, one of these mechanisms usually predominates, or can be enhanced to optimize contaminant removal. In both remediation mechanisms, oxygen transport in the saturated zone plays a key role. Although the exact nature of the saturated zone vapor phase is not completely understood, Ardito and Billings (1990), as well as Brown and Fraxedas (1991), theorize that sparging creates air bubbles which move through the groundwater to the unsaturated soil analogous to bubbles in an aeration basin whereas Middleton and Hiller (1990) describe the movement of air through irregular pathways in the saturated zone and ultimately to the surface of the water table as discrete pockets of air. The nature of the air sparging physics will determine the effectiveness of mass transfer to and from the groundwater regime.

Transfer of oxygen to the groundwater or dissolution of volatiles from groundwater would be expected to be related to bubble volume to total air volume ratios than continuous irregular pathways of air flow.

SITE EVALUATION

The transport and fate of organic contaminants in the subsurface environment continues to be the subject of major research efforts. Although the behavior of non-aqueous phase contaminants in the subsurface and unsaturated flow is not yet fully understood, some very useful descriptions are available including those by Mercer and Cohen (1990), USEPA (1989) and Lyman, Reidy and Levy (1991).

Contaminants released to the subsurface environment are acted upon by numerous forces that influence the degree and rate at which they migrate from the source or point of release. The extent to which the released products partition into the vapor phase is influenced by: the quantity of product released; time over which the release took place, or since the release occurred; contaminant physicochemical properties; soil characteristics; and the nature of the subsurface environment.

Physical Factors

Critical to the application of SVE technology is the ability to achieve adequate vapor flow through the contaminated zone. Vapor flow rates are dependent upon soil characteristics such as porosity, moisture content, and permeability, as well as the gas viscosity, density, and pressure gradients.

Coarse-textured, highly permeable soils are best suited to SVE application although SVE can work successfully in fine textured soils, where interbedded permeable layers exist or macropores and secondary structure exist. High vacuum systems have been used to remove volatiles and groundwater in very slowly permeable soils. Soil water content has a significant effect on the air permeability. In general, higher water contents reduces the air-filled porosity thereby decreasing the connected pores through which air can flow by advection. SVE is generally more successful at lower moisture contents since high water content reduces the air-filled porosity available for airflow.

Since air permeability will control the decision to implement SVE or bioventing technology at a contaminated site to a large degree, the importance of the air permeability measurement or estimation technique is evident. Numerous methods have been advanced for determining soil-air permeabilities for sites at which SVE techniques might be applied. Some SVE technology vendors utilize proprietary air permeability test methods for estimating cleanup times and establishing system design criteria.

Contaminant Factors

The physical and chemical properties of the contaminant affects its movement and ultimate fate soil micropores. The degree to which the contaminant partitions into the vapor phase is described by the contaminant's volatility, its tendency to become sorbed to soil particles, and its ability to dissolve in pore water. The contaminants distribution between product, soil particles, pore water, and pore gases will vary over time in response to weathering.

SVE has the ability to remove soil vapors resulting from the spill, disposal, or leakage of non-aqueous phase liquids (NAPLs). Those NAPLs with densities less than water are termed light LNAPLs whereas those denser than water are termed DNAPLs. LNAPLs float on the water table and DNAPLs may sink through groundwater and hence have also been described by the terms floaters and sinkers. Although the density of the NAPL product will affect the redistribution in the subsurface environment, numerous other soil factors enter into the behavior of these products. In many cases, the NAPLs will not behave as conceptually depicted due to soil macropore flow or discontinuities. Floating DNAPLs may therefore be present under some conditions.

Weathering changes the nature of a chemical mixture after its release into the environment. The product composition will change over time and affect the ease with which that product may be removed via SVE. The more volatile, soluble, and degradable compounds will be subject to removal from the mixture initially, leaving the resultant mixture relatively richer in less-volatile, less-soluble, and more-refractory compounds. As SVE progresses and volatile fractions are removed ganglia, or isolated globules of product may form in soil pores. These globules of product may develop resistant skins which slow diffusion of vapors to the soil pores. Highly weathered petroleum products may therefore require implementation of enhanced SVE approaches.

Perhaps the most important contaminant characteristic affecting the applicability of soil vapor extraction is its volatility. Vapor pressure and Henry's Law Constant are used to describe this tendency. Vapor pressure is the force exerted by the vapor of the chemical in equilibrium with its pure solid or liquid form. Henry's law governs the volatilization of a solvent from an aqueous solution, rather than from a pure product. Henry's Law Constant is a more appropriate partitioning constant for evaluating partitioning outside of the free product zone, where product is likely to exist in solution with pore water. Compounds with Henry's Law constants above 0.01 (dimensionless) will tend to move from the aqueous to gaseous phase and will be acted upon by SVE systems (4). Comprehensive discussion of Henry's Law constants vapor pressure as well as other important physicochemical properties of compounds and methods for estimating chemical properties can be found in Lyman, Reehl and Rosenblatt (1990).

Sorption of contaminants to soil particles and organic matter will influence distribution and movement of released products. Organic carbon, being the most effective soil component with respect to organic sorption, is generally used in equations used to predict partitioning of contaminants between soil and aqueous phases. As the soil organic content increases, sorption of most organic product increases.

The product's solubility controls the degree to which a product dissolves into groundwater and pore water present in the vadose zone. Soluble products are more likely to dissolve in infiltrating precipitation and migrate from the source.

SVE APPLICABILITY ASSESSMENT

Although SVE and bioventing are often implemented without conducting pilot studies, the data obtained through field piloting is invaluable in developing full system design. Pilot programs may be as simple as conducting air permeability tests at a potential SVE site. Such a test provides critical site specific data which allows for an effective full scale system design.

The air permeability of the soil is perhaps the single most important soil parameter with respect to the success of vapor extraction. The permeability incorporates the effects of several soil and vapor characteristics. Among the important soil characteristics to be considered are the stratigraphy, air-filled porosity, particle size distribution, water content, residual saturation, and the presence or absence of macropores or preferred flowpaths; important product characteristics include the vapor viscosity and vapor density. Soil-air permeability plays a key role in determining SVE applicability and also in system design. The soil-air permeability incorporates many soil characteristics including porosity, structure, grain size distribution, water content, and preferred flow paths.

Soil-air permeability may be estimated from known physical characteristics of the soil sample, such as the grain size distribution or saturated hydraulic conductivity (14). Massman (1989) discusses the use of a correlation between both soil grain size distribution analyses or saturated hydraulic conductivity and soil air permeability. These methods do not account for decreases in the air permeability due to increased moisture contents or vice versa, nor do they account for in situ bulk density, soil structure, or heterogeneity of the subsurface soils.

The use of saturated hydraulic conductivity values to estimate air permeability is subject to several additional sources of error including soil moisture content, swelling soils, and gas slippage. Both air permeability and saturated hydraulic conductivity are influenced by the soil water content and hydraulic conductivity generally increases while air permeability generally decreases as the water content of a soil increases. Correlation of saturated hydraulic conductivity values and air permeability would not be expected to be valid for soils with an appreciable expandable clay content. The “slippage” of gas as it passes along the soil pore wall is commonly known as the “Klinkenberg effect”. This phenomenon accounts for greater soil-air permeabilities than the aqueous permeability at low flows in fine grain soils. Correlation methods provide a quick means of assessing the relative permeability of soil but are generally not appropriate for SVE system design criteria development.

In situ field soil-air permeability methods rely on measuring the difference between the ambient atmospheric pressure and the soil-air pressure during vapor extraction. The methods used for SVE evaluations are modifications of oil field natural gas pressure build-up and drawdown tests. Johnson et. al. (1990 a&b) developed a soil-air permeability test for SVE evaluations which is similar to the oil field drawdown gas permeability test. The drawdown, or vacuum pressure, is measured in a monitoring point at a known distance from the vapor extraction well, while extracting vapors at a constant rate. Soil-air permeability is estimated graphically from field data by calculating the slope of the regression line that relates gauge pressure, measured at a sample probe well to the natural logarithm of the time, from the initiation of vapor extraction. All of the parameters used to estimate permeability are measured in the field with the exception of the dynamic viscosity of air which is estimated as a function of air temperature.

Soil-air permeability determination using the method suggested by Johnson et. al. (1990 a&b) assumes that as the time from initiation of soil vapor extraction increases, the vacuum pressure in the subsurface increases (i.e., the absolute pressure becomes more negative). The time interval over which air permeability measurements are made should be long enough to extract at least one pore volume of air, yet short enough not to be hampered by: variations in atmospheric pressure, and effective porosity changes that occur after rainfall and when soil air moisture condenses and evaporates during diurnal temperature changes. Because

it is often difficult to maintain a constant vapor extraction rate during SVE operation, variations in the vapor extraction rate should be recorded and used when evaluating data. The sensitivity of the air permeability measurement will be reduced as the variations in the vapor extraction rate increase. Permeability values should be measured at a number of locations around the vapor extraction well and then averaged to provide a reasonable estimate of the areal variability soil air permeability.

Air permeability tests are relatively simple procedures similar to groundwater pumping tests. A vacuum (or sometimes positive pressure) is applied to a vapor extraction well screened in the vadose zone. The pressure distribution, which is established in the subsurface due to the application of the vacuum, is measured by collecting soil pressure data from probes located at various horizontal and vertical distances from the extraction well. Knowledge of the soil pressure data is used along with the pressure at the extraction well to calculate a soil-air permeability.

In addition, trailer mounted SVE pilot units may be used for full scale treatment unit at sites where the volume of contaminated soil is small and the cleanup time is short. Many retail gas station sites fall into this category and trailer mounted systems which allow everyday business activities to continue uninterrupted at the site. The units are also useful on a pilot scale in cases where data concerning contaminant removal rates are needed before proceeding with full scale design.

TRENDS

SVE has found widespread application for remediation of soils impacted through the release of gasoline and other petroleum products from underground storage tanks. SVE systems will find wider application to complex subsurface conditions as a better understanding of vapor flow physics and contaminant fate is gained. Models for subsurface vapor flow prediction will continue to become more sophisticated and provide needed tools for understanding soil/vapor/contaminant behavior. Advances in analytical and field investigation approaches will allow for more accurate assessment of contaminant transport and clean up attainment evaluation will be advanced through the use of innovative statistical techniques.

Horizontal well systems and high vacuum techniques will continue to expand SVE application to more restrictive subsurface conditions. Subsurface modification by pneumatic fracturing and bioaugmentation will also be applied at an increasing number of sites in the future. Steam injection, subsurface radio frequency, or other radiation sources to effect increase volatilization, and the use of gases other than ambient air will broaden the types of contaminants that will be amenable to removal by SVE. Advances in discharge air treatment technologies will allow for SVE implementation in areas where regulatory discharge limitations previously restricted SVE technologies.

The overall trend in SVE is towards increased sophistication in the assessment of subsurface conditions, simplification of system design, coupling of treatment technologies and application to increasingly complex situations.

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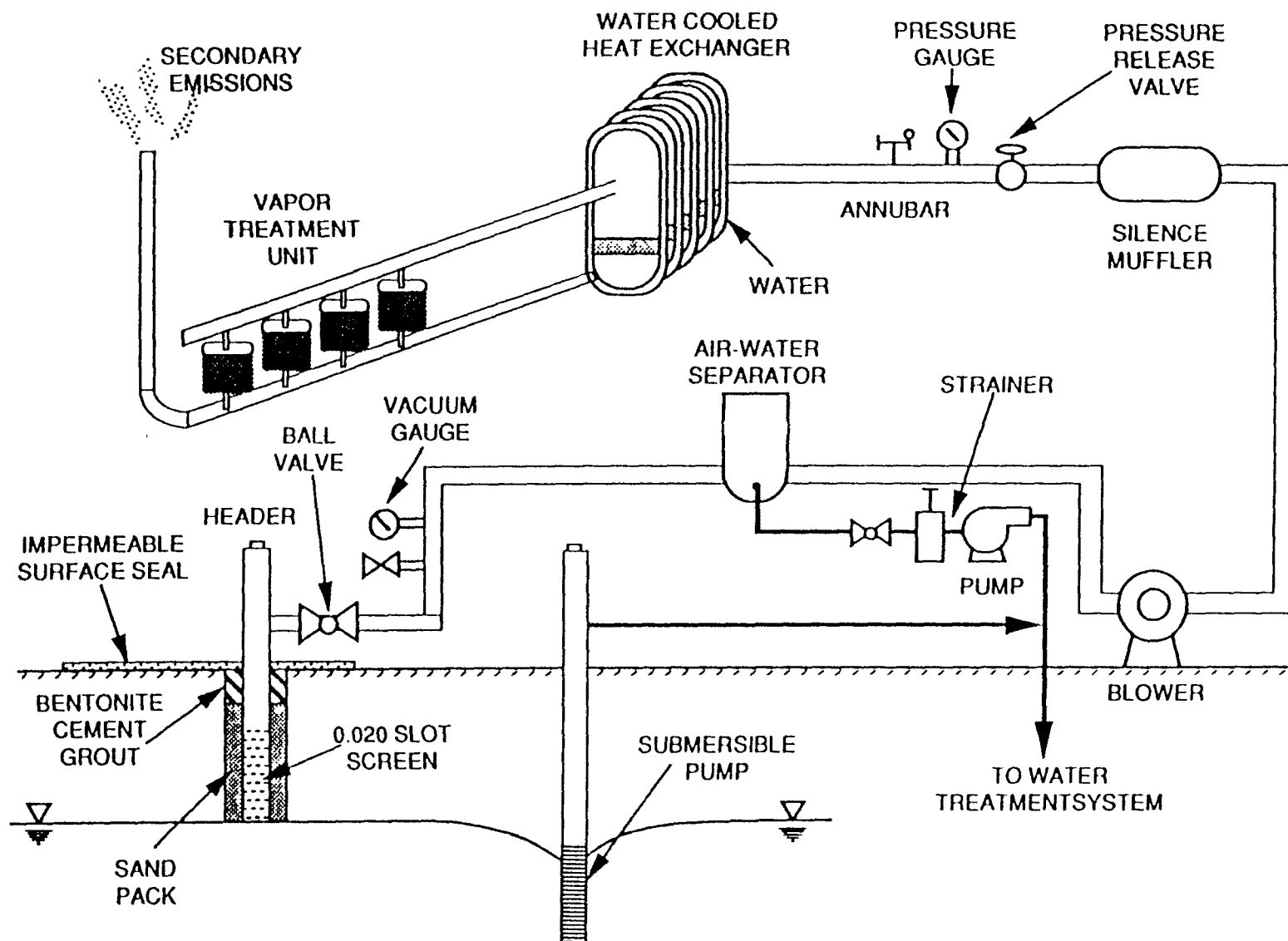


Figure 1. Soil Vapor Extraction System Schematic

SOIL, SITE, AND WASTE CHARACTERISTICS CONTROLLING THE VOLATILIZATION OF ORGANIC CONTAMINANTS IN THE VADOSE ZONE

R. RYAN DUPONT

Utah State University

ABSTRACT

Soil vacuum extraction (SVE) has found wide application in the in-place treatment of fuels and solvent contaminated soils, but its effectiveness and limitations under a wide range of soil/site/waste conditions is not well understood. The fate of hazardous contaminants subjected to this remediation alternative is controlled by the complex interaction of physical, chemical and biological process taking place under vacuum induced flow conditions. The overall effectiveness of conventional high rate SVE systems is determined in large part by the tendency of soil contaminants to move into the vapor phase, a property which is described by a contaminant's vapor pressure, aqueous solubility and distribution among the various compartments existing within the vadose zone. The physical performance of an SVE system, i.e., its ability to provide contact between extracted soil gas and the contaminated soil zone, also impacts the overall efficiency of site remediation using SVE, and is limited by subsurface heterogeneities in both soil and contaminant distribution.

Fundamental soil, site and waste characteristics that impact both constituent volatilization and vapor flow through soils will be reviewed. Particular emphasis will be placed on a discussion of mass transfer limitations that may result from these subsurface heterogeneities. The potential magnitude of such transfer limitations will be presented, and practical field methods for the identification of potential limitations to SVE system performance will be reviewed as they relate to system design, and operation for optimal site remediation.

THE EFFECT OF MOISTURE ON ADSORPTION OF TRICHLOROETHYLENE VAPOR ON NATURAL SOILS

KAROL J. OJA¹, DAVID K. KREAMER²

¹ Salt River Project, P.O.Box 52025, Phoenix, AZ 85072

² Director, Water Resources Management Program,
University of Nevada, Las Vegas; Las Vegas, NV 89154-4029

ABSTRACT

The vapor sorption of trichloroethylene (TCE) on three recompacted natural soils at various moisture contents ranging from air dried to 20% ($\text{gH}_2\text{O/gsoil}$) was determined at room temperature using a static adsorption procedure. Vapor uptake on the soils was determined at a single initial concentration of 97.8 ppb TCE in nitrogen. Soil-vapor partition coefficients for the air dried soils were observed to be a factor 2-4 times greater than that for the moist soils. Above 5% water content, the TCE partition coefficient was found to be relatively independent of the degree of saturation. The observed increased adsorption of TCE vapor on dry natural soils suggests that optimal design of vapor leak detection systems in unsaturated subsurface environments, such as those used around underground storage tanks should use models based on dry soils. This is because the greater vapor adsorption exhibited in dry environments would constitute a conservative estimate of vapor migration and the effectiveness of vapor monitors.

INTRODUCTION

An understanding of adsorptive processes in natural soil environments is an important parameter in describing contaminant transport in soil and ground water. Although a considerable amount is known about the sorptive behavior of organic contaminants in aqueous solutions or saturated soils (13, 24), and dry adsorbents with no free liquid water content (5), much less is known about sorption reactions of gaseous pollutants in unsaturated soils. Such reactions, however, are of considerable significance because a large class of groundwater contaminants are volatile organic compounds (VOC's), which can readily distribute between the liquid phase in saturated soils and the vapor phase in unsaturated soil regions (22). Understanding the transport and fate of these chemicals in unsaturated zones has become increasingly important in recent years.

Soil-gas surveys, designed to measure VOC vapor in the soil atmosphere in unsaturated zones, are gaining wide acceptance as a tool for delineating subsurface contamination by VOC's (17). A knowledge of the factors affecting vapor-soil adsorption in unsaturated zones is necessary to accurately describe the diffusive flux of gaseous pollutants that can move into unsaturated porous media from, for example, contaminated groundwater, leaking underground storage tanks, or hazardous waste sites. Determination of such vapor

phase interactions may have significant implications for effectively detecting or monitoring chemical leaks from potential sources of contamination.

In saturated soils or aqueous solutions laden with sediment, uptake of nonionic organic compounds has been correlated to essentially two parameters: 1) degree of compound hydrophobicity (or aqueous solubility) and 2) the fraction of organic carbon or organic matter associated with the soil or sediment (22, 14). Isotherm linearity over a wide range of relative concentration is characteristic in this situation, and it is arguable as to whether partitioning into soil organic matter or linear adsorption is the mechanism responsible for the uptake from aqueous systems (3, 18). In unsaturated soils, uptake of organic vapors may be controlled by the mineral fractions and also by competitive effects between water and organic vapors for adsorption sites on mineral surfaces. Recent experimental studies (2, 4) which determined the organic vapor adsorption on natural soils at various humidities indicate that at least two different uptake mechanisms are involved. For example, isotherms determined for a natural soil under dry and low humidities are distinctly nonlinear, however, at high relative humidities the isotherms are linear over a wide range of relative concentration. Furthermore, isotherms of organic vapor on soil humic acid (i.e., pure humic acids with no mineral fraction present), a major constituent of soil organic matter, are linear. These findings imply that adsorption of organic vapors on mineral matter is important for dry soils or soils of relatively low moisture contents. These results also provide more conclusive evidence of a partitioning process to explain uptake of hydrophobic compounds in wet soils. Because of the large surface areas provided by soil minerals, markedly greater sorptive capacities are observed for dry soils compared to that for saturated soils. Specifically, solid-vapor partition coefficients have been found to be several orders of magnitude greater than corresponding solid-liquid coefficients (22). This finding suggests that vapor-soil interactions can be of considerable significance in describing contaminant transport in unsaturated zones.

The purpose of this work was to determine from a series of experiments, effective adsorption parameters of a selected pollutant vapor, trichloroethylene, for three recompacted natural soils under varying degrees of water content. Trichloroethylene was selected for this study because it is one of the most commonly found groundwater contaminants in the U.S. It has been detected in highest concentration and greatest frequency in several states surveyed (9). It is widely used as a degreaser in the semi-conductor industry. TCE is of environmental concern because it is a suspected carcinogen.

THEORY

Understanding the effects of moisture on adsorption becomes critical when considering the movement of gases through natural soils. Diffusive transport equations usually contain a "lumped parameter" called the Effective Diffusion Coefficient, and this coefficient in turn contains, either explicitly or implicitly, a sorption term.

Weeks, et al. (1982) described gaseous diffusion theory in a three-phase medium, in one dimension with a modified form of Fick's second law by replacing the general diffusion coefficient D with an effective (apparent) diffusion coefficient D' :

$$D' = \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \quad (1)$$

where C is the concentration of vapor (g/cm^3), x is distance (cm) and t is time (sec). D' (cm^2/sec) can be described in a non-reactive media by (Weeks et al., 1982):

$$D' = \frac{\tau \theta_D D}{\theta_D + (\theta_T - \theta_D) \rho_w k_w + (1 - \theta_T) \rho_s k_s} \quad (2)$$

where τ = the tortuosity factor accounting for the added resistance to diffusion imposed by the structure of the porous medium (dimensionless). θ_D = drained or gas-filled porosity (dimensionless), θ_T = total porosity (dimensionless), ρ_w = density of water (g/cm^3), ρ_s = particle density of granular material making up solid matrix (g/cm^3), k_w = liquid-gas partitioning coefficient (often taken as the Henry's Law Coefficient) that describes the ratio of the concentration of the gas under consideration in solution to its concentration in overlying gas phase under equilibrium conditions, (moles/gm water ÷ moles/ cm^3 gas), $k_s = k_w k_D$ = gas-liquid-solid distribution product describing the ratio of the moles of the gas under consideration sorbed on the solid phase per unit mass or solid phase to the concentration of the gas in the soil atmosphere (moles/g solid ÷ moles/ cm^3 gas), and k_D = solid-liquid distribution coefficient describing the ratio of the moles of solute under consideration sorbed on the solid phase per unit mass of solid phase to the concentration of the solute in the water (moles/gm solid ÷ moles/gm water).

In the more generalized form of Fick's second law appearing in equation (1), it is assumed that the liquid phase is immobile and completely wets the solid phase, and rapid (immediate) equilibration occurs between the gaseous phase and the dissolved and sorbed concentrations in the liquid and solid phases. This also means that it is assumed the gaseous diffusion through the liquid film prior to sorption on the solid phase is essentially instantaneous with respect to the overall diffusion process (26). Recent studies have shown equilibration to take approximately ten minutes for the VOC's to absorb onto soil (12).

Kreamer (1982) analytically solved the three-dimensional form of equation (1) for a point source which continuously emits a vapor at a constant rate. The solution for a given radial distance from a gaseous source, and at a known time after vapor emission began is

$$C = \frac{q}{4\pi D' A_r} \operatorname{erfc} \sqrt{\frac{r^2}{4D't}} \quad (3)$$

where C is the concentration of vapor (g/cm^3), q is a constant vapor release rate (g/sec), A is the denominator of D' (dimensionless) called the Sorption-Corrected Porosity, r is the radial distance from the source (cm), erfc is the complimentary error function, t is time (sec) since release began, and the other parameters are as defined before.

A graphical curve match procedure for calculation of D' and A from a field tracer test was developed by Kreamer (1982) and expanded upon by Kreamer et al. (1988). This technique is analogous to Theis curve matching for the inverse solution of the basic groundwater equation. It provides a means of field testing for determination of diffusive properties of a given site, just as the Theis equation provided, by means of a pumping well test, a way to determine aquifer properties. Laboratory procedures, used in this study, were developed (12), to verify the "lumped parameters" obtained by field tracer tests. Laboratory sorption tests

for organic vapor adsorption on unsaturated soils provide a means of calculating the subcomponents of the Effective Diffusion Coefficient.

The effect of adsorption of organic vapors on soils does not only impact transport equations, adsorption itself can be modeled. Crittenden et al. (1989) described thermodynamic adsorption models for gas-phase adsorption equilibria of solvent vapors in unsaturated media. These researchers used the models to predict single component adsorption capacity, competitive interaction between VOC's and water vapor, and competitive interaction between individual VOC's. Single component adsorption equilibria was described using the Dubinin-Radushkevich equation (1947), which is based on the Polanyi potential theory. Crittenden et al. (1989) extended the Polanyi potential theory to predict multicomponent adsorption equilibria. Ideal absorbed solution theory has also been used to describe binary and ternary gas-phase adsorption system using single solute isotherm data (19, 23).

In the experiments associated with this paper, adsorption of a single solvent vapor was measured on natural soils at high moisture contents. In order to simulate real-world condition, these soils had free water contents ranging from just under 2% to 20% by weight. Much previous work has been done on competition between VOC's and water vapor at various humidities in the very dry range of free water content. While this approach is applicable to a variety of chemical engineering problems, including the adsorption of gaseous compounds on granular activated carbon, it has poor applicability to gaseous movement through unsaturated natural soils.

It has been recognized the adsorption of VOC's in the presence of water vapor is unlike single component or multicomponent (competitive) adsorption of several VOC's. Okazaki et al. (1978) proposed a model to predict the effect of competition between VOC's and water vapor. The model was based on the idea that organic gases adsorbed in an unsaturated medium, have three unique components. These components are: (1) adsorption on "dry" surfaces, (2) absorption on "wet" surfaces, and (3) dissolution into liquid capillary water. Total adsorptive capacity is then said to be the sum of these three mechanisms (5).

However, for very wet soils the analogy is questionable as VOC loading on "dry" surfaces may be minimal. In Okazaki et al. (1978), the VOC loading on dry surfaces is determined using the Dubinin-Radushkevich equation. This equation has the form:

$$Q = \left[\frac{W_o \rho_1}{10^{-3}} \right] \exp \left[\frac{-B}{\beta^2} \left\{ RT \ln \frac{P_o}{P_f} \right\}^2 \right] \quad (4)$$

where Q = concentration of gas adsorbed onto the solid phase (mg/g solid), W_o = the maximum adsorption space on the adsorbent (cm^3/g solid), ρ_1 = the liquid density of the pure adsorbate (g/cm^3), B = the microporosity constant of the adsorbent ($\text{mol}^2/\text{cal}^2$), β = the affinity coefficient of the adsorbate (dimensionless), R = the gas constant ($1.987 \text{ cal}/\text{mol } ^\circ\text{K}$), P_o = saturation vapor pressure of solute (atm), P_f = equilibrium partial pressure of solute in the gaseous phase (atm), and T = temperature ($^\circ\text{K}$). Dubinin (1965) has shown that the affinity coefficient, β , and the maximum adsorption space, W_o , are properties of the absorbent (in this case the soil), and are independent of temperature and adsorbate.

Okazaki et al. (1978) were concerned with water vapor competition with organic vapors for adsorption sites. Any regions of water condensation were treated with a Henry's law approximation of organic vapor dissolution into the aqueous phase. While in dry adsorbents this factor has sometimes been found to be negligible (5), the wetted soils of this study were projected to dissolve approximately half the vaporous adsorbate in many cases (20).

The adsorptive capacity of organic vapors onto "wetted" pore walls is usually estimated from an aqueous phase isotherm. The total adsorptive capacity is then the sum of: (A) the Dubinin-Radushkevich predicted loading multiplied by the dry area fraction; (B) the Henry's prediction of the aqueous VOC concentration times the water volume; and (C) the amount predicted from an aqueous-phase isotherm times the fraction of wet surface area.

The partitioning of TCE in this study is described by a single partitioning coefficient, K_a , defined at a known temperature as:

$$K_a = \frac{Q}{P/P_o} \quad (5)$$

where K_a is the equilibrium soil-vapor adsorption (mg VOC adsorbed/g soil ÷ mg of VOC in gaseous phase/g of VOC in vapor phase at saturation) and the concentration of adsorbed gas on the solid phase, Q , and the relative vapor concentration P/P_o are as defined previously. The use of this single partitioning coefficient, does not include the extensive computation (and associated error in estimation) of parameters required in the more rigorous and descriptive approach by Okazaki et al. (1978).

The use of a single partitioning coefficient, K_a to describe both adsorption onto the solid-phase and dissolution into liquid capillary water would reduce Equation (2) to

$$D' = \frac{\tau \theta_D D}{\theta_D + (1 - \theta_T) \rho_{sw} k_a} \quad (6)$$

where ρ_{sw} is a weighted average density of the combined solid and liquid phases.

EXPERIMENTAL METHOD

Vapor Sorption Apparatus

The method used in this work to determine vapor phase adsorption coefficients was a static adsorption method developed by Houston et al. (1989) in which the adsorbent was placed in a chamber, the adsorbate gas introduced, and the chamber isolated to achieve a static equilibria between soil and vapors. The equilibrium vapor phase concentration in the soil chamber was measured by a direct injection of the vapor into a gas chromatograph.

Measurement of the vapor phase sorption of a selected organic compound onto dry and partially saturated soils was carried out by a static equilibrium adsorption apparatus at room temperature (Fig 1). The test gas, a commercially prepared mixture of TCE in nitrogen, was connected by stainless steel tubing (0.635 cm o.d.) to a series of 34mm x 60mm (inner dimensions) stainless steel solid chambers that housed the sample. The entire system was evacuated (down to 10^{-3} Torr) by a vacuum pump connected to the system. The test compound was brought to contact with the soil sample at a constant pressure, which was controlled by a regulator at the vapor source. The sorption chambers were then isolated from the system by closing valves designated V3, V5, etc. to attain a static equilibria between vapors and soil.

Several concentrations of the commercially prepared TCE vapor were obtained, so that when needed, the concentration of vapor could be varied. To do this, the test gas source was disconnected from the system at the regulator and replaced by a source with different vapor concentration. Amounts of the organic vapor adsorbed by the soil samples were determined by the difference between initial and final TCE concentrations in the gas phase of the soil chamber. Soil-vapor adsorption coefficients were calculated from the resulting data.

Some of these important physicochemical properties for TCE are listed in Table 1.

Table 1. Physicochemical Properties of TCE

PROPERTY	VALUE
Structural Formula	$\text{ClHC}=\text{CCl}_2$
Molecular Weight	131.39
Boiling Point	87°C
Vapor Pressure	71mm Hg ^a
Solubility	1100mg/l ^b
Henry's Law Constant	619 atm
Dipole Moment	0.77 ^c

^aValue at 24°C from Weast (1986).

^bValue at 25°C from Dean (1987).

^cValue at 30°C from Dean (1987).

The equilibrium vapor phase was measured by a direct injection procedure. This was accomplished by allowing the equilibrated gas to expand and fill a Valco 10 port sample valve (connected to the soil chamber by 0.159 cm o.d. stainless steel tubing) of known volume and temperature directly to a chromatograph column. Once filled, the vapor was then swept by a flow of nitrogen carrier gas into a gas chromatograph and analyzed. This sampling methodology has been previously developed and described elsewhere and was only slightly modified in this study. Changes to the apparatus included the addition of a sample blank used as a control in the sample analysis, addition of a cold trap to keep the vacuum system clean, and replacement of filter paper by a metal filter gasket to contain soil particles during evacuations. The gas samples were analyzed for TCE with a Perkin Elmer Sigma 300 gas chromatograph with a column of 10% SP21-- on 80/100 Supelcoport (Supelco, Inc.) operated isothermally at 135°C. Both ⁶³Ni electron capture and flame ionization detectors were used for the analyses.

The basic soil chamber design was previously developed (15) and an extensive study on the best choice of materials to use for these chambers in adsorption measurements was conducted by Houston et. al. (1989). To ensure containment of soil particles during evacuation of the soil chamber, filter paper was placed between the gasket and the top of the soil. However, difficulties were encountered with the filter paper “bulging” as a vacuum was drawn and was especially a problem with soils of finer particles (<50 μ). The problem was remedied by replacing the filter paper with a filter constructed from copper metal and copper wire mesh.

All pressure measurements are made with either an Ashcroft or Matheson pressure gauge (designated as G1 in Fig. 1). The valves were stainless steel. All fittings were stainless steel. A liquid nitrogen trap was added to the vacuum system to reduce contamination from pump oil and grease.

The test compound was derived from a mixture of TCE vapor and nitrogen prepared and analyzed gravimetrically by Scott Specialty Gases. The TCE concentration employed for this study was a standard 0.0978 ± 0.005 ppm by weight.

The Area 5 Alluvium, Desert Rock, and Clay soils (<40 mesh fraction) used in this study were from the same batch employed in a previous sorption study by Houston et. al. (1989). In the previous study, the mineralogic content of the soils was obtained. Houston et. al. (1989) also estimated the surface areas of these soils. This was done by computing the ratios of the surface areas of the soils from the ratios of the adsorption coefficients determined for air-dried soils. In their experiments, adsorption coefficients for the above soils and a sand were measured. The adsorption coefficient ratio was computed comparing these soils with that for the sand. Then, from the surface area of the sand, which was estimated assuming a spherical shape, the surface areas of the soils were computed. A list of all adsorbents used in this study and their estimated surface areas and soil classifications are presented in Table 2.

A soil compaction procedure was performed on the three natural soils: Area 5 Alluvium, Desert Rock, and Clay. Also, the water content was varied. The soils were compacted in the chambers to obtain a desired bulk density to replicate a field condition. A procedure developed by Houston et al. (1989) to obtain the partially saturated soils and bulk densities was followed. The desired volume of deionized water was added and mixed with the soil prior to compacting the sample in the sorption chamber. A final water content was measured immediately following each experiment to take into account evaporative losses during compaction of the soil and evacuation of the sorption chamber. Air dried Areas 5 Alluvium, Desert Rock, and Clay soils contained about 2.5, 1.5, and 2.4 percent moisture, respectively.

Table 2. Adsorbent Properties

ADSORBENT	MESH SIZE	ESTIMATED SURFACE AREA (cm ² /g)	SOIL CLASSIFICATION
Area 5 Alluvium	<40	620 ^a	Silty Sand
Desert Rock	<40	900 ^a	Sandy Loam
Clay	<40	1360 ^a	Clay

^aHouston et. al. (1989)

Adsorption Measurements by Direct Injection Technique

The test compound was brought into contact with soil by the following operations (referring to the apparatus in Fig. 1):

- 1) The test gas was regulated to a constant absolute pressure of 200 kPa (2.0 atm) according to pressure gauge, G1, and then valve V1 was closed.
- 2) The system from valve V1 to V8 was evacuated. The sorption chambers were evacuated separately from the system with flow out of the chamber through valves, V2, V4, etc.
- 3) Valve V1 was opened which refilled the system with test gas to 200 Kpa of total pressure up to valve V8. The gas was brought in contact with the soil by opening valve V3 for 15 seconds. A reduced exposure time was kept to minimize diffusion of vapors into the soil chamber, which may occur as a result of immediate adsorption. The system was then evacuated and refilled again with test vapor and the next soil sample was exposed to the gas by opening V5, etc. The adsorbent and vapor were equilibrated for 12 hours or more. To measure the vapor phase equilibrium TCE concentration in the soil chamber, the gas was expended by opening valves V3 or V5 etc. into a previously evacuated sample loop of known temperature and volume and then swept by a nitrogen carrier gas into the gas chromatograph and analyzed. The pressure drop resulting from the volume expansion was recorded by pressure gauge, G1. The pressure drop was about 50 Kpa (0.5 atm) in normal runs. To determine whether expanding the equilibrated gas into a relatively large volume (40-80 percent of chamber volume) caused significant desorption, the expansion volume was reduced to a minimum allowed by the system which resulted in a corresponding pressure drop of 10 kPa (0.1 atm).

Standard calibration curves were established before each set of soil gas analysis by directly injecting a given concentration of test gas as a function of pressure and plotting the number of moles of test compound versus peak area. This was done by evacuating the sample loop and filling with test gas at some known pressure according to gauge G1 and then analyzing the solute at that pressure. The procedure was repeated for different gas pressures. If the soil gas peak area was not within the range of the curve, a different test vapor concentration was connected to the system and a new calibration curve was generated. Due to the large concentration range studied in associated experimentation (6 orders of magnitude), it was necessary to employ two detectors because it was not practically feasible to sufficiently dilute the gas in order to stay within the dynamic range of one detector. As a result, lower concentrations (0.0978 and 1.2 ppm) were analyzed with an electron capture detector and higher concentrations (10.5, 109, 1070, and 5010 ppm) were analyzed using a flame ionization detector which has a lower sensitivity for the test compound. Standards were run in duplicate. During all evacuations, the system was flushed several times with high purity nitrogen to thoroughly clean sample loop and line. Also, blanks of pure nitrogen were run to ensure the sample loop and line were clean.

To determine the amount of adsorption on the chambers walls, an empty soil chamber was evacuated, filled with test gas, and then analyzed following the same procedure as described above.

RESULTS AND DISCUSSION

Vapor Sorption on Natural Soils

Equilibrium soil-vapor partition coefficients were determined for the vapor phase uptake of TCE on Area 5 Alluvium, Desert Rock, and Clay soils at various water contents, ranging from air-dried to 20% (g H₂O/g soil). For these experiments on natural soils, the direct injection technique (described earlier) was used to determine the equilibrium TCE concentration in the soil gas. All sorption determinations were made from a single, initial TCE concentration of 97.8 ppb. The experimental data obtained from these experiments are tabulated in Oja, 1988. From these data, the equilibrium partition coefficient, K_a , as defined by Equation (5) was computed. Values of K_a for the soils at each water content are given in Table 3.

The error in the calculation of K_a was estimated from standard error propagation methods. On average, the standard deviations are about 20% of K_a . The difficulty associated with obtaining and measuring accurate water contents is manifested by inconsistencies in the void volume, which are greater at higher water contents. The error in the void volume was evaluated by comparing the calculated void volume, determined from the difference in the total system volume and the combined solid and water volume with that computed according to the pressure drop during expansion of the gas. This latter volume was calculated based on an average value of the expansion volume determined for the dry soils and the pressure volume relationship for an ideal gas. The average of these two volume determinations was used in computing K_a . The void volume discrepancies do not affect trends in the partition coefficient, however, they do contribute substantially to the uncertainty in K_a .

Table 3. Equilibrium Partition Coefficient K_a Describing the Vapor Uptake of TCE on Three Natural Soils as a Function of Water Content.

SOIL	WATER CONTENT (wt%)	K_a (MG/G)
Area 5 Alluvium	<i>Air-Dried</i>	1.4
	5	0.34
	10	0.42
	15	0.60
	20	0.41
Desert Rock	<i>Air-Dried</i>	4.4
	5	0.96
	10	1.0
	15	0.75
	20	0.45
Clay	<i>Air-Dried</i>	3.2
	5	0.71
	10	0.60
	20	0.45

Upon introducing TCE vapor to soil in the sorption chamber, a minimum exposure time was maintained by closing the valve that controlled the flow into the container after 30 seconds. This was done in order to prevent additional vapor from entering by diffusion as a result of a concentration gradient. Such a condition may exist if the adsorption rate is very rapid, however, the amount of TCE that may diffuse into the sorption chamber after 30 seconds as a result immediate adsorption was calculated to be insignificant compared that entering by advection.

A significant reduction in the initial TCE gas phase concentration was observed in these experiments, indicating there is a large uptake by the soil. The data indicate greater than 80% sorption occurring when the initial moles of TCE are compared to the number of moles adsorbed, suggesting that the number of adsorbent sites is still very large relative to the amount of vapor present. Considering the very low partial pressure of TCE ($\sim 10^{-7}$ atm) used in these experiments, the large change observed in the TCE concentration might be expected. At these pressures, linear adsorption may be anticipated.

The effect of water content on the vapor sorption of TCE by Area 5 Alluvium, Desert Rock, and Clay soils at 24°C is illustrated in Fig. 2. In general, the air-dried soils exhibit a greater sorptive capacity for vapor compared to their moist counterparts. For example, the adsorption partition coefficient for TCE onto air-dried Area 5 Alluvium, Desert Rock, and Clay soils was found to be 1.4 mg/g, 4.4 mg/g, and 2.4 mg/g, respectively. Partition coefficients for all moist soils (5-20 percent saturations) were less than or equal to 1 mg/g. Figure 2 shows a plot of K_a as a function of water content for all soils.

The influence of moisture on sorption indicates that water successfully competes for the active adsorption sites on minerals. This behavior is consistent with the fact that adsorption on minerals is enhanced by adsorbate polarity (4). Water molecules may effectively displace the less polar TCE. The results are also consistent with Peterson et. al.(1988) who found that TCE vapor sorption on a synthetic soil is highly dependent on water content. In their study, the partition coefficient for TCE vapor onto an oven-dried porous alumina oxide coated with humic acids was found to be 1-2 orders of magnitude greater than that for 8.2% and 11.6% water contents; the value for 8.2% is 4 times greater than for 11.6%. Results from Figure 2 of the present study reveal that the air-dried soils possess a distinctly greater sorptive capacity for TCE vapor than do the bulk of the moist soils. However, the decrease in adsorption with increasing water content assuming equal distribution is not as pronounced as that found by Peterson et. al. In fact, the variation in K_a from 5 to 20 percent moisture contents is insignificant, given the error in K_a , and this suggests that uptake by the moist soils is essentially independent of water content.

The much greater difference in uptake observed by Peterson et. al. between the dry and moist simulated soil may be explained by the much greater surface area of the soil (206 m²/g) compared to that of soils in this study (0.136 m²/g). For example, an average of a few monolayers of water were estimated to be present on the synthetic surface at 8.2% and 11.6% moisture contents. In comparison, several hundred monolayers of water are estimated to be present on the soils used here for a similar water content (20). These estimates are based on 11.4 Å² as the surface area occupied by a water molecule (11, 22). The latter estimate is also based on the soil surface areas given in Table 3. If the ratio of the partition coefficients for the air-dried natural soils and oven-dried simulated soil is compared to the ratio of the above soil surface areas, the surface areas estimated for the natural soils appear reasonable. A further possibility for the large difference in uptake observed between the synthetic soil and natural soils may be explained if equilibrium between the natural soils and

TCE vapor in the present work was not fully attained. This would result in a lower (relative to that at true equilibrium) measured value of K_a .

Gas-liquid partition coefficients for TCE in water were not experimentally determined in this laboratory, however, the amount of TCE dissolved in water at 25°C was estimated based on Henry's Law

$$P_f = X_{f,l} K_H \quad (6)$$

where P_f is the equilibrium partial pressure of TCE, $X_{f,l}$ is the final mole fraction of TCE in water and K_H is Henry's Law constant equal to 619 atm at 25°C (Table I). The results suggest that a 20 weight percent water content, about half of the measured uptake may be attributed to dissolution (or adsorption at the water interface) in water (20). Since this estimate accounts for only a portion of that observed, and K_a appears to be relatively independent of the degree of saturation above 5% water content, residual uptake may be a result of partitioning into the soil organic phase or adsorption on mineral matter in the presence of water (site specific adsorption).

If it is assumed that residual uptake is predominately a result of partition into the soil organic matter at moisture contents above 5% and that relationships for partitioning in saturated media are analogous to partitioning relationships in unsaturated media, then the fraction of organic carbon associated with these soils may be estimated. For example, under the assumption of negligible mineral uptake, in saturated systems, the soil-liquid partition coefficient, K_p , can be normalized to soil organic carbon ($K_{oc} = K_p/f$ where f is the fraction of organic matter) (2, 13). The K_{oc} value has been found to be fairly constant for a particular adsorbate and valid for a wide range of organic matter content (24). Using as a value for K_p , the average value of the partition coefficient measured in this study for the soils above 10% water content (assuming that K_a is linear) and using a K_{oc} value for TCE of 61 units as reported by Garbini and Lion (1986), the percent of organic carbon contributing to the soil uptake is estimated to be less than or equal to 1% (g organic matter/g soil) for all three soils. The validity of using specified assumptions to make this calculation, however, remain unproven.

The uptake capacities of the air-dried soils appear to be controlled by soil minerals. It might be predicted that the sorptive capacities of a (dry) soil would be different for different soil types largely because of differences in mineralogy. For example, a clay-rich soil would be expected to have a higher uptake than a sandy soil. In a study by Call (1957), the vapor sorption of the ethylene dibromide on two different soil types (0% moisture content) was highly variable largely in response to the clay content. Desert Rock soil contains 17% clay, 19% silt, and 64% sand; Area 5 Alluvium contains 14% clay, 15% silt, and 71% sand; the Clay soil contains 52% clay, 18% silt, and 30% sand by weight (Houston et al., 1989). The Clay soil has 3 times more clay minerals than Desert Rock or Area 5 Alluvium, yet Desert Rock soil was found to have the greatest sorptive capacity for TCE vapor relative to the other soils as Fig. 2 illustrates. Thus, it appears that although the air-dried uptake is affected by soil minerals, a correlation of clay content and soil uptake cannot be made from the samples studied here.

CONCLUSIONS

The sorption on natural soils was found to decrease with an increase in water content indicated by noticeably greater soil-vapor partition coefficients for the air-dried soils compared to moist soils. However, compared

to air-dried, above 5% moisture contents, the uptake was observed to be relatively independent of the degree of saturation indicated by an nearly constant TCE partition coefficient. This effect suggests that above 5% water contents, the surfaces of these soils are fully covered by water and that residual uptake may be controlled by soil organic matter (or specific adsorption sites favorable to TCE in the presence of water). In all cases, a very high uptake was observed by the soils at the low sub-parts per million level of TCE employed.

The greater adsorption of TCE vapor on dry soils suggests that optimal design of vapor leak detection systems in unsaturated subsurface environments, such as those used around underground storage tanks, should use models based on dry soils. This is because the greater vapor adsorption exhibited in dry environments would constitute a conservative estimate of vapor migration. Designs of leak detection systems based on dry soil would therefore underestimate the effectiveness of gaseous monitoring.

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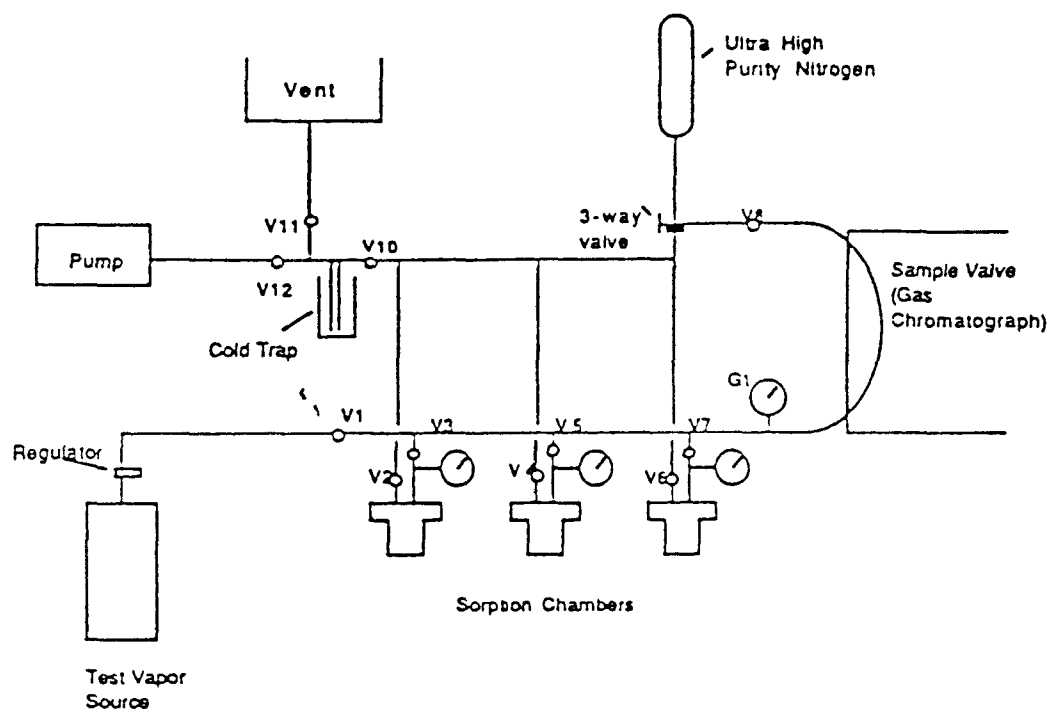


Figure 1. Schematic diagram of the static vapor sorption apparatus.

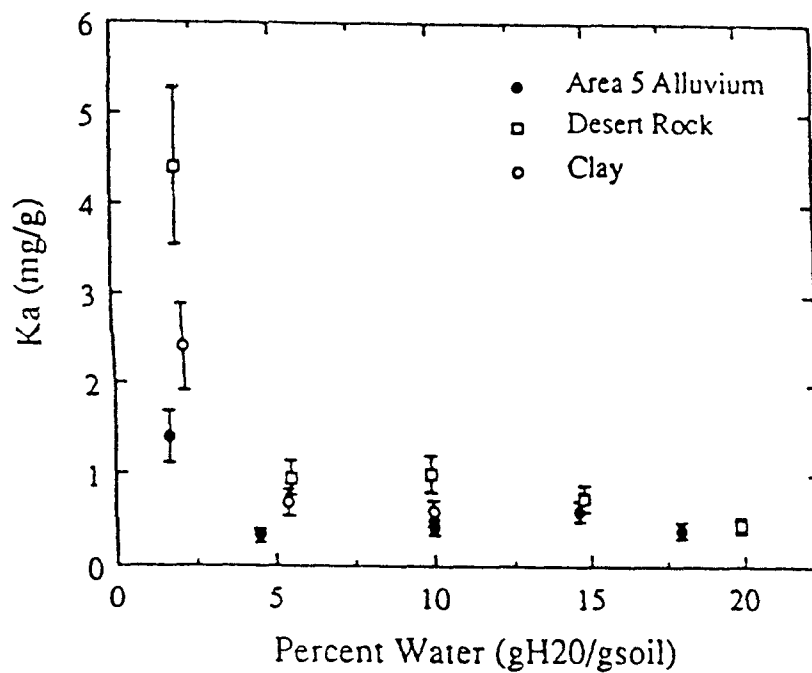


Figure 2. Plot of the soil-vapor partition coefficients for TCE on Area 5 Alluvium, Desert Rock, and Clay soils as a function of water content

USE OF IN-SITU OZONATION FOR THE REMOVAL OF VOCs AND PAHs FROM UNSATURATED SOILS

SUSAN J. MASTEN

Department of Civil and Environmental Engineering
Michigan State University
East Lansing, MI 48824-1326

The contamination of soils has resulted in a complex problem which necessitates novel engineering approaches. In this project we have investigated the applicability of ozone for the oxidation of volatile organic chemicals (VOCs) and polycyclic aromatic hydrocarbons (PAHs) when these chemicals are present in aqueous solutions containing humic acid or in soils.

The oxidation of several PAHs in the presence of humic acid and soils is described. The oxidation of four olefinic VOCs and naphthalene occurred in solutions containing up to 12.0 mg/L humic acid, however, the extent to which each of the compounds reacted is very much compound specific. The effect of pH and ozone dosage on these reactions was considered. The effects of pH were weak for all compounds except trichloroethane. Ozone dosage had a significant effect on the extent to which each of the VOCs and naphthalene was oxidized.

Experiments were also conducted by adding aqueous ozone solutions to soil slurries containing the compound of interest. Complete oxidation of cis-dichloroethylene by ozone (22 mg/L) occurred in solutions containing 1.0 g of Eustis soil suspended in 10.0 mL water. However, only 40% oxidation of tetrachloroethylene was achieved using an ozone dosage of 17.3 mg/L when 1.0 g of Eustis soil was present. Complete oxidation of naphthalene was achieved in solutions of a sandy loam soil (0.4% organic matter) containing 1.0 g of soil suspended in 10.0 mL water. Similar results were also obtained in slurries of Ottawa sand and alumina oxide.

The oxidation of PAHs by ozone in dry soils was studied. Complete removal of phenanthrene from a soil using an ozone dosage of 80 mg/hr for one hour was observed. Chrysene and pyrene were removed to a lesser extent. The work described here suggests that ozone may be applicable for the treatment of contaminated soils and waters containing naturally occurring organic matter.

INTRODUCTION

Vapor extraction (also referred to as in situ air stripping and vacuum extraction) techniques have been developed for the removal of vapor phase contaminants from an unsaturated aquifer (1-5). In order for this technique to be effective, the contaminant must be volatile and not strongly sorbed by the soil particles. With conventional treatment systems, remedial activities can result in gaseous effluents which have concentrations of volatile organic chemicals (VOCs) that are well above that which can be safely discharged into the

atmosphere. While activated carbon units can be added to treat the off-gases, this additional treatment approximately doubles the cost of remediation (6).

To alleviate some of the problems of the conventional system, a modified vapor extraction system has been proposed and is illustrated in Figure 1. The principal design features of conventional vapor extraction system are maintained. However, the major change is that instead of pumping air into the unsaturated zone, ozonated air or oxygen would be used. This would require the installation of an ozone generation system as shown in this figure. Despite the expense involved in the generation of ozone, such a system would have some definite benefits. Ozone, being a strong oxidant, would react with most olefinic and aromatic compounds which might be present. This should alleviate the need for post-treatment of the off-gases, or if treatment were necessary, the excess ozone generated could be used. Additionally, in transport-limited situations, where pump-and-treat technologies might not be feasible, the need to remove the pollutants from the soil system would be negated as the ozone would react with compounds in the subsurface environment. Finally, while capital costs for the ozone generation system are high, since the generation system would outlast the life of the remediation project, such a system could be transported from site to site. This would significantly reduce the costs of using this technique for remediation.

THEORY

Among the types of compounds that could be treated by this modified vacuum extraction system are the chlorinated olefins, such as *cis*-dichloroethylene, trichloroethylene and tetrachloroethylene, the chlorinated aromatics such as chlorobenzene and o-chlorophenol, and the polycyclic aromatic hydrocarbons, such as pyrene and chrysene. The results of work on the treatment of soils contaminated with chlorinated olefins and aliphatic compounds (VOCs), and polycyclic aromatic hydrocarbons are presented here. The chlorinated compounds are commonly used solvents while the polycyclic aromatic hydrocarbons (PAHs) are components found in petroleum products. Both groups of compounds have been identified in many aquifers and in the unsaturated soils in a variety of locations throughout the U.S. (7). The compounds studied are listed in Table 1.

The mechanism of the ozonolysis reaction involving olefins and aromatic compounds has been well studied and is documented in a number of review articles (8-11). This mechanism, also referred to as the Criegee Mechanism, involves a 1,3-dipolar cyclic addition of ozone across the double bond of the olefinic or aromatic compound to yield an unstable intermediate, known as a molozonide. These intermediates rapidly decompose to form aldehydes, ketones and carboxylic acids. In the case of the highly chlorinated olefinic compounds, chlorinated carboxylic acids or ketones may result. These compounds are rapidly hydrolyzed in water to form carbon dioxide and HCl (12). Dreher and Klamberg (1988) studied the ozonation of PAHs. Among the products identified were phthalic acids, carboxylic acids and methyl esters.

For volatile chemicals, the gas phase reactions involving ozone must be considered. However, since much work has been done in this area, and extensive reviews are available (see for example, Atkinson and Carter (1984)) these reactions were not studied. The availability of gas phase rate constants for the reaction of ozone and VOCs permits the prediction of the efficiency of this process. Additionally, as these reactions would be much more rapid than the oxidation of the same compounds in water, gas-phase reactions would not control the removal rates or efficiencies of VOCs from unsaturated soils.

In the system described here, the decomposition of ozone must be considered since the concentration of ozone present at any time, t , will affect the decomposition of the particular VOC. If the oxidation of the VOC occurs by a direct (Criegee) mechanism, then an increase in the ozone decomposition rate will result in a decrease in the extent to which the organic chemical of interest reacts.

Understanding the mechanism of ozone decomposition is important from the standpoint of knowing what oxidizing species are formed. A number of researchers (15-26) have studied these reactions and recently Staehelin and Hoigne (1985) developed a schematic for the decomposition of ozone in "pure" water. Based upon this schematic it is clear that the most important oxidizing species present in solution are ozone, OH radicals and superoxide. Both superoxide and OH radicals enter into the cyclic reaction which then enhances the decomposition of ozone. Additionally, hydroxide will react with ozone to form superoxide and, as such, will result in an enhancement of the rate of ozone decomposition.

An understanding of the reactions involving ozone that may occur in the presence of a solute is important in terms of designing and optimizing such a treatment system. As is the case in "pure" water, ozone, superoxide and OH radicals are present as three of the oxidizing species, termed promoters, which can react with OH to form carboxyl radicals. The carboxyl radicals react with oxygen to form organoperoxides. Staehelin and Hoigne (1985) found that the naturally occurring matter obtained from Greifen Lake and from the Dubendorf ground-water, acted as a chain promoter. In contrast, other species may react with OH radicals in such a way that they do not enter into the cyclic reaction. The production of OH radicals in such systems is significant since OH radicals are much more powerful and less selective oxidants than ozone, and as such, their formation may result in the oxidation of compounds that would not react appreciably with ozone. Since solutes may act as either chain promoters or scavengers; in such a complex mixture as soil, the rate of ozone decomposition cannot be predicted, but must be measured.

Figure 2 illustrates some of the reactions that would occur in a soil. These reactions include transfers of chemical from one phase to another, for example, if free product is present, it may volatilize. Gas phase oxidation reactions, as discussed previously, would occur; as would the oxidation of the solubilized natural organic matter with dissolved ozone. Additionally, the reaction of ozone with organic matter and the organic chemical that is sorbed onto the soil surface may play a significant role in ozone decomposition and in VOC oxidation. Clearly such a system is extremely complex and would require a great deal of work to completely elucidate the kinetics and mechanisms of these reactions. Since it was felt that the gas-phase reactions involving ozone and the VOCs were well understood and not rate limiting, no gas-phase work was planned in the study. The PAHs studied are sufficiently non-volatile that the gas-phase reactions are unimportant. In an attempt to simplify the system, most of the work conducted with VOCs was performed in homogeneous aqueous systems containing humic acid as a model of naturally occurring organic matter. Limited work was conducted in heterogenous systems containing either Eustis soil or a simulated soil (28). The work conducted with PAHs was done by treating contaminated soils with gaseous ozone.

EXPERIMENTAL PROCEDURES

Materials. Unless otherwise specified, all solutions were prepared from water which had been treated using reverse osmosis (RO water). The RO water was boiled for 20 minutes to remove any volatile contaminants. Ozone was prepared from high purity oxygen (>99.99%) which had been dried through a molecular sieve trap (Molecular Sieve 5A, Supelco, Bellefonte, PA). A Polymetrics Ozone Generator (Model T-408, San

Jose, CA) was used. The VOCs and PAHs used in these experiments were obtained from either Aldrich Chemical Co. (Milwaukee, WI) or from Chem Service Inc. (West Chester, PA) and were at least 95% pure, although most were >99% pure. Humic acid was obtained from Aldrich Chemical Co. as the sodium salt. The simulated soil was prepared by the method described by Garbarini and Lion (1985). The TOC of the soil was 0.70%. Prior to use, the simulated soil was dried overnight at 105°C. The other soil used in the VOC study was the <250 µm fraction of a surface soil from Florida, Eustis sand, (Typic Quartzipsamments). Since the moisture content of the air-dried soil was found to be <0.5%, no additional drying was required. The TOC of the Eustis soil was 0.66%. The physical and chemical characteristics of this soil are presented elsewhere (29). The soil used in the PAH experiments was a sandy soil containing 0.5% organic matter. The characteristics of this soil are presented in Table 2.

Methods. Quantification of the ozone concentrations in the stock solutions of aqueous ozone were determined spectrophotometrically at 258 nm, the peak maximum for ozone. An extinction coefficient of 3000 M⁻¹ cm⁻¹ (30) was used to convert the absorbance units to concentration.

To prepare aqueous ozone solutions, gaseous ozone (approximately 4% in oxygen) was bubbled into water at a flow rate of approximately 1 mL/min. The water had been previously acidified to a pH of 2 (or 3, depending on the experiment) and was chilled to approximately 4°C. During the bubbling of the gas, the ozone solution was kept chilled on ice. After one hour, the system was shut down and the ozone solution (approximately 30-35 mg/L) was ready for use.

Solutions of Aldrich humic acid (sodium salt) were prepared by dissolving the humic acid in water followed by filtration through a 0.45 µm filter. Stock solutions were stored in the dark. A 10 mg/L solution of Aldrich humic acid had an absorbance of 0.227 at 258 nm using a 1 cm path length.

Stock solutions of VOCs were prepared according to the method described by Masten (1991). The stock solution was kept at 4°C during storage and on ice while dispensing the solution into the samples. Stock solutions were kept for no longer than 10 days. Naphthalene was prepared by dissolving the solid in methanol, then, diluting the stock solution in distilled water (pH 3) to 10⁻⁴ M.

The soil samples used to study the reaction of ozone with VOCs were prepared according to Masten (1991). The PAH contaminated soils were prepared in the following manner. The soils were air - dried, then sieved through a 0.5 mm sieve. 50 mg of the target PAHs were dissolved in <35 ml methanol. A known volume of PAH solution was added to a known amount of soil. The mixture was shaken by hand. The solution was added until the total soil weight was 500.0 g and all of PAH solution was added. After rotating the soil sample at 30 rev/min for 1 hour, the soil containing 100 µg/kg of PAHs was ready for use.

VOC concentrations were determined in the samples using a gas chromatograph equipped with an FID (31). PAH concentrations were determined using direct injection onto a gas chromatograph equipped with an FID (32).

Procedure. Details of the experimental procedure for the VOC experiments are presented elsewhere (31). Experiments with naphthalene were conducted in a similar manner, except that the naphthalene was first dissolved in a 0.66% methanol/water mixture, then diluted into water to achieve the desired concentration.

Glass columns (21.2 mm I.D., 25 cm length) were packed with the contaminated soil. The treatment system was set up as shown in Figure 3. Gaseous ozone (produced at a concentration of approximately 3% in oxygen) was passed through the soil. Flows were measured using a rotameter calibrated using a bubble flow meter. The concentration of ozone generated was monitored by trapping the ozone into potassium iodide traps (33). After ozone passed through the column for a period of time at a certain flow rate (depending on experimental design), the soil was removed from the column and well mixed. The concentration of PAHs remaining in the soil was tested by conventional soxhlet extraction techniques (34, 35) followed by GC analysis.

RESULTS AND DISCUSSION

Effect of ozone dosage. The ozonation of *cis*-dichloroethylene (*c*-DCE) was studied at two ozone dosages. As expected, increasing the ozone dose resulted in an increase in the extent to which the *c*-DCE reacted as indicated in Figure 4. At 300 mg/L humic acid, a 2.6 fold increase in the ozone dosage resulted in almost a 5 fold increase in the amount of compound which reacted. If the disappearance of *c*-DCE occurred purely by a direct reaction with ozone, than one would expect a 1:1 stoichiometry. The complexity of the reactions suggests that secondary oxidants are important and that *c*-DCE is able to successfully compete with the humic acid for these oxidants. Similar results were observed with the other VOCs (31).

Effect of pH. The effect of pH can be observed by comparing results obtained for *trans*-dichloroethylene (*t*-DCE) and tetrachloroethylene (PCE). *t*-DCE will react by both the direct and indirect reaction mechanisms while PCE does not react appreciably with ozone, but only with OH radicals. With *t*-DCE, at pH 3 (see Figure 5), there appears to be a significant portion of the DCE which reacts by the direct mechanism. Increasing the pH from 3 to 6 had a much greater effect than did raising the pH from 6 to 8. Increasing the pH of a 0.05 M phosphate buffer solution (measured at 25 C) from 4 to 6 results in a 7-fold decrease in the ozone half-life; whereas increasing the pH from 6 to 8, resulted in a 15-fold decrease in the half-life (36). Based upon this, one would expect that increasing pH from 6 to 8 would have a greater effect on the extent to which *t*-DCE is oxidized, since the rate at which ozone decomposes "autocatalytically" changes most dramatically in this pH range. The fact that this is not observed is further evidence that some mechanism other than the direct reaction involving ozone and the VOC is occurring.

As is illustrated in Figure 6, the effect of pH appears to be much less with tetrachloroethylene (PCE) than observed with *t*-DCE. Since the rate constant for the reaction between ozone and PCE is over than three orders of magnitude greater than the rate constant for the ozone - *t*-DCE reaction, one would expect that the extent to which PCE reacts would be much less than that for *t*-DCE, in the presence of similar concentrations of humic acid. Thus, it can be postulated that the PCE which reacted, reacted via an indirect mechanism, most probably involving OH radicals. Similar results were obtained with the other VOCs studied (31).

Oxidation of VOCs and Naphthalene in Soil Slurries. The oxidation of PCE and *cis*-DCE was studied in Eustis and simulated soil. Neither PCE nor *cis*-DCE sorbed onto the soils. This is illustrated in Figures 7 and 8. When no ozone was added, the recovery of *cis*-DCE was 101 ± 3.7%, while the recovery of PCE was 100 ± 3.6%. The Eustis soils were treated with 20.9 mg/L ozone while the simulated soils were treated with 23.1 mg/L ozone. In both cases, almost complete oxidation of the *cis*-DCE occurred with up to 1.0 g soil per 10.0 mL (total volume) of water. Thus, in the systems containing 300 mg TOC/L water, complete oxidation of *cis*-DCE occurred. Alternatively written, 0.22 mg ozone added to 1 g of soil (0.66% TOC by weight) would result in complete oxidation of *cis*-DCE.

The oxidation of PCE was studied in both buffered and unbuffered Eustis soil. The extent of reaction of PCE was less than that of *cis*-DCE. Nevertheless, at pH 6.6 the application of 0.17 mg of ozone did result in approximately 40% decomposition of PCE in the presence of 1.0 g of soil. As in the case for the humic acid, at low organic concentrations, pH did not appear to effect the extent of oxidation. It is interesting to note though, that at higher organic contents, the extent to which the PCE reacted (at the pH's studied) varied somewhat. It is also interesting to note that in the simulated soil system, increasing the pH resulted in a slight decrease in the extent to which the PCE reacted. On the contrary, in the Eustis soil system, a greater extent of reaction occurred in the system buffered at pH 6.6 than at the lower pH. Results such as these are indicative of the complexity of such systems, and may imply that natural soils are less capable of terminating the radical chain reaction than is Aldrich humic acid or that the reactions are surface-catalyzed.

Effect of OH radical scavengers. Several experiments were conducted to better understand the mechanism by which the oxidations of the target compounds occurred. To determine the extent to which PCE and naphthalene reacted via a free radical mechanism, *tert*-butyl alcohol (0.5 mM) was added as a scavenger of OH radicals. If the direct reaction predominated then the addition of *tert*-butyl alcohol should have no effect on the extent to which these compounds reacted. The addition of *tert*-butyl alcohol reduced the extent to which target compound was degraded. From Figure 9, it can be observed that approximately 30% of the PCE was oxidized even at a humic acid concentration of 100 mg/L. This suggests that some of the target compound which reacts, does so by the direct reaction with ozone; or that *tert*-butyl alcohol does not completely scavenge the OH or other radicals. The amount of PCE that degraded when the OH radical mechanism was insignificant was also much higher than predicted using rate constants available in the literature. As shown in Figure 10a, the extent to which naphthalene reacted with ozone was reduced approximately 27%. The difference in the amount of naphthalene which reacted in the presence and absence of *tert*-butyl alcohol vs. the initial humic acid concentration added is plotted in Figure 10b. The linear relationship observed suggests that the importance of the indirect mechanism over the direct mechanism increases with increasing humic acid concentration.

Oxidation of PAHs Sorbed onto Soils. The oxidation of PAHs in soils was studied by passing gaseous ozone through a soil column which had been packed with a sandy soil contaminated with the target PAHs. During each experiment, the ozone flux was measured and calculated by two different methods: (1) based on gas being 3.5% ozone in oxygen, and (2) based on empirical results using KI traps. Several experiments were conducted during the study to ensure that the gas was 3.5% ozone in oxygen. The discrepancies in the results are most likely due to poor pH control of the KI traps. It is important to maintain a pH of less than 3 in the KI solutions and this was not always done. As a result, the ozone fluxes which were calculated based on the empirical results were less than the ozone fluxes which were calculated based on the ozone being 3.5% in oxygen. The following discussion is based on the ozone flux as calculated based upon the ozone gas being 3.5% in oxygen.

The experimental results for phenanthrene are presented in Table 3. Before treating the soil using ozone, a control experiment was performed by passing air through a phenanthrene contaminated soil at a flow rate of 2.64 L/hr for 7 hours. No phenanthrene was removed by the air. After passing ozone through the soil at a flux of 253 mg O₃/hr for 2.3 hours, greater than 95% of the phenanthrene had disappeared. The final concentration of phenanthrene in the soil was below detection limits. The gas chromatographic scans revealed no degradation products. When the ozone dosage was reduced to a flux of 151 mg O₃/hr and the soil was treated for one hour, 60-84% removal was still obtained. It was also observed that 5.8 mg of ozone degraded 1 mg of phenanthrene.

The results of the ozonation experiments conducted on soils contaminated with chrysene and pyrene are presented in Table 4. In this case, less than 20% removal of chrysene and pyrene occurred with an ozone dosage of 177 mg O₃/hr for one hour. It appears that when the target compounds are present together, as they were in this studies with pyrene and chrysene, the ozone dosage must be increased in order to achieve the same levels of removal as that obtained when phenanthrene was the soil contaminant present in the soil. When the ozone dosage was increased to a flux of 217 mg O₃/hr and the soil was treated for one hour, 34% removal of pyrene was obtained while no removal of chrysene was found. Increasing the ozone dosage to 549 mg O₃/hr for one hour, resulted in no removal of chrysene while 94% removal of pyrene was obtained. These findings seem to suggest the importance of the direct ozone reaction in the dry soil, since the results follow the order of reactivity of chrysene and pyrene with ozone (11).

The experimental results for chrysene oxidation are presented in Table 5. After passing ozone through the soil at a flux of 500 mg O₃/hr for one hour, the total ozone dosage was approximately that used when the phenanthrene contaminated soil had been treated with a flow rate of 253 mg O₃/hr for 2.3 hours. Only 40% removal of chrysene was achieved as compared to greater than 95% removal of the phenanthrene (when either PAH was present as the sole contaminant). When the ozone dosage was increased to a flux of 594 mg O₃/hr and the soil was treated for four hours, only 50% removal of chrysene was achieved. Thus, chrysene requires more than eight times the ozone dosage of phenanthrene. These results follow the order of reactivity for chrysene and phenanthrene with ozone (11). The gas chromatographic scans showed peaks for what appears to be two major degradation products.

The results for experiments with pyrene-contaminated soil are presented in Table 6. When these results are compared to those obtained with chrysene, it is observed that pyrene is much more efficiently oxidized. For example, the passage of ozone through the soil at a flux of 26.3 mg O₃/hr for one hour, resulted in 53% removal of pyrene while the treatment of a chrysene contaminated soil at flow rate of 253 mg O₃/hr for 2.3 hours resulted in only 40% removal of the chrysene. However, pyrene is not as efficiently oxidized as is phenanthrene. For example, when the ozone dosage was 581 mg O₃/hr and the soil was treated for one hour, only 83% removal of pyrene was achieved, compared to greater than 95% removal of phenanthrene. These inconsistencies with the order of reactivity as indicated by Bailey (1982) may because the soil absorbed pyrene much strongly than it absorbed phenanthrene. The partition coefficients (log K_{ow}) for phenanthrene and pyrene are 6.12 and 6.51, respectively (37). Thus, a higher ozone dosage is required for treated pyrene. The gas chromatographic scans of the pyrene treated soils revealed no degradation products.

CONCLUSIONS

This work indicates the feasibility of using ozone as an oxidant in solutions containing high concentrations of humic acid or soils. It is important to note that in both situations the oxidation reactions appear to occur predominately by the indirect reaction involving some oxidant other than ozone. The effects of the addition of tert-butyl alcohol support this hypothesis.

The compounds studied all reacted to a much greater extent than one would predict assuming that only the direct ozone reaction occurred. Both c-DCE and PCE reacted to a much greater extent in soils slurries than in aqueous solutions containing humic acid. There is very strong evidence that the indirect reaction involving some free radical, such as the OH radical, plays a significant role in the oxidation of these compounds. This finding is extremely significant since it suggests that in-situ treatment of contaminated soils may be feasible,

despite the highly reactive nature of humic acid or naturally occurring soil organic matter with ozone. It appears that the organic matter acts, essentially, as a reservoir of OH radicals which can then react with the olefinic anthropogenic compounds found in the soil.

From the results of the soil column experiments, it is apparent that the removal efficiency of the PAH of interest depends on the reactivity of the PAH. Based upon the results presented here, it appears reactivity decreases with increasing bond-localization energy (11) and with increasing partition coefficients (K_{oc})

ACKNOWLEDGEMENTS

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Table 1. Organic Chemicals Studied

<i>VOCs</i>	<i>PAHs</i>
1,1-trichloroethane (TCA)	naphthalene
trichloroethylene (TCE)	phenanthrene
tetrachloroethylene (PCE)	chrysene
cis-dichloroethylene (c-DCE)	pyrene
trans-dichloroethylene (t-DCE)	

Table 2. Soil Characteristics

<i>Soil Characteristic</i>	<i>Results</i>
Organic Matter Content	0.5%
pH	6.6
Lime index	71.0
Sand	82.3%
Silt content	10.0%
Clay content	7.7%
Residual PAHs	negligible
Specific gravity	2.55

Table 3. Treatment of Phenanthrene In Soil Columns
(Initial Concentration = 100 µg PH/g soil)

Ozone Flux ^a (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal
(1)	(2)			
0.00	0.00	2.64	7.0	[-]
940	879	13.6	8.0	>95%
882	1010	12.8	6.0	>95%
253	111	3.66	2.3	>95%
170	73.0	2.46	2.5	87%
151	78.4	2.35	1.0	* 60% ** 84%

Phenanthrene Recovery Rate From Soil: 78.8%

* 12 extracts analyzed

** 6 extracts analyzed

^a Ozone Flux (1): flux based on 3.5% ozone in oxygen
(2): flux based on KI trap measurements

Table 4. Treatment of Chrysene And Pyrene In Soil Columns
(Initial Concentration = 100 µg PY+100 µg C/g soil)

Ozone Flux ^a (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal	
(1)	(2)			PY	C
549	78.4	8.53	1.0	94%	[-]
217	121	3.25	1.0	34%	[-]
177	107	2.56	1.0	3%	18%

PY Recovery Rate From Soil: 63.3%

C Recovery Rate From Soil: 80.1%

^a Ozone Flux (1): flux based on 3.5% ozone in oxygen
 (2): flux based on KI trap measurements

Table 5. Treatment of Chrysene In Soil Columns
(Initial Concentration = 100 µg Chr/g soil)

Ozone Flux ^a (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal
(1)	(2)			
594	48.4	8.65	4.0	50%
558	250	8.68	2.0	43%
611	278	8.97	1.0	33%
501	27.1	7.45	1.0	40%
412	32.9	6.00	1.0	39%
339	166	4.94	1.0	* 39 ** 65%

Chr Recovery Rate from Soil: 82.7%

* 12 extracts analyzed

** 6 extracts analyzed

^aOzone Flux: (1): flux based on 3.5% ozone in oxygen
(2): flux based on KI trap measurements

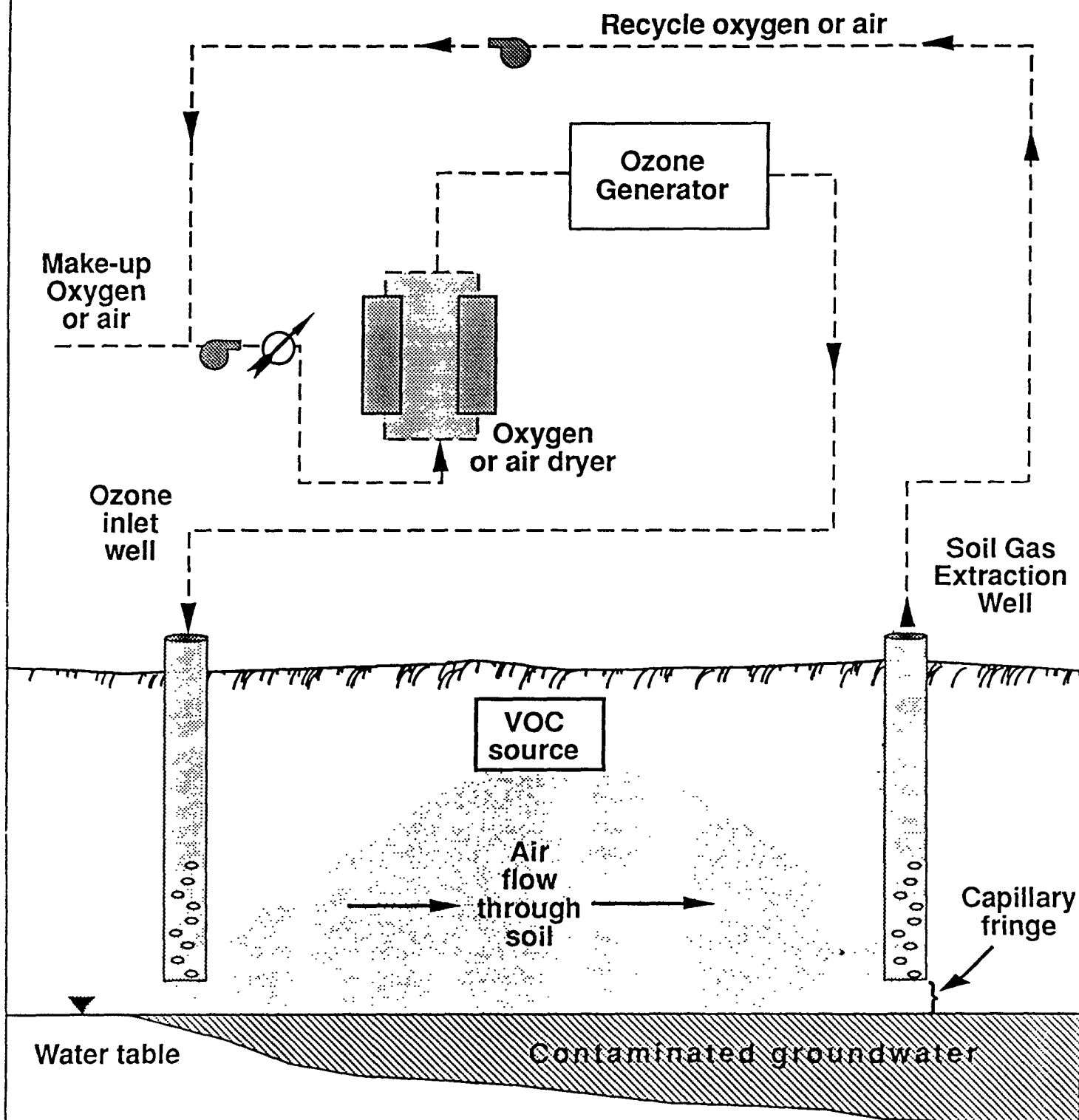
Table 6. Treatment of Pyrene In Soil Columns
(Initial Concentration = 100 µg PY/g soil)

Ozone Flux ^a (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal
(1)	(2)			
598	238	8.65	4.0	91%
581	266	8.40	1.0	83%
315	20.7	4.55	1.0	79%
218	8.91	3.22	1.0	>95%
119	8.79	1.72	1.0	71%
26.3	1.40	0.38	1.0	53%

PY Recovery Rate from Soil: 105%

^aOzone Flux: (1): flux based on 3.5% ozone in oxygen
(2): flux based on KI trap measurements

Figure 1. Schematic of a modified vapor stripping system.



(adapted from Bennedsen, 1987)

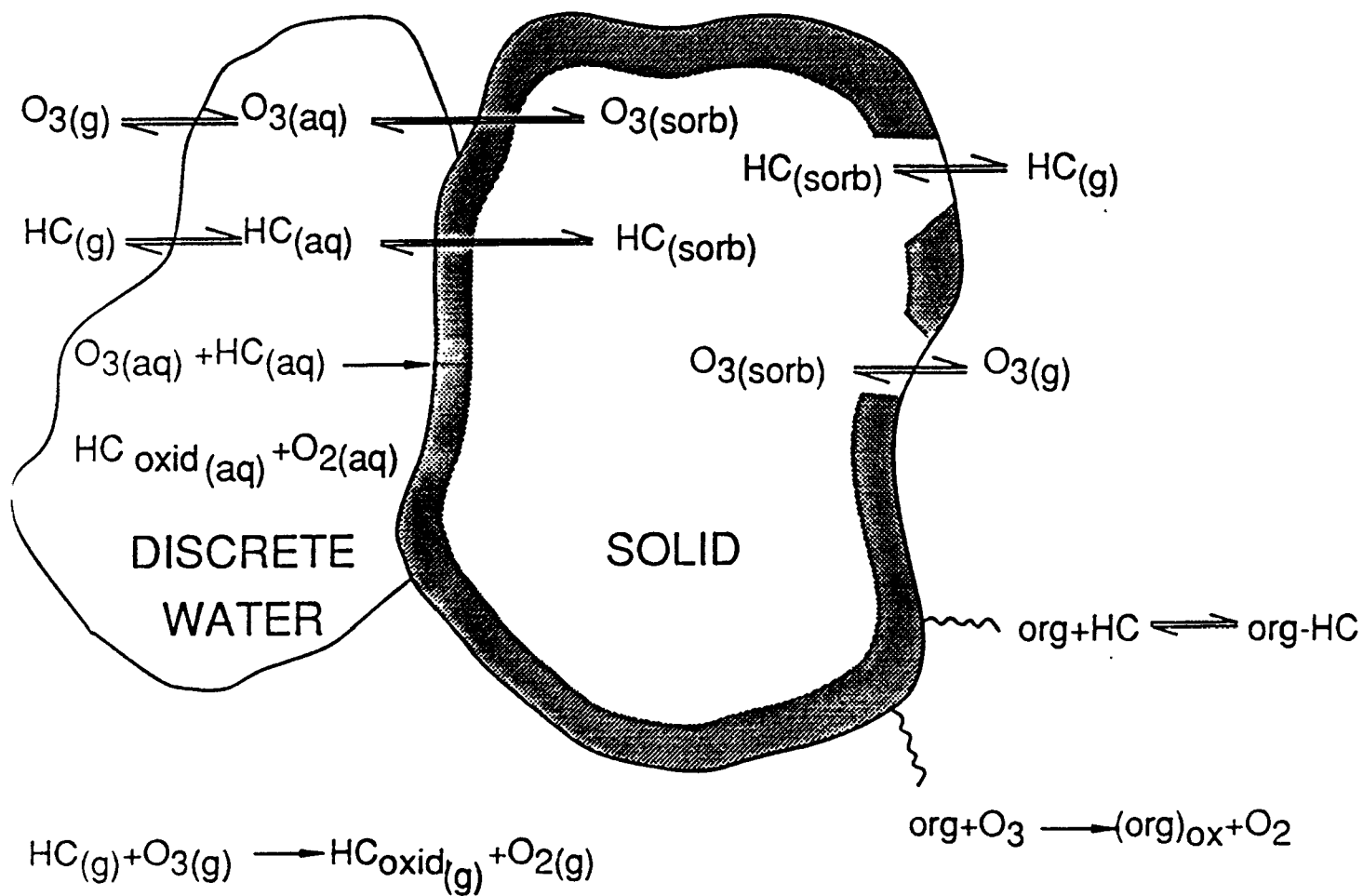


Figure 2. Reactions involving ozone in a soil system.

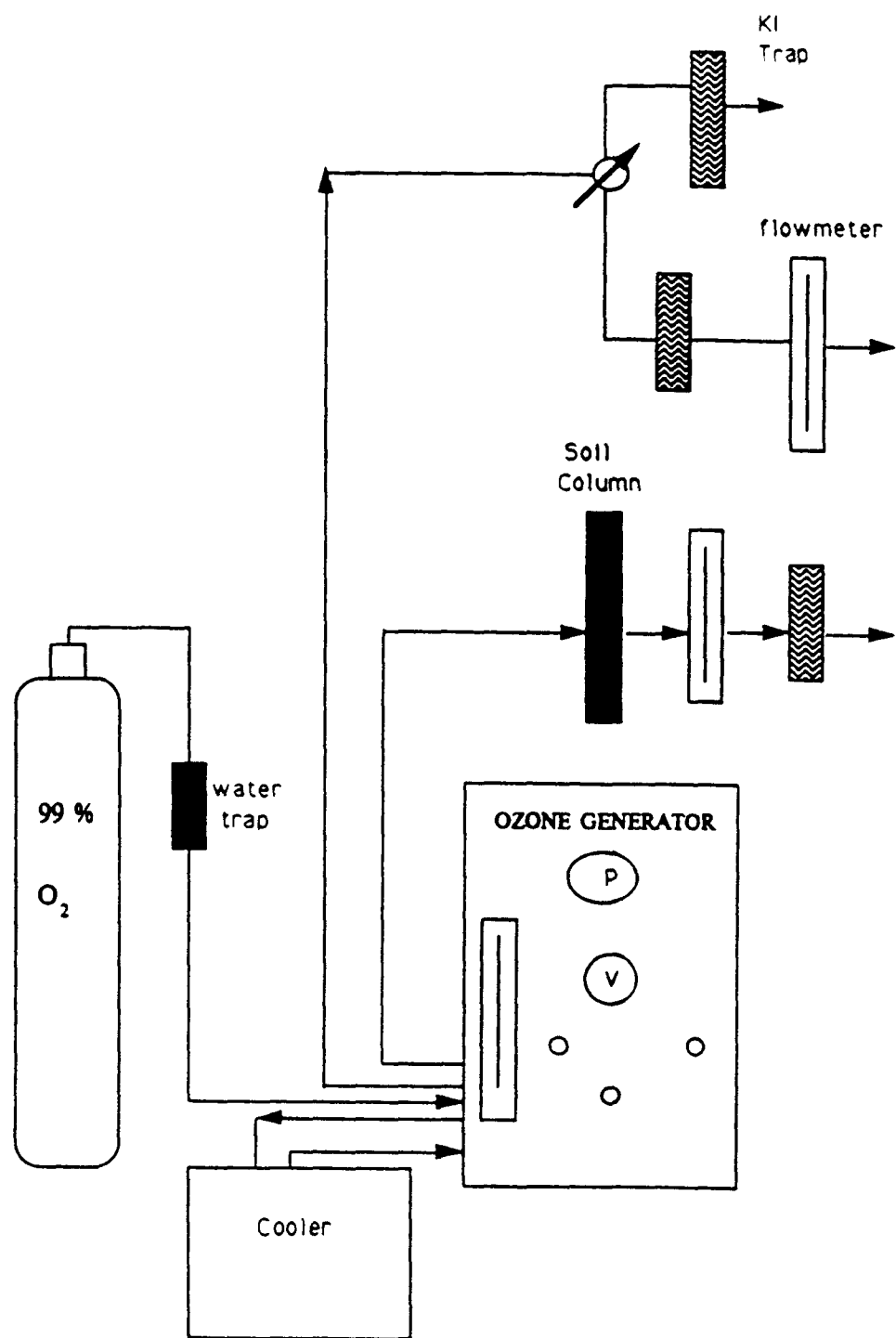


Figure 3. Experimental setup used in soil column work.

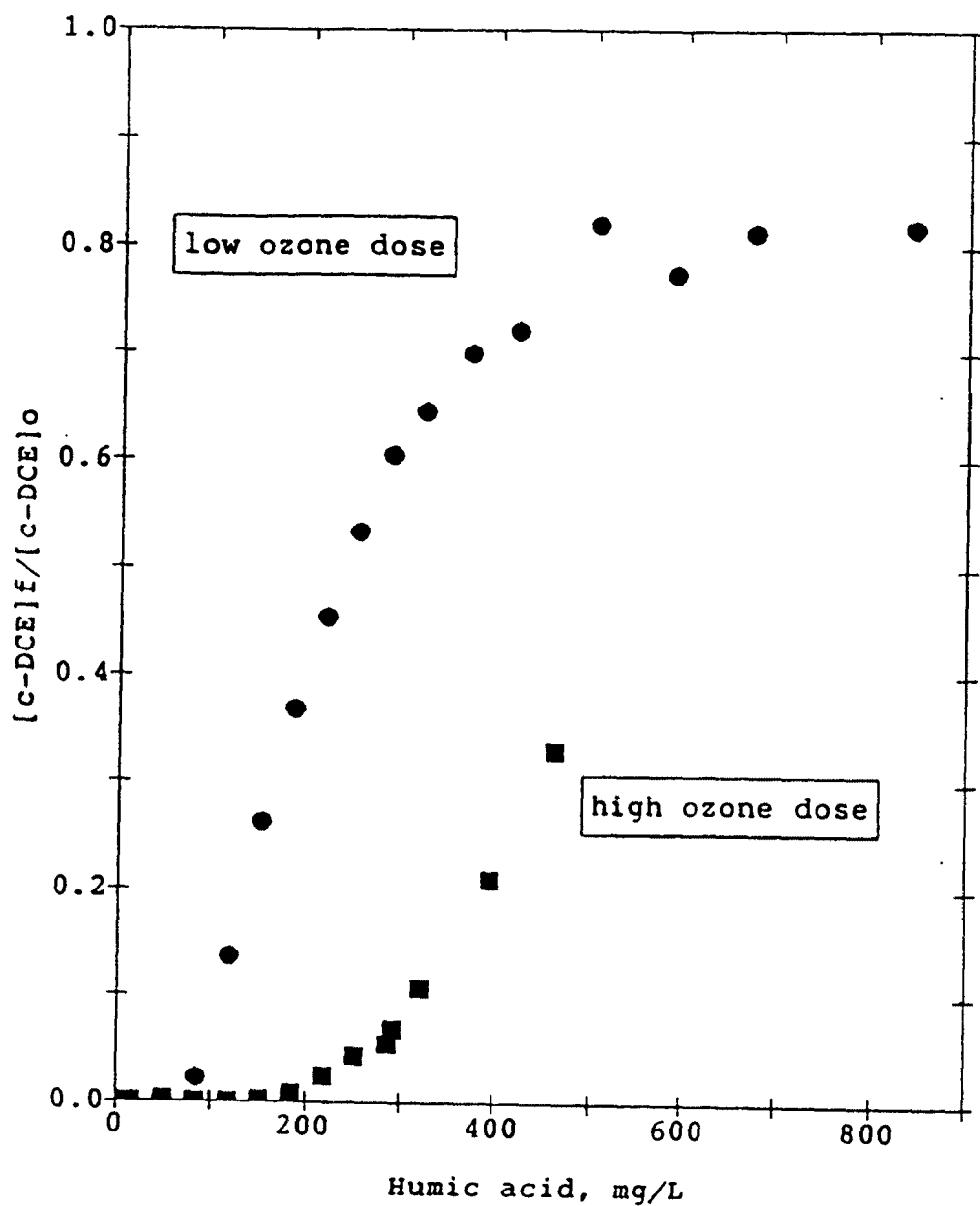


Figure 4. Effect of ozone dosage on the ozonolysis of *cis*-DCE in the presence of Aldrich humic acid (pH 3.2, 10°C). Initial concentrations were (n) [*cis*-DCE] = 2.22 mg/L, [O₃] = 16.5 mg/L; (•) [*cis*-DCE] = 2.12 mg/L, [O₃] = 6.20 mg/L.

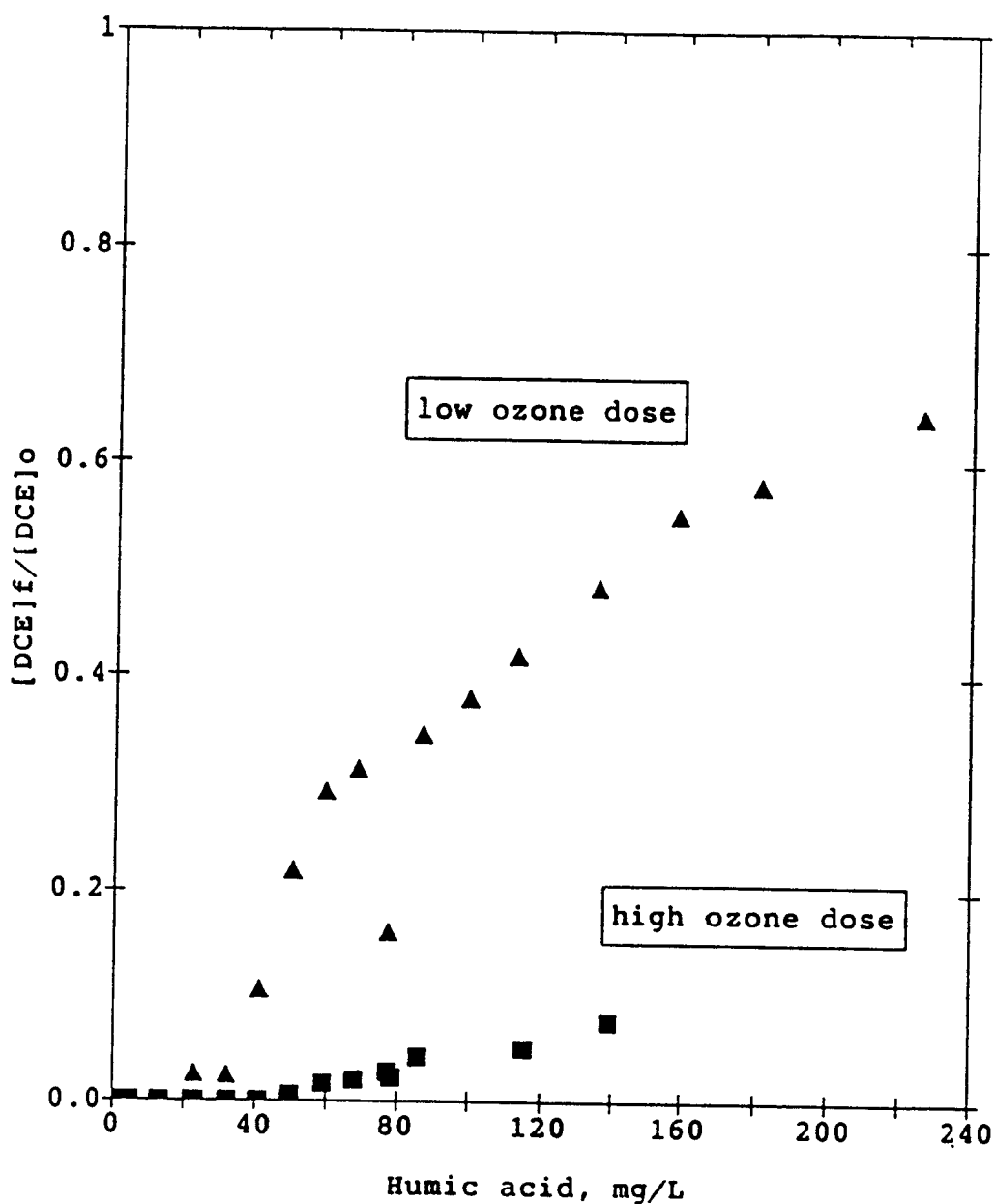


Figure 5. Effect of pH on the ozonolysis of trans-DCE in solutions containing Aldrich humic acid (10°C). Initial concentrations were (s) pH 3.2, [trans-DCE] = 2.07 mg/L, [O₃] = 5.75 mg/L; (n) pH 3.1, [trans-DCE] = 1.71 mg/L, [O₃] = 6.60 mg/L; (•) pH 8.0, [trans-DCE] = 1.71 mg/L, [O₃] = 6.60 mg/L.

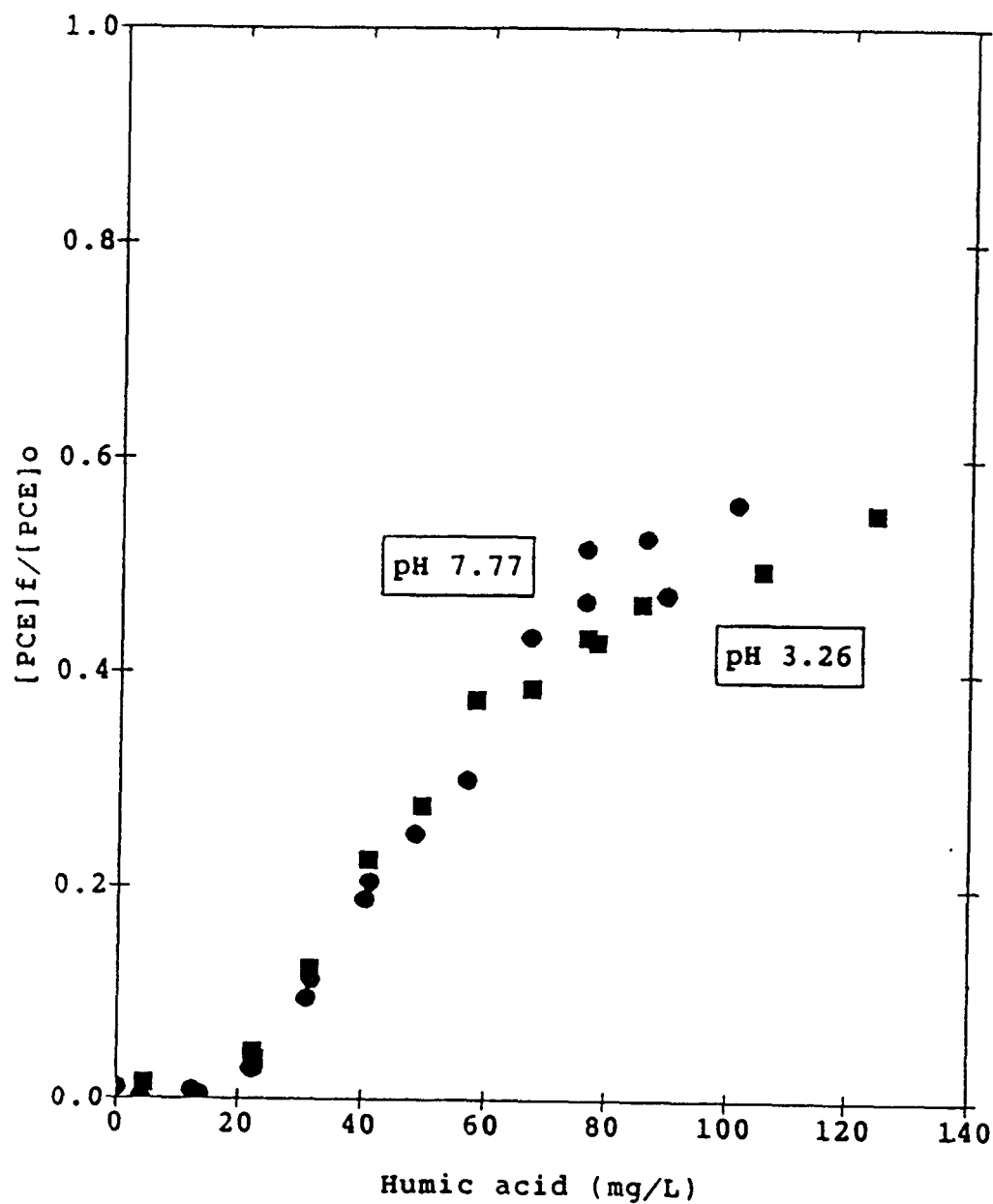


Figure 6. Effect of pH on the ozonolysis of PCE in solutions containing Aldrich humic acid (10°C). Initial concentrations were (n) [PCE] = 1.81 mg/L, [O₃] = 18.8 mg/L; (•) [PCE] = 1.68 mg/L, [O₃] = 21.7 mg/L.

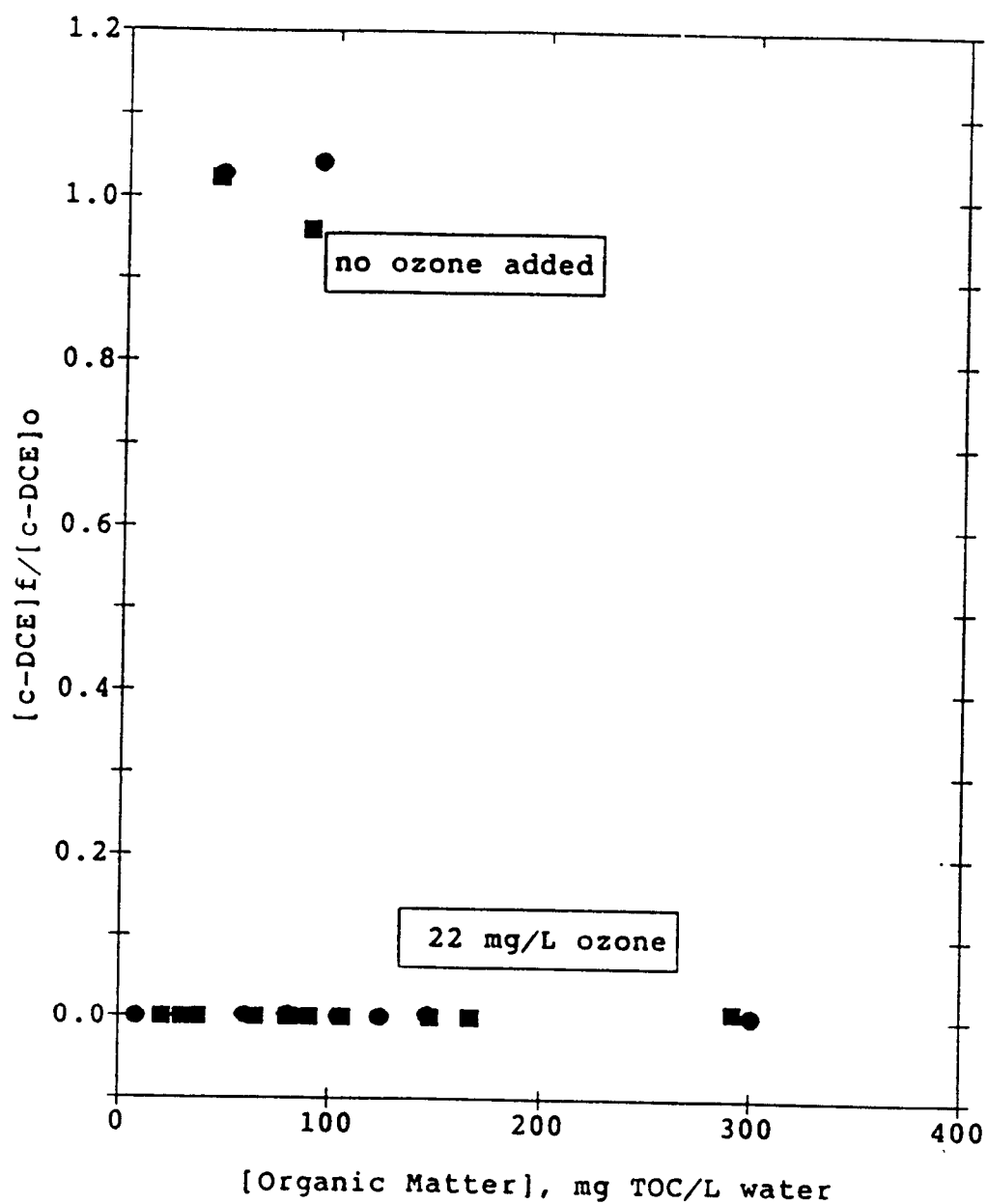


Figure 7. Effect of two soils on the ozonolysis of *cis*-DCE (10°C). The soil, pH and initial concentrations used were (•) Eustis soil, pH 3.4-4.8, [*cis*-DCE] = 2.05 mg/L, [O₃] = 20.9 mg/L; (n) simulated soil, pH 6.1-6.8, [*cis*-DCE] = 1.89 mg/L, [O₃] = 23.1 mg/L.

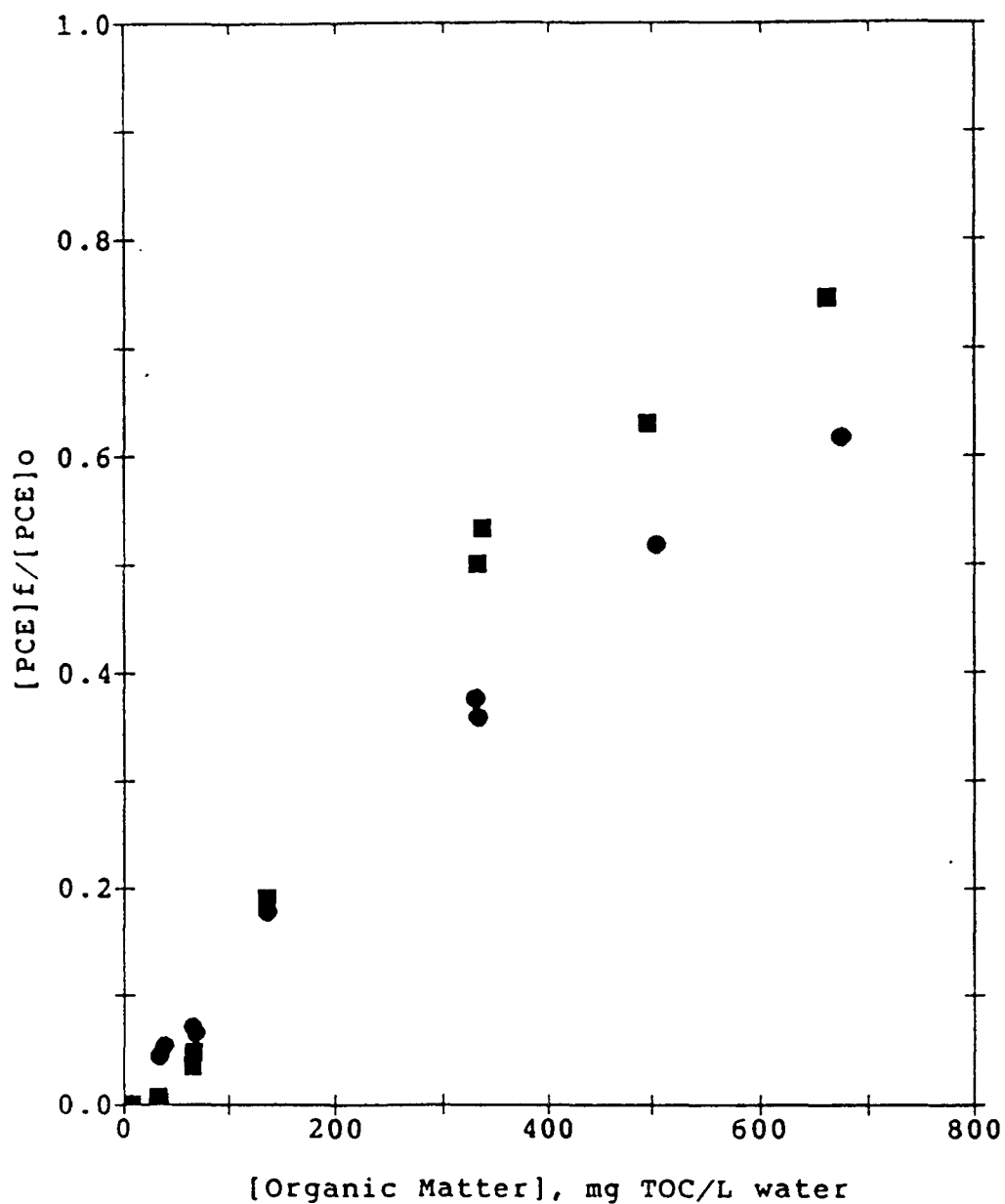


Figure 8. Ozonolysis of PCE in the presence of Eustis soil (10°C). The pH and initial concentrations used were (n) pH 3.4-4.8, [PCE] = 2.05 mg/L, [O₃] = 17.0 mg/L; (•) pH 6.6, [PCE] = 1.63 mg/L, [O₃] = 17.6 mg/L.

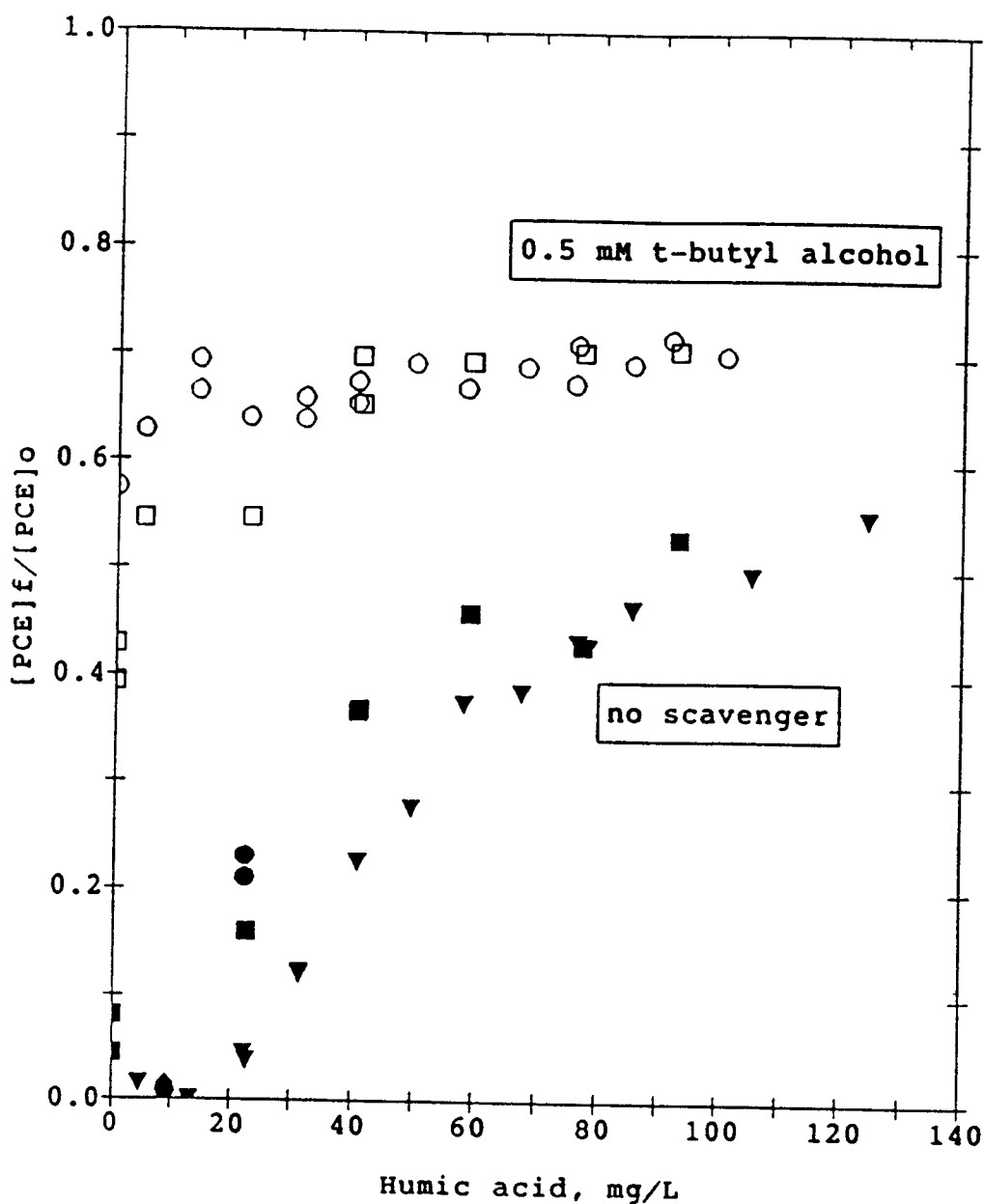


Figure 9. Effect of OH radical scavengers on the ozonolysis of PCE in the presence of Aldrich humic acid (pH 3.2, 10°C). Initial concentrations were (rn) [PCE] = 2.14 mg/L, [O₃] = 25.5 mg/L; (m) [PCE] = 2.24 mg/L, [O₃] = 25.0 mg/L; (s) [PCE] = 1.68 mg/L, [O₃] = 20.6 mg/L; (•) [PCE] = 2.24 mg/L, [O₃] = 24.4 mg/L; (u) [PCE] = 1.97 mg/L, [O₃] = 23.3 mg/L.

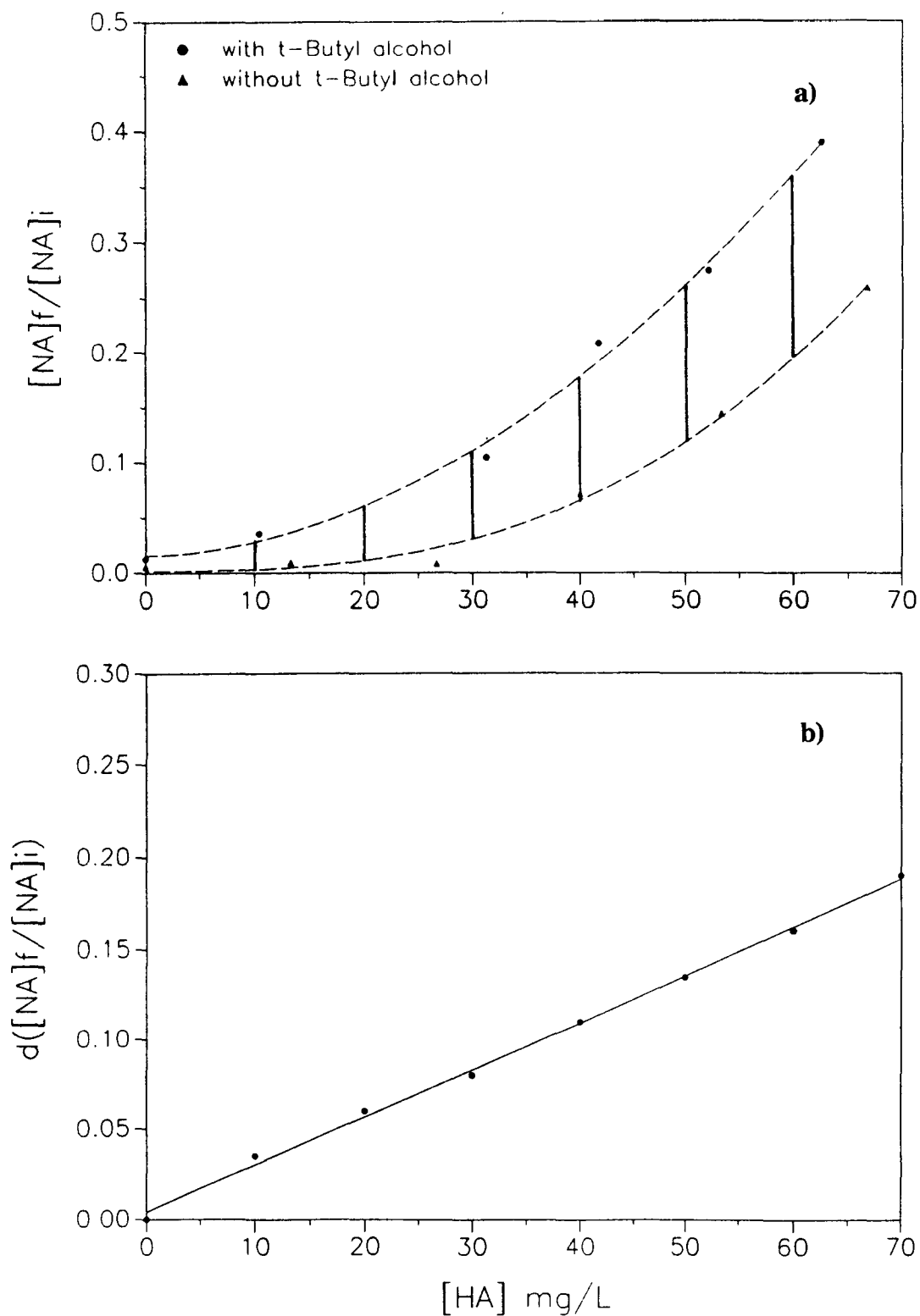


Figure 10a. Effect of OH radical scavengers on the ozonolysis of naphthalene in the presence of Aldrich humic acid (pH 3.2, 10°C). Initial concentrations were $[t\text{-BuOH}] = 2.8 \times 10^{-4} \text{ M}$, $[NA] = 3.3 \times 10^{-5} \text{ M}$, $[O_3] = 1.5 \times 10^{-4} \text{ M}$.

Figure 10b. The effect of *tert*-butyl alcohol on the extent to which naphthalene reacts via the direct and indirect mechanisms in the presence of humic acid. Conditions as given in Figure 10.

HABITAT CONDITIONS AFFECTING BIOVENTING PROCESSES

DARWIN L. SORENSEN AND RONALD C. SIMS

Bioprocess Engineering Program and Utah Water Research Laboratory

Utah State University

Logan, Utah

THE ROLE OF HABITAT CONDITIONS IN CONTROLLING MICROBIAL ACTIVITY

Natural Boundaries Control Microbial Degradative Activity

Soil venting may be viewed as a process to enhance microbial metabolic activity to degrade organic contaminants. Microbial metabolism, including contaminant decomposition, is a complex network of chemical reactions controlled by the same kinds of physical and thermodynamic limits that all chemical reactions follow. Enzymes produced by microorganisms act as catalysts, lower reaction energy barriers (Figure 1), and greatly accelerate reaction rates. It is this increase in rate of degradative reactions that makes biodegradation attractive for soil remediation.

The Niche

The physical location of an organism is its habitat. The dimensions of a microorganism's habitat is on the order of a cubic millimeter or less and may be best described as a microhabitat (Figure 2). The combination of an organism's habitat and what it does there defines the concept described as a niche (2). In theory, every population of microorganisms present in the microbial community of a given habitat fills a niche. Some overlap in functions of organisms and their habitats may exist, but in general, each niche is unique. If a niche is not available, microorganisms from other habitats (i.e., allocthonous organisms) are likely to face competition and may not become part of the community. The introduction of contaminant organic matter into a habitat may expand an existing niche or serve to create more new niches in the community. If the contaminant is biodegradable, populations already in the microbial community will expand to fill the niche. In some cases, physical or chemical (e.g., toxicity) boundaries may exclude organisms with the appropriate biochemistry to degrade the contaminant(s). Over time, physical and chemical processes, including activities of the microbial community, may change the niche including those affected by contamination making new niches available. For example, rapid oxygen consumption by microorganisms degrading a soil contaminant may change the habitat from aerobic to anaerobic allowing anaerobic or facultatively anaerobic microbial communities to occupy the habitat.

General Requirements for Microbial Activity

Before bioventing is selected as a treatment process, physical and chemical conditions conducive to growth and/or maintenance of bacterial and fungal populations in the contaminated soil must be assured. Although microorganisms that inhabit extreme environmental are known, it is not likely that those organisms will

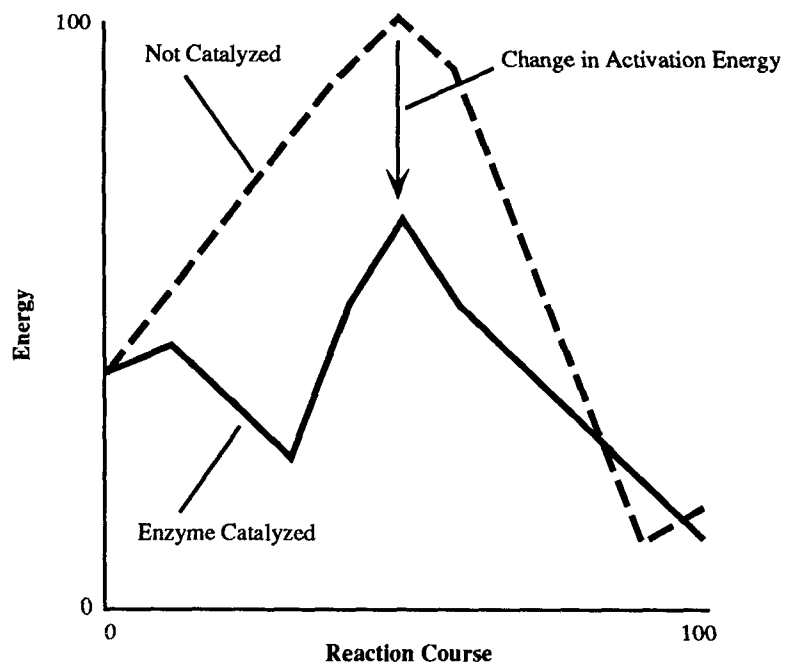


Figure 1. Schematic illustration of the decrease in reaction activation energy facilitated by enzymes (adapted from Rawn 1989).

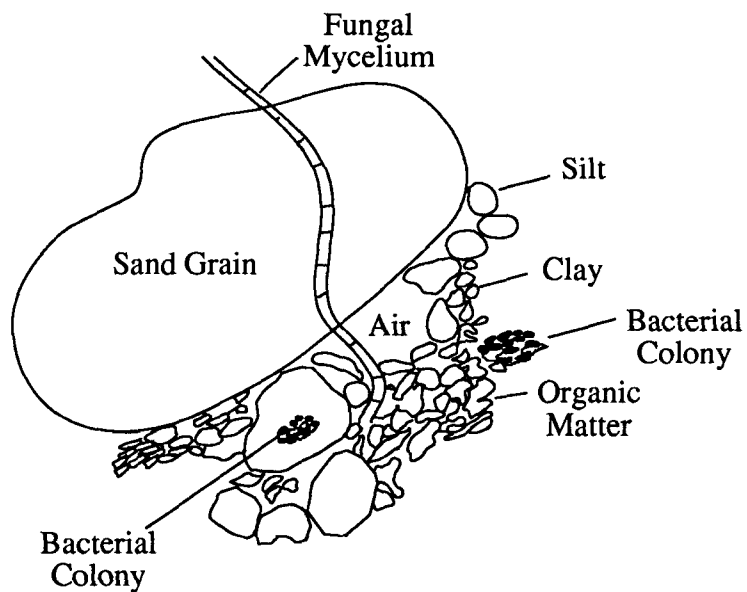


Figure 2. Conceptual illustration of the microbial soil habitat. Bacterial distribution tends to be in microcolonies and organic matter may be closely associated with clays (adapted from Brock 1979).

become important in the degradation of contaminants in most soils. Certain soil conditions should be available, either through natural occurrence or through engineered controls if biodegradation is likely to be successful. Moisture must be available; temperature, pH, and redox potential must not be extreme; nutrients and terminal respiratory electron acceptors must be available; and the habitat must be not toxic. It is reasonable to assume that if conditions are appropriate for an organism(s) to grow in a habitat, the degradative enzymes produced by the organism(s) will be active.

Factors Affecting Enzymatic Activity

Biodegradation activity is dependent on the presence of the appropriate enzyme(s) and enzyme activity. Activity is dependant on enzyme stability or appropriate conformation and chemical conditions at the catalytic site on the enzyme molecule(s). For biodegradation to occur, many conditions must be met. Obviously, the microorganisms present must produce enzymes that will catalyze the reaction(s) of interest. Assuming that the enzyme is produced, activity will be affected by environmental factors including soil moisture, temperature, pH, redox potential, nutrients, and availability of terminal electron acceptor.

In general, enzyme activity increases with increasing temperature to the point where the structure of the enzyme is affected by the temperature. At temperatures above the normal operating range for an enzyme, the protein(s) which makes up the enzyme may become denatured resulting in loss of catalytic activity. This leads to the observation that all enzymatic activities may have an optimum temperature (Figure 3). Optimum enzyme activities are often found at temperatures that are near optimum for the growth of the organism in which they are produced. However, appreciable activity may exist at temperatures below optimum.

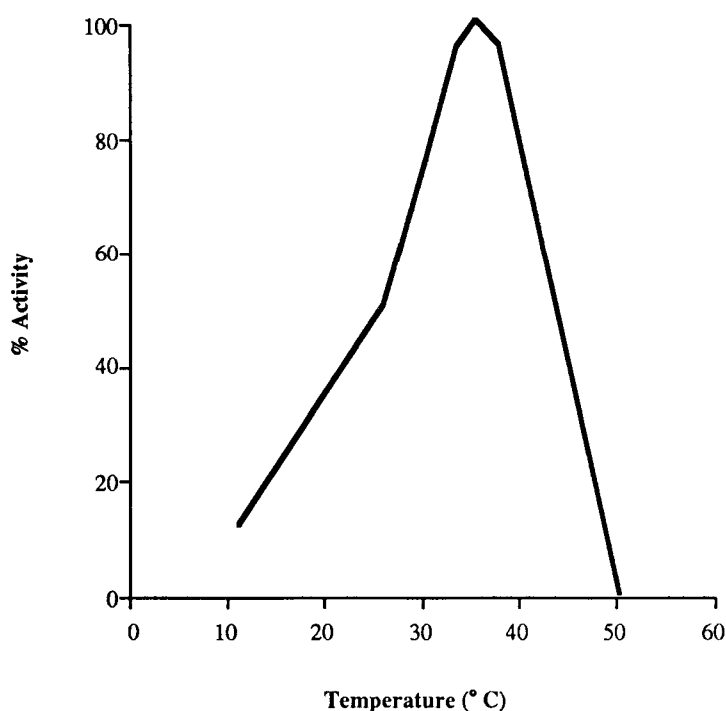


Figure 3. Schematic illustration of the effect of temperature on microbial activity.

The proton activity, pH, of the enzyme environment also affects the conformation of the catalytic protein. Since protonation of protein function groups (carboxyl, amino, and sulfhydryl) is affected by pH, the charge distribution of the active region of the enzyme is affected by pH. These affects result in a pH optimum for enzyme activity (Figure 4). Within the cell, the pH environment of the enzyme may be modified and protected from the extracellular environment. For extracellular enzymes, however, the pH of the microenvironment has control.

Salinity also affects protein conformation through the interactions of ions functions groups of the protein. In the laboratory, proteins can be “salted out” of solution by increasing ionic strength causing them to denature. Ionic affects may also alter the electronic charge distribution at the catalytic region of the enzyme and cause activity to cease (Figure 5). Within limits, the cell can control the salinity of the environment for intracellular enzymes. This is not the case for extracellular enzymes. If the salinity of the cell environment significantly exceeds the salinity inside the cell, osmotic forces will cause the loss of water from the cell (plasmolysis) and metabolic activity will cease.

Many reactions catalyzed by enzymes are oxidation-reduction reactions. An enzyme cannot catalyze reactions if electron and proton flow are affected by the redox state of the environment. The redox environment inside the cell is protected by extracellular enzymes encounter competition with redox couples in microenvironments.

Subsurface Characterization Requirements for Bioventing

The vadose zone is the region extending from the ground surface of the earth to the upper surface of the principal water-bearing formation, and is divided into three belts. The uppermost belt consists of soil and other materials that lie near enough to the surface to discharge water into the atmosphere in perceptible quantities by the action of plants or by soil evaporation and convection. The lowest belt, the capillary fringe, is located immediately above the water table and contains water drawn up from the zone of saturation by capillary action. The intermediate belt lies between the belt of soil water and the capillary fringe. This paper addresses bioventing of the vadose zone and conditions where the saturated zone is engineered to become unsaturated, e.g., when ground water is pumped out to create an unsaturated zone.

A promising aspect of soil vacuum extraction is the application for bioventing, i.e., enhancement of biodegradation of volatile and semi-volatile organic chemicals in a natural or engineered vadose zone. In the process of bioventing, SVE provides air to the vadose zone, and thus carries oxygen that can be used as the terminal electron acceptor by soil microorganisms to biodegrade chemicals aerobically. Air has a much greater potential than water for delivering oxygen to soil on a weight-to-weight basis and volume-to-volume basis. Oxygen provided by air is more easily delivered since the fluid is less viscous than water; higher oxygen concentration in air also provides a larger driving force for diffusion of oxygen into less permeability areas within a soil formation.

Hinchee (1989) and Hinchee and Downey (1990) successfully applied SVE for enhancement of biodegradation of petroleum hydrocarbons in JP-4 jet fuel at Hill Air Force Base, Ogden, Utah, by increasing subsurface oxygen concentrations. Soil moisture was found to be a sensitive variable affecting biodegradation, with increased soil moisture (from 20 percent to 75 percent field capacity) related to increased biodegradation.

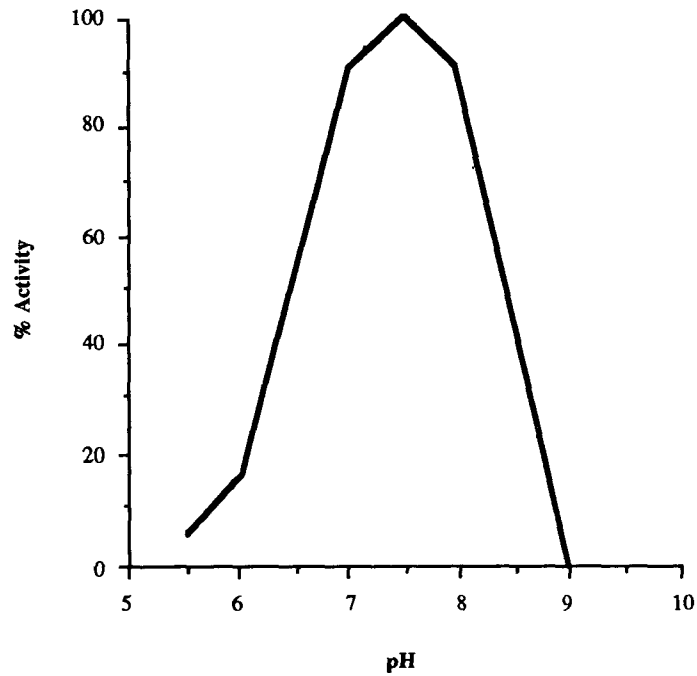


Figure 4. Schematic illustration of the effect of pH on microbial activity.

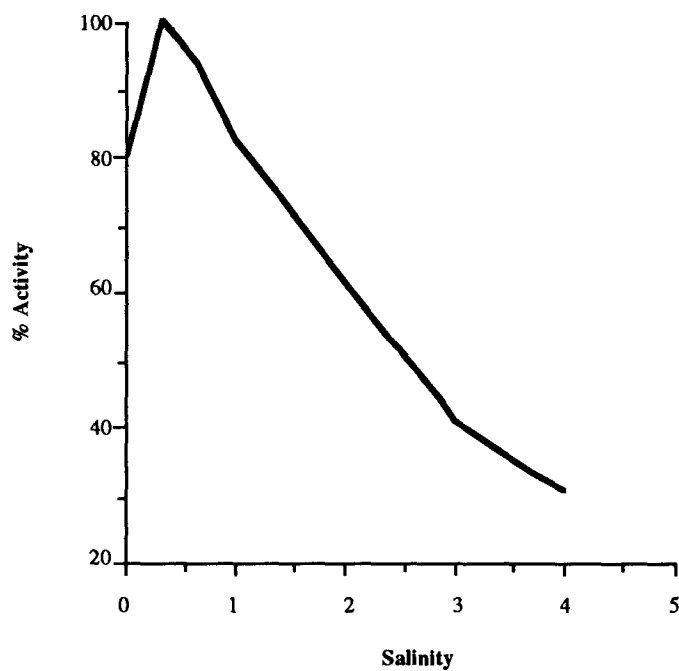


Figure 5. Schematic illustration of the effect of salinity on microbial enzyme activity. Considerable variations in this response have been observed (Atlas and Bartha 1978). Salinity expressed as electrical conductivity (EC) measured in units of mmhos/cm at 25°C.

Monitoring of carbon dioxide production and oxygen utilization was used to monitor biodegradation under field-scale conditions.

Microbial ecologists have identified ranges of critical environmental conditions that affect aerobic activity of soil microorganisms (Table 1). Many of these conditions are controllable and can be modified to enhance activity (10, 18, 20, 22). Each of the critical environmental conditions identified in Table 1 is considered in more detail below.

Table 1. Critical environmental factors for microbial activity (Sims et al. 1984, Huddleston et al. 1986, Rochkind and Blackburn 1986, Paul and Clark 1989)

<i>Environmental Factor</i>	<i>Optimum Levels</i>
Available soil water	25 - 85% of water holding capacity; -0.01 MPa
Oxygen	Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimum air-filled pore space of 10%; Anaerobic metabolism: O ₂ concentrations less than 1%
Redox potential	Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts
pH	5.5 - 8.5
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth (Suggested C:N:P ratio of 120:10:1)
Temperature	15 - 45° C (Mesophiles)

Soil Moisture and Oxygen Concentration

Water is necessary for microbial life, and the soil water matric potential against which microorganisms must extract water from the soil regulates their activity. Soil matric potential is the energy required to extract water from the soil pores to overcome capillary and adsorptive forces. Soil water also serves as the transport medium through which many nutrients and organic chemicals diffuse to the microbial cell, and through which metabolic waste products are removed. Soil water also affects soil aeration status, nature and amount of soluble materials, soil water osmotic pressure, and the pH of the soil solution (18).

Microbial respiration, plant root respiration, and respiration of other organisms remove oxygen from the soil atmosphere and enrich it with carbon dioxide. Gases diffuse into the soil from the air above it, and gases in

the soil atmosphere diffuse into the air. However, oxygen concentration in a soil may be only half that in air while carbon dioxide concentrations may be many times that of air. Even so, a large fraction of the microbial population within the soil depends on oxygen as the terminal electron acceptor in metabolism. When soil pores become filled with water, the diffusion of gases through the soil is restricted. Oxygen may be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil may become anaerobic. Clay content of soil and the presence of organic matter also may affect oxygen content in soil. Clayey soils tend to retain a higher moisture content, which restricts oxygen diffusion, while organic matter may increase microbial activity and deplete available oxygen. Loss of oxygen as a metabolic electron acceptor induces a change in the activity and composition of the soil microbial population. Facultative anaerobic organisms, which can use oxygen when it is present or can switch to alternative electron acceptors such as nitrate or sulfate in the absence of oxygen, and obligate anaerobic organisms become the dominant populations.

Redox Potential

Another soil parameter that describes the effect of the soil environment on metabolic processes is the redox potential of the soil (18). Biological energy is obtained from the oxidation of reduced materials. Electrons are removed from organic or inorganic substrates to capture the energy that is available during the oxidative process. Electrons from reduced compounds are moved along respiratory or electron transport chains composed of a series of compounds. In an aerobic process, O_2 acts as the terminal electron acceptor. In some cases where O_2 is not available, nitrate (NO_3^-), iron (Fe^{3+}), manganese (Mn^{2+}), and sulfate (SO_4^{2-}) can act as electron acceptors if the organisms have the appropriate enzyme systems. A measurement of the oxidation-reduction potential (redox potential) of a soil provides a measurement of the electron density of the system. As a system becomes reduced, O_2 is depleted, and other substances are used as terminal electron acceptors. There is a corresponding increase in electron density, resulting in a progressively increased negative potential. Redox potential is measured as Eh, expressed in millivolts, or as pe, which is equal to $-\log [e^-]$, where $[e^-]$ is the concentration of negatively charged electrons. Redox potential is measured in a subsurface system with a reference electrode in combination with a metallic electrode, such as platinum, which is sensitive and reversible to oxidation-reduction conditions. Very well oxidized soils have redox potentials of 400 to 800 mV, while extremely reduced soils may have potentials of -100 to -500 mV (4).

Eh defined as follows (Dragun 1988):

$$Eh = pe (2.3 RT/F)$$

where Eh	=	redox potential, Volts
pe	=	negative log of electron concentration
R	=	gas constant, 0.001987 kcal/ $^{\circ}$ K
T	=	temperature, $^{\circ}$ K
F	=	faraday constant, 23.06 kcal/V equivalent

thus

$$pe = 16.9 (Eh)$$

Since electrons neutralize protons, many reactions in the subsurface are both Eh and pH dependent. Therefore, Eh-pH diagrams are often used to indicate the predominant dissolved and mineral species as functions of the Eh and pH values a system.

Soil pH

Soil pH also affects the activity of soil microorganisms. Fungi are generally more tolerant of acidic soil conditions (below pH 5) than are bacteria. Near neutral pH values are most conducive to microbial functioning in general. The solubility of phosphorus, an important nutrient in biological systems, is maximized at a pH value of 6.5. A specific contaminated soil system may require management of soil pH to achieve levels that maximize microbial activity. Control of pH to enhance microbial activity may also aid in the immobilization of hazardous metals in a soil system (a pH level greater than 6 is recommended to minimize metal transport).

Buffering capacity of soil reflects the ability of the soil components to hold large number of ions in adsorbed or reserve form. This, adsorption or inactivation of H^+ ions or the release of adsorbed ions to neutralize OH^- ions provides protection against abrupt changes in pH when acidic or basic constituents are added to soil. Varying buffer capacities among soils reflects differences in the soil cation exchange capacities and will directly affect the amount of material required for addition to change pH as well as the length of time before additional material must be added to maintain pH at a desired level.

pH also affects the molecular structure for chemicals that ionize. Comparison of the soil pH value with chemical K_a value will indicate the distribution of chemical between ionized and un-ionized form. Generally, ionized forms of chemicals are more water soluble and therefore less available for volatilization, and for anionic species, less available for sorption to the soil solid phase.

Nutrient Availability

Microbial metabolism and growth is dependent upon adequate supplies of essential macro- and micronutrients. Required nutrients must be present and available to microorganisms in (1) a usable form; (2) appropriate concentrations; and (3) proper ratios (4). If the wastes present at the site are high in carbonaceous materials and low in N and P, the soils may become depleted of available nitrogen (N) and phosphorus (P) required for biodegradation of the organic constituents. Fertilization may be required at some contaminated sites as a management technique to enhance microbial degradation.

In agriculture, fertilizer is added to hasten the decomposition of crop residues (1). This procedure also has been used in the treatment of soil contaminated with hazardous wastes as a result of an oil spill (25). Skujins et al. (1983) studied the biodegradation of waste oils at a disposal site where soils were amended with calcium hydroxide, phosphate, and urea; within four years, 90 percent of the applied oil was degraded.

Although most microorganisms can efficiently extract inorganic nutrients from their environment, their activity may be limited by the availability of nutrient. This is especially true if available carbon is excessive relative to the amount of nitrogen or phosphorus required to degrade the carbon. If soil organic carbon, organic nitrogen, and organic phosphorus are determined, the C:N:P ratio can be determined and nutrient availability can be evaluated. If the ratio of C:N:P is wider than approximately 300:15:1 (weight basis) and available (extractable) inorganic forms of N and P do not narrow the ratio to within these limits, supplemental nitrogen or phosphorus should be added (1).

Temperature

Biodegradation of organic constituents declines with lowering of soil temperature due to reduced microbial growth and metabolic activity. Biodegradation has been shown to essentially stop at a temperature of 0° C. Soils exhibit a variation in the temperature of the surface layers, both diurnally and seasonally. Diurnal changes of temperature decrease with depth of the soil profile. Due to the high specific heat of water, wet soils are less subject to large diurnal changes than dry soils (18). Factors that affect soil temperature, and therefore microbial activity at a site, include soil aspect (direction of slope), steepness of slope, degree of shading, soil color, and surface cover.

Soil temperature also influences the rate of volatilization of compounds from soil. As the rate of volatilization increase, the residence time of the volatilized organic chemical in soil may decrease and result in reduction of the mass of chemical available for biodegradation. However, if volatilization is increased due to increased temperature, engineering controls, such as reduction in vacuum extraction rate, can be utilized to maintain volatilized chemicals in the soil environment (i.e., increase soil residence time) for a longer period of time to allow biodegradation to occur.

The effect of temperature on the biodegradation rate often can be described quantitatively by the change in the degradation constant term using the Arrhenius expression:

$$k = A_0 e^{(E_a/RT)} \quad (1)$$

where k is the rate constant, A_0 is a frequency factor, E is the energy of activation, R is the universal gas constant, and T is absolute temperature.

Rate of degradation, k in equation (1), is often expressed as a function of the concentration of one or more of the constituents being degraded or the change in concentration of the terminal electron acceptor, or the rate of generation of a product of biodegradation, e.g., CO_2 . This is termed the order of the reaction and is the value of the exponential used to describe the reaction (18). Either zero or first order power rate models are often used in environmental studies.

Zero order reactions are ones in which the rate of transformation of an organic constituent is unaffected by changes in the constituent concentration because the reaction rate is determined by some other factor than the constituent concentration. If a constituent C is transformed to X , the rate of change of C is:

$$dC/dt = -k \quad (2)$$

On integration, the equation becomes:

$$C_t = C_0 - kt \quad (3)$$

where C_t = concentration of constituent remaining at time t ; and C_0 = initial concentration of constituent, and k = zero order rate constant. A useful term to describe the reaction kinetics is the half-life, $t_{1/2}$, which is the time required to transform 50% of the initial constituent:

$$C_t = C_o/2, \quad \text{then} \quad t_{1/2} = C_o/2k \quad (4)$$

The first order rate model (Equation 5) is widely used because of its effectiveness in describing observed results as well as its inherent simplicity. Its use also allows comparison of results obtained from different studies. In a first order rate reaction, the rate of transformation of a constituent is proportional to the constituent concentration:

$$dC/dt = -kC \quad (5)$$

where C = contaminant concentration (mass/mass); t = time; and k = first order rate constant (1/time). After integration of Equation 4 and rearrangement of the integrated equation, Equation 5 may be used to graphically determine the rate constant, k :

$$\ln(C_t/C_o) = -kt \quad (6)$$

where C_t = concentration of constituent remaining at time t ; and C_o = initial concentration of constituent. A plot of $\ln(C_t/C_o)$ versus t is linear with a slope of $-k$. The rate constant k is independent of the concentration of constituent, since the slope is constant over time. To calculate the time required to transform one-half of the initial constituent ($C_t = C_o/2$), the following equation is used:

$$\ln((C_o/2)/C_o) = -kt_{1/2} \quad (7)$$

which is equal to:

$$t_{1/2} = 0.693/k \quad (8)$$

where $t_{1/2}$ = half-life of the constituent.

First order kinetics generally apply when the concentration of the compound being degraded is low relative to the biological activity in the soil. However, very low concentrations may be insufficient to initiate enzyme induction or support maintenance requirements necessary for microbial growth, even if the compound can be used as an energy source. (21).

A second model used to describe degradation in soils is the hyperbolic rate model, which is similar to Michaelis-Menten enzyme kinetics. This model is expressed as:

$$dC/dt = -k_1 C/(k_2 + C) \quad (9)$$

where k_1 and k_2 are constants. The constant k_1 represents the maximum rate of degradation that is approached as the concentration increases. This model simulates a catalytic process in which degradation may be catalyzed by microorganisms.

Toxicity Assessment

Bioassays to quantify toxicity measure the effect of a chemical on a test species under specified test

response of the test organism(s). Often a battery of bioassays is utilized that may include measurements of effects on general microbial activity (e.g., respiration, dehydrogenase activity) as well as assays relating to activity of subgroups of the microbial community (e.g., nitrification, nitrogen fixation, cellulose decomposition). Bioassays utilizing organisms from different ecological trophic levels may also be used to determine toxicological effects. However, use of a single assay as a screening test to identify relative toxicity assessment and toxicity reduction in the environment is a common procedure employed in treatability studies. Assays utilizing microorganisms are often used due to their speed, simplicity, ease in handling, cost effectiveness, and use of a statistically significant number of test organisms that is required to detect the effects of potentially toxic materials in the environment (5, 13).

The Microtox™ assay is an aqueous general toxicity assay that measures the reduction in light output produced by a suspension of marine luminescent bacteria in response to an environmental sample. Bioluminescence of the test organism depends on a complex chain of biochemical reactions. Chemical inhibition of any of the biochemical reactions causes a reduction in bacterial luminescence. Therefore, the Microtox™ test considers the physiological effect of a toxicant and not just mortality. Matthews and Bulich (1984) have described a method of using the Microtox™ assay to predict the land treatability of hazardous organic wastes. Matthews and Hastings (1987) described a method using the Microtox™ assay to determine an appropriate range of waste application loading for soil-based treatment systems. Symons and Sims (1988) utilized the assay to assess the detoxification of a complex petroleum waste in a soil environment. The assay was also included as a recommended bioassay in the U.S. EPA Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations (26).

Soil respiration is generally accepted as a measure of overall soil microbial activity and has been used as an indicator of the toxicity or of the utilization of organic compounds added to the soil environment. Respiration may also act as an indicator for microbial biomass in soil because the transformations of the important organic elements (C,N, P, and S) occur through the biomass. Measurement of CO₂ evolution from soil samples is a commonly used indicator of soil respiration, although measurement of O₂ uptake is also an option for short-term evaluations.

Determination of soil respiration through CO₂ evolution or O₂ utilization are inexpensive and simple approaches for indicating general soil microbial activity and acute effects of the presence of organic chemicals on general microbial activity. This approach has been used for evaluation of the biological component in removal of organic chemicals in bioventing systems (8, 9, 17).

Dehydrogenation is the general pathway of biological oxidation of organic compounds. Dehydrogenases catalyze the oxidation of substrates which produce electrons able to enter the electron transport system of a cell. The type and quantity of carbon substrates, present and introduced, will influence dehydrogenase activity. This assay involves the incubation of soil with 2,3,5-triphenyltetrazolium chloride (TTC). The water-soluble colorless TTC intercepts the flow of electrons produced by microbial dehydrogenase activity and is reduced to the water-insoluble, red 2,3,5-triphenyltetrazeolium formazan (TTC-formazan). TTC-formazan is extracted from the soil with methanol and quantified colorimetrically.

The soil dehydrogenase activity assay is simple and efficient, and is convenient. Major equipment required include a spectrophotometer, centrifuge, and an incubator.

Nitrification activity represents another assay for evaluating biological activity and toxicity in subsurface soils using bioventing technology. Nitrification, the oxidation of ammonium nitrogen to nitrite and nitrate, is accomplished by environmentally sensitive chemoautotrophic bacteria. Energy substrates as well as oxidized products are easily extracted from soil and measured, and therefore the nitrification process may be used as a bioassay for microbial activity, as well as toxicity, in the soil.

No single assay of soil microbial activity is likely to indicate the activity of the broad spectrum of soil microorganism. Measurements of respiration and general toxicity (e.g., Microtox™) may represent the broadest community of microorganisms. Therefore a battery of bioassays, including an activity assay as well as a toxicity assay, are useful in determining the potential for biodegradation as well as the intensity of biological degradation of organic chemicals at a site and for determining the influence of environmental variables on the rate and extent of biodegradation achieved through engineered bioventing at a site.

Interaction of Environmental Factors

The environmental factors presented in Table 1, as well as soil and waste characteristics, interact to affect microbial activity at a specific contaminated site utilizing bioventing as a treatment technology. Computer modeling techniques are useful to attempt to describe the interactions of environmental factors and their effects on treatment of organic constituents in a site-specific bioventing situation.

RESEARCH EFFORTS TOWARD INCREASING BIOVENTING EFFICIENCY

Is There an Advantage to Alternating Aerobic and Anaerobic Processes?

Aerobic habitats are conducive to some microbial activities that may be advantageous in bioventing. Reductive dechlorination of some compounds under anaerobic conditions may be advantageous where chlorinated compounds are the contaminant or part of the contamination (6, 7). The reduced products of these transformations may be susceptible to mineralization under aerobic conditions. Nitrogen fixation by free-living anaerobic bacteria may add to the available nitrogen pool and may be a low cost, effective way of providing nutrients in systems that have become carbon rich because of contamination with organic chemicals. Organic acids produced in anaerobic fermentations may aid in solubilizing phosphorus and other mineral nutrients from soil minerals thus promoting microbial growth and activity.

We have observed nitrogen fixation activity from free living bacteria, as measured by the acetylene reduction assay in jet fuel (JP-4) contaminated soil. Acetylene reduction activity at a contaminated site at Tyndall Air Force Base, Florida, averaged $200 \text{ nmol kg}^{-1} \text{ h}^{-1}$ under anaerobic conditions at 20°C (Miller 1990). Assuming a 3:1 ratio of acetylene reduced to nitrogen fixed, an average of up to $16 \text{ mg N kg}^{-1} \text{ yr}^{-1}$ could be added to this soil from nitrogen fixation. Free living nitrogen fixing bacteria require relatively high amounts of carbon and energy substrates to be available (1) and, for this reason, their activity is often limited in subsurface soil systems. In contaminated environments where degradable organic matter may be abundant however, nitrogen fixation activity may be significant.

Alternating periods of anaerobiosis may provide opportunity for the following reactions in subsurface contaminated soil: (1) fixation of significant amounts of nitrogen (2) dehalogenation of chlorinated organics (3) solubilization of mineral nutrients, and (4) denitrification of excess nitrate. Based upon preliminary results obtained by Utah State University researchers, these reactions are considered potential advantages of "pulsed venting." Characterization and evaluation of "pulsed venting," as described above, at the field-scale level represents a research need that may have immediate application to sites considering bioventing for remediation.

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OPPORTUNITIES FOR BIOTREATMENT OF TRICHLOROETHYLENE IN THE VADOSE ZONE

JOHN T. WILSON

DON H. KAMPBELL, AND

JONG CHO

U.S. EPA-Ada, Oklahoma

ABSTRACT

Trichloroethylene (TCE) vapors in air can be amended with gaseous alkanes, then injected into the unsaturated zone. The unsaturated zone acts as a natural in-situ bioreactor. During natural biodegradation of the alkanes, the TCE is co-oxidized to carbon dioxide and chloride. The technology is most appropriate for sites with a deep and homogeneous unsaturated zone. If necessary, a fertilizer solution can be applied to encourage rapid rates of hydrocarbon oxidation.

The technology is well established at the bench scale. Commercial propane or LPG gas can be used as the feedstock; however, the best results have been obtained with a propellant mixture designed for use in aerosol cans. Prior work by Kampbell et al. (Journal of the Air Pollution Control Association, 37(10)1236-1239, 1987) demonstrated removal of volatile aliphatic hydrocarbons in a soil bioreactor. In a laboratory system, acclimated soil was exposed to air amended with the propellant mixture and TCE vapors. TCE removal was rapid and extensive compared to controls constructed from soil that was not acclimated to the hydrocarbons. Current work attempts to optimize the rate and extent of biodegradation of the feedstock at field scale.

SOIL VENTING DESIGN: MODELS AND DECISION ANALYSIS

MARIAN W. KEMBLOWSKI AND

SHYAMAL CHOWDERY

Utah State University

ABSTRACT

Venting of hydrocarbon-contaminated soils is a frequently used and generally efficient technology for soil cleanup. Proper design of soil venting requires two major components: (1) understanding of the processes that control venting efficiency, and (2) information related to relevant chemical and physical soil and contaminant parameters. In this paper we present several simple models that describe the principal venting processes, including air flow, hydrocarbon-vapor partitioning, ground water upwelling, and diffusion-limited hydrocarbon removal. These models are used to determine which of the physical and chemical soil and contaminant parameters determine the venting efficiency.

Ideally, one would like to know the spatial distribution of such parameters (for example: soil permeability, contaminant concentration, contaminant composition, etc.) as precisely as possible. Incomplete and/or inaccurate information may result, under some circumstances, in significant losses related to improper design of a venting system. On the other hand, obtaining complete and accurate information is hardly ever possible, let alone practical, mostly due to the cost of subsurface investigation and chemical analyses. Thus, the whole design process consists of several modeling and investigation phases.

At the end of each evaluation (modeling) phase, a decision(s) regarding the need for and expectations from further field investigation has to be made. The problem is even more complicated by the fact that one cannot predict the success of subsurface investigation in a deterministic way. Due to this fact, and the intrinsic random character of subsurface parameters, the process of venting design and related investigation should be performed in a stochastic framework. This can be done using the Bayesian decision analysis approach. Applicability of this methodology to venting design is discussed. Some examples are presented.

MODELING TRANSPORT OF ORGANIC CHEMICALS IN GAS AND LIQUID PHASES

A. K. KATYAL, P. K. PATEL AND J. C. PARKER

Virginia Polytechnic Institute & State University

ABSTRACT

The basic principles of modeling fluid flow and transport in multiphase systems relevant to the analysis of in situ gas venting are discussed. The assumption of equilibrium phase partitioning enables multiphase transport equations to be reduced to a single phase-summed equation that has the form of the conventional single phase transport equation with lumped coefficients which reflect contributions from various mobile and immobile phases. Due to diffusive limitations on the rate of mass transfer between phases at the pore scale and between regions of high and low permeability at the field scale, apparent nonequilibrium interphase mass transfer may occur. A first-order kinetic formulation for interphase mass transfer is described which can be incorporated into the phase-summed transport equation by defining apparent partition coefficients, which are functions of the actual local mass transfer rate. A numerical model has been developed which enables solution of water, NAPL and gas flow and transport equations with nonequilibrium mass transfer. An example problem is presented involving a spill of chlorinated solvent which penetrates the unsaturated and saturated zones. Two remediation scenarios are simulated involving 1) gas venting only, and 2) gas venting combined with water pumping. In the former case, water table upwelling occurs due to the reduction in gas pressure near the vacuum well. Water pumping enables water upwelling to be controlled and increases the gas phase recovery while also enabling aqueous phase recovery of solvent in the saturated zone. Simulations with different mass transfer rate constants show that mass recovery rates decrease as nonequilibrium effects become more pronounced.

INTRODUCTION

Organic liquids enter the subsurface environment through a variety of sources which include accidental spills, leaking underground storage tanks, pipeline leaks and other releases. These nonaqueous phase liquids (NAPLs), which may be complex mixtures of different organic compounds, may migrate downward and spread laterally on the water table if less dense than water, or they may penetrate into the aquifer if more dense than water. NAPLs pose a serious threat to water quality due to the gradual release of components to the aqueous phase.

A number of researchers have developed multiphase models with different capabilities and limitations. Most models have been restricted to two-dimensional vertical sections (1, 6, 13, 14, 16, 19) and vertically integrated models for areal analyses of oil-water flow (9, 15, 20, 21). Abriola and Pinder (1985) presented a computationally intensive model, which was later modified by Reeves and Abriola (1988) to improve its efficiency. Corapcioglu and Baehr (1987) presented a multicomponent transport model with steady water flow and immobile oil and air phases including oxygen-limited biodegradation. Most of the above

researchers assumed local equilibrium partitioning between various phases. Falta and Javandel (1987) presented a three-dimensional model which considered nonequilibrium phase partitioning, and Sleep and Sykes (1989) presented a similar two-dimensional model. Miller et al. (1990) presented a comparison between equilibrium and nonequilibrium oil-water partitioning models.

Under conditions of high oil saturation and low flow velocities, the assumption of local equilibrium partitioning may be valid (10, 22). On the other hand, nonequilibrium conditions have been reported by Schwille (1975), Feenstra and Coburn (1986), Miller and Weber (1986), Hunt et al. (1988b) and Geller and Hunt (1989) in systems with low residual oil saturations.

Various researchers have addressed the problem of in situ air venting for remediation of volatile compounds from soil. Baehr et al. (1989) presented a model for air venting based on equilibrium partitioning. Johnson et al. (1990) presented a screening model for designing air venting systems, also based on equilibrium partitioning. Recently, Powers et al. (1991) compared the removal efficiency of pump and treat systems with equilibrium and nonequilibrium partitioning between water and NAPLs. Powers et al. (1991) concluded that the important parameters that controlled the removal efficiency were the mass transfer coefficient and the flow velocity.

This paper extends the multiphase model of Kaluarachchi and Parker (1990) to include nonequilibrium interphase partitioning with a dynamic gas phase. Emphasis is placed on impacts of nonequilibrium partitioning on the removal efficiency for air venting systems. A hypothetical spill of dense chlorinated hydrocarbon is simulated and two different scenarios are studied involving air pumping only or combined air and water pumping. Water pumping enables control of the water table upwelling at the vacuum well to increase the air removal efficiency. In each scenario, removal efficiency is compared with different nonequilibrium partitioning coefficients and with equilibrium partitioning.

MODEL DESCRIPTION

Flow model. The mass conservation equations for water (w), organic liquid (o) and air (a) phases, assuming an incompressible porous medium, incompressible liquid phases and compressible gas phase, may be written in summation convention for a two dimensional Cartesian domain as

$$\phi \frac{\partial S_w}{\partial t} = - \frac{\partial q_{wi}}{\partial x_i} + \frac{R_w}{\rho_w} \quad (1a)$$

$$\phi \frac{\partial S_o}{\partial t} = - \frac{\partial q_{oi}}{\partial x_i} + \frac{R_o}{\rho_o} \quad (1b)$$

$$\phi \frac{\partial \rho_a S_a}{\partial t} = - \frac{\partial q_{ai}}{\partial x_i} + R_a \quad (1c)$$

where ϕ is porosity, S_p is the p-phase saturation, x_i (and x_j) are Cartesian spatial coordinates ($i, j = 1, 2$), q_{pi} is the Darcy velocity of phase p in the i -direction, ρ_p is the density of phase p, R_p is the net mass transfer per unit porous media volume into (+) or out of (-) phase p, and t is the time. Darcy velocities in the p-phase are defined by

$$q_{pi} = -K_{p_{ij}} \left\{ \frac{\partial h_p}{\partial x_j} + \rho_{rp} u_j \right\} \quad (2)$$

where $K_{p_{ij}}$ is the p-phase conductivity tensor, $h_p = P_p / g \rho_w^*$ is the water height equivalent pressure head of phase p where P_p is the p-phase pressure, g is gravitational acceleration and ρ_w^* is the density of pure water, ρ_p is the density of phase p, $\rho_{rp} = \rho_p / \rho_w^*$ is the p-phase specific gravity, and $u_j = \partial z / \partial x_j$ is a unit gravitational vector measured positive upwards where z is elevation. Initial and boundary conditions for each phase may be specified as a prescribed head or a prescribed flux.

Two-phase air-water saturation-capillary pressure relations are described by the van Genuchten (1980) function

$$\bar{S}_w = [1 + (\alpha h_{aw})^n]^{-m} \quad (3)$$

where α and n are porous medium parameters, $m = 1 - 1/n$ and $h_{aw} = h_a - h_w$. Following the occurrence of oil at a given location, the system is described by the three phase relations

$$\bar{\bar{S}}_w = [1 + (\alpha \beta_{ow} h_{ow})^n]^{-m} \quad (4a)$$

$$\bar{S}_t = [1 + (\alpha \beta_{ao} h_{ao})^n]^{-m} \quad (4b)$$

where $h_{ow} = h_o - h_w$ and $h_{ao} = h_a - h_o$, β_{ao} and β_{ow} are fluid-dependent scaling factors and $\bar{\bar{S}}_w$ and \bar{S}_t are "apparent" water and total liquid saturations which account for effects of irreducible water saturation, S_{wr} and the maximum trapped oil saturation, S_{or} , as described in detail by Kaluarachchi and Parker (1991). Phase conductivities are described by

$$K_{wij} = k_{rw} K_{swij} \quad (5a)$$

$$K_{oij} = k_{ro} K_{swi} / \eta_{ro} \quad (5b)$$

$$K_{aij} = k_{ra} K_{swi} / \eta_{ra} \quad (5c)$$

where k_{rp} is the relative permeability of phase p, η_{rp} is the viscosity ratio between phase p and water, and K_{swij} is the saturated conductivity tensor for water. We shall assume here that the coordinate system is oriented with the conductivity tensor, or otherwise that off-diagonal components may be disregarded, so that $K_{swij} = 0$ for $i \neq j$. Phase relative permeabilities are described by

$$k_{rw} = \bar{S}_w^{1/2} [1 - (1 - \bar{S}_w^{1/m})]^2 \quad (6a)$$

$$k_{ro} = (\bar{S}_t - \bar{S}_w)^{1/2} \left[(1 - \bar{S}_w^{1/m})^m - (1 - \bar{S}_t^{1/m})^m \right]^2 \quad (6b)$$

$$k_{ra} = (1 - \bar{S}_t)^{1/2} [1 - \bar{S}_t^{1/2}]^{2m} \quad (6c)$$

where $m = 1 - 1/n$ is the van Genuchten parameter.

Transport model. Mass conservation of species α in the p-phase requires that

$$\phi \frac{\partial C_{\alpha p}}{\partial t} = - \frac{\partial J_{\alpha p i}}{\partial x_i} + R_{\alpha p} \quad (7)$$

where $C_{\alpha p}$ is the concentration of the noninert α component in p-phase expressed as the mass of α per phase volume [ML^{-3}], $J_{\alpha p i}$ is the mass flux density of α in p-phase per porous media cross section in the i-direction [$\text{ML}^{-2} \text{T}^{-1}$], and $R_{\alpha p}$ is the net mass transfer rate per porous medium volume of species α into (+) or out of (-) the p-phase [ML^{-3}].

The mass flux density of component a in phase p due to convection, diffusion and mechanical dispersion is described by

$$J_{\alpha p i} = C_{\alpha p} q_{p i} - \phi S_p D_{\alpha p i j} \frac{\partial C_{\alpha p}}{\partial x_j} \quad (8)$$

where $D_{\alpha p i j}$ is a dispersion tensor given by

$$D_{\alpha p i j} = g_{\alpha p} \left(D_{\alpha p}^{dif} + D_{p i j}^{hyd} \right) \quad (9)$$

in which $D_{\alpha p}^{dif}$ is the molecular diffusion coefficient of α in the p-phase of the porous medium, $D_{p i j}^{hyd}$ is a mechanical dispersion coefficient, and $g_{\alpha p}$ is a nonadulst solution correction factor. For the case of transport of low solubility organic components, small volume fractions of organic components in water and gaseous phases will occur and $g_{\alpha w} = g_{\alpha a} = 1$ is assumed. For nonaqueous phase liquids, the phase composition may reach 100% (e.g., single component organic liquid) at which point dispersive transport becomes nonexistent. We accommodate nondilute solution diffusion-dispersion by approximating the oil phase nonideal solution factor by

$$g_{\alpha o} = 1 - C_{\alpha o} / \rho_o \quad (10)$$

Employing the tortuosity model of Millington and Quirk (1959) yields the expression for $D_{\alpha p}^{dif}$ as

$$D_{\alpha p}^{dif} = \phi^{1/3} S_p^{7/3} D_{\alpha p}^o \quad (11)$$

where $D_{\alpha p}^o$ is the diffusion coefficient of α in bulk p-phase. The mechanical dispersion coefficient is shown by Bear (1972) to have the form

$$D_{p ij}^{hyd} = \frac{1}{\phi S_p} \left(A_T \bar{q}_p \delta_{ij} + (A_L - A_T) \frac{|q_{pi} q_{pj}|}{q_p} \right) \quad (12)$$

where A_L and A_T are longitudinal and transverse dispersivities [L], q_{pi} and q_{pj} are p-phase Darcy velocities in the i and j directions, $q_p = |\Sigma q_{pi}^2|^{1/2}$ is the absolute magnitude of the p-phase velocity, and δ_{ij} is Kroonecker's delta.

Combining the phase continuity equation and the mass flux equation for transport of component α in the p-phase yields

$$\phi \frac{\partial C_{\alpha p} S_p}{\partial t} = \frac{\partial}{\partial x_i} \left(\phi S_p D_{\alpha p ij} \frac{\partial C_{\alpha p}}{\partial x_j} \right) - \frac{\partial C_{\alpha p} q_{pi}}{\partial x_i} + R_{\alpha p} \quad (13)$$

Expanding the first and third terms in (13), employing the bulk p-phase continuity equation (1), and assuming density derivative terms to be of second order importance within a given time step yields

$$\phi S_p \frac{\partial C_{\alpha p}}{\partial t} = \frac{\partial}{\partial x_i} \left(\phi S_p D_{\alpha p ij} \frac{\partial C_{\alpha p}}{\partial x_j} \right) - q_{pi} \frac{\partial C_{\alpha p}}{\partial x_i} + R_{\alpha p} - \frac{R_p}{\rho_p} C_{\alpha p} \quad (14)$$

To accommodate adsorption of α by the solid phase, an additional continuity equation is required which may be written as

$$\frac{\partial C_{\alpha s}}{\partial t} = R_{\alpha s} \quad (15)$$

where $C_{\alpha s}$ is the solid phase concentration expressed as mass of adsorbed component α per porous medium volume [ML^{-3}] and $R_{\alpha s}$ is the mass transfer rate per porous medium volume to (+) or from (-) the solid phase [$ML^{-3}T^{-1}$]. The total phase mass transfer rate, R_p , is related to the individual component mass transfer rates by

$$R_p = \sum_{\alpha=1}^{n_s} R_{\alpha p} \quad (16)$$

where n_s denotes the number of “noninert” or partitionable species. In the present context, we will use the term “inert” to refer to components of the NAPL phase which are for practical purposes insoluble and nonvolatile.

We introduce *equilibrium* phase partition relations of the form

$$C_{\alpha o}^e = \Gamma_{\alpha o} C_{\alpha w}^e \quad (17a)$$

$$C_{\alpha a}^e = \Gamma_{\alpha a} C_{\alpha w}^e \quad (17b)$$

$$C_{\alpha s}^e = \Gamma_{\alpha s} C_{\alpha w}^e \quad (17c)$$

where superscript e denotes an equilibrium concentration, $\Gamma_{\alpha o}$ is the equilibrium partition coefficient for species α between water and organic liquid (Raoult’s constant), $\Gamma_{\alpha a}$ is the equilibrium partition coefficient between water and gas (Henry’s constant), and $\Gamma_{\alpha s}$ is a dimensionless equilibrium partition coefficient between water and solid phase.

Under transient field conditions actual phase concentration ratios may differ from the true equilibrium ratios defined by [17]. With this in mind, we define *apparent* partition coefficients — which will vary in time and space — by analogs of [17] as

$$C_{\alpha o} = \Gamma_{\alpha o}' C_{\alpha w} \quad (18a)$$

$$C_{\alpha a} = \Gamma_{\alpha a}' C_{\alpha w} \quad (18b)$$

$$C_{\alpha s} = \Gamma_{\alpha s}' C_{\alpha w} \quad (18c)$$

For any two phases which are in physical contact, the rate of mass transfer will be described by first order mass transfer functions of the form

$$R_{\alpha 12} = k_{\alpha 12} (C_{\alpha 1} - C_{\alpha 1}^e) \quad (19a)$$

$$= -k_{\alpha 12} (C_{\alpha 2} - C_{\alpha 2}^e) \quad (19b)$$

where $R_{\alpha 12}$ is the rate of mass transfer of α per porous medium volume from phase 1 to phase 2, $C_{\alpha 1}$ is the actual concentration of α in phase 1, $C_{\alpha 1}^e$ is the concentration of α which would occur in phase 1 if it were in equilibrium with phase 2, $C_{\alpha 2}$ is the actual concentration of α in phase 2, $C_{\alpha 2}^e$ is the concentration of α that would occur in phase 2 if it were in equilibrium with phase 1, and $k_{\alpha 12}$ is a mass transfer rate coefficient [T^{-1}].

Consider first, the case of mass transfer between oil and water phases when both phases exist at a point in time and space. Employing [19a] along with [18a] for the actual oil phase concentration and [17a] for the equilibrium concentration gives

$$R_{\alpha ow} = k_{\alpha ow} (\Gamma_{\alpha o}' C_{\alpha w} - \Gamma_{\alpha o} C_{\alpha w}) \quad (20)$$

which may be solved in terms of $\Gamma_{\alpha o}'$

$$\Gamma_{\alpha o}' = \Gamma_{\alpha o} + \frac{R_{\alpha ow}}{k_{\alpha ow} C_{\alpha w}} \quad (21)$$

which indicates that the apparent partition coefficient may be expressed in terms of the actual partition coefficient plus a correction term, which depends on the sign and magnitude of the actual mass transfer rate and on the concentration in the water phase.

If free oil is present in the system at a given point in time and space, so that air and oil are physically in contact, mass transfer between oil and gas phases may be described in a similar fashion. Employing in this case [19b] we obtain

$$R_{\alpha oa} = -k_{\alpha oa} (\Gamma_{\alpha a}' C_{\alpha w} - \Gamma_{\alpha a} C_{\alpha w}) \quad (22)$$

which yields

$$\Gamma_{\alpha a}' = \Gamma_{\alpha a} - \frac{R_{\alpha oa}}{k_{\alpha oa} C_{\alpha w}} \quad (23)$$

In the absence of free oil in the porous medium at a given location, mass transfer will occur between water and gas phases rather than between oil and gas phases. Proceeding in the same manner as for oil-gas mass transfer yields

$$\Gamma_{\alpha a}' = \Gamma_{\alpha a} - \frac{R_{\alpha wa}}{k_{\alpha wa} C_{\alpha w}} \quad (24)$$

Note that *either* (23) or (24) will be relevant at a given location and time, depending on whether free oil occurs. Finally, mass transfer between water and solid phase may be considered by employing [19b] to obtain

$$\Gamma_{\alpha s}' = \Gamma_{\alpha s} - \frac{R_{\alpha ws}}{k_{\alpha ws} C_{\alpha w}} \quad (25)$$

Using (17) to eliminate oil, gas and solid phase concentrations from (14) and summing the equations noting that

$$R_{\alpha w} + R_{\alpha o} + R_{\alpha s} + R_{\alpha a} = 0 \quad (26)$$

leads to the α -component phase-summed transport equation in terms of water phase concentrations

$$\phi_{\alpha}^* \frac{\partial C_{\alpha w}}{\partial t} = \frac{\partial}{\partial x_i} \left[D_{\alpha ij}^* \frac{\partial C_{\alpha w}}{\partial x_j} \right] - q_{\alpha i}^* \frac{\partial C_{\alpha w}}{\partial x_i} - \mu_{\alpha}^* C_{\alpha w} \quad (27a)$$

where

$$\phi_{\alpha}^* = \phi S_w + \phi S_o \Gamma_{\alpha o}' + \phi S_a \Gamma_{\alpha a}' + \Gamma_{\alpha s}' \quad (27b)$$

$$D_{\alpha ij}^* = \phi S_w D_{\alpha wij} + \phi S_o D_{\alpha oij} \Gamma_{\alpha o}' + \phi S_a D_{\alpha aij} \Gamma_{\alpha a}' \quad (27c)$$

$$q_{\alpha i}^* = q_{wi} + q_{oi} \Gamma_{\alpha o}' + q_{ai} \Gamma_{\alpha a}' \quad (27d)$$

$$\mu_{\alpha}^* = \frac{R_w}{\rho_w} + \frac{R_o \Gamma_{\alpha o}'}{\rho_o} + \frac{R_a \Gamma_{\alpha a}'}{\rho_a} \quad (27e)$$

Note that (27) has the same form as the simple single-phase equilibrium transport equation. However, the coefficients represent pooled effects of transport in all phases and the equation is nonlinear due to dependence of apparent partition coefficients on concentrations. Note also that interphase mass transfer terms occur in the phase summed equation only as a sum over all components.

Solution approach. The basic approach for solving the coupled multiphase flow and multicomponent transport problem with nonequilibrium mass transfer is as follows

1. Solve the fluid flow equations simultaneously for the current time-step using time-lagged phase densities and interphase mass transfer rates.
2. Solve the phase-summed transport equation using current values of apparent partition coefficients, interphase mass transfer rates and phase densities.
3. Back-calculate interphase mass transfer rates, update phase densities and apparent partition coefficients and repeat (2) until transport solution converges.
4. Proceed to the next time step.

An upstream-weighted finite element formulation for the coupled flow and transport problem was developed and implemented in a computer code (details available from authors on request).

APPLICATION TO SOLVENT SPILL REMEDIATION

This problem involves a spill of tetrachloroethylene (PER) in a radial domain and remediation using vacuum extraction. The simulation is performed in three stages with two restarts as follows:

Stage 1:	Oil infiltration event
Stage 2:	Redistribution and transport under natural gradients
Stage 3:	Remediation using gas vacuum extraction and/or water pumping

The first stage of the problem involves infiltration of PER on a circular area with a radius of 2.0 m at the soil surface. A total of 3 m³ of PER is assumed to infiltrate under a water-equivalent oil head of -0.25 m. A water table occurs at a depth of 3.2 m and an impermeable layer occurs 5 m below the surface. The soil is uniform and has properties given in Table 1. Properties for PER are also given in the table. The problem is analyzed as a 2-D radial section with an inner radius of 0.1 m (in order to facilitate subsequent analysis of pumping from a well of the same radius) and an outer radius of 8 m. A mesh with 12 nodes in the vertical direction and 16 nodes in the horizontal direction is employed.

Initial conditions for the water phase are assumed to correspond to equilibrium with the water table with no oil. Boundary conditions for the water phase involve a type-1 condition on the right side below the water table corresponding to vertical hydrostatic conditions (i.e., same as the initial conditions). All other boundaries are no flow for the water phase. Boundary conditions for the oil phase are a type-1 condition with $h_o = 0.25$ m on the 5 nodes on the upper surface between $r = 0$ and $r = 2.0$ m. All other nodes are no flow for oil. Gas flow was not considered during infiltration. Termination of Stage 1 occurred at $t = 6.48$ d after infiltration of 3.13 m³ of oil.

Stage 2 of the problem involves a continuation from the final conditions of Stage 1. Redistribution of PER is permitted for a period of 25 d under no flow boundary conditions for the oil phase on all boundaries. Boundary conditions for the water phase are maintained as in the infiltration stage. Gas phase flow is again disregarded. Transport is considered with the initial aqueous concentration of PER at nodes where oil phase is present set to the solubility of 150 g m⁻³. Boundary conditions for transport impose zero dispersive flux on all boundaries which is equivalent to zero flux since there is essentially no flow on the boundaries during Stage 2. By the end of the redistribution period, the NAPL plume has reached the lower aquifer boundary. However, a substantial volume of the spill is still retained in the zone above the water table as “residual saturation” retained by capillary forces (Figure 1).

In Stage 3, remediation is simulated with vacuum pumping in the unsaturated zone. A vacuum well with a 0.1 m radius is assumed to be placed at the left boundary screened from the surface to a depth of 3.2 m and regulated at a pressure head of $h_a = -1.5$ m. The gas boundary at the well is treated as a type-1 boundary condition (specified pressure). Gas inflow is permitted along the upper surface from $r = 3.5$ m to the outer perimeter under a type-1 condition for gas with a constant pressure of $h_a = 0$ (atmospheric pressure). The inner 3.5 m of the surface is assumed to be covered and is treated as no-flow. No flow conditions are imposed for the oil phase on all boundaries. Boundary conditions for transport are type-3 with zero influent concentration on the top and right side boundaries and zero dispersive flux elsewhere.

Two different scenarios are evaluated to assess alternative designs of the gas venting system. In the first scenario, only gas pumping is considered. The water head is prescribed on the right boundary at the initial conditions below the water table as in the earlier simulations and all other boundaries are treated as no flow for water. During this simulation, the gas flow rate stabilizes at 319 m³ d⁻¹ after 2 days. The simulations were analyzed with three different values of nonequilibrium partitioning coefficients: 0.2 d⁻¹, 2.0 d⁻¹ and 20.0 d⁻¹.

The variation of PER mass remaining in the system versus time for all the three cases is presented in Figure 3. It is clear that the mass removed during venting is reduced due to nonequilibrium partitioning between PER and air. From Figure 2, it is evident that constant gas pumping results in water table upwelling which will affect recovery in the gas phase since the gas transmissivity, and hence the gas flow rate, is reduced, and the amount of PER which is exposed to gas flow is also reduced.

The second scenario is performed to evaluate the effects of simultaneous pumping of air and water on removal efficiency. The boundary conditions on the entire domain are the same as in the first scenario, except on the left edge, where the water head is specified with a 50 cm drawdown to induce water pumping. As before, the simulation is repeated for three different values of nonequilibrium partitioning coefficients. The mass remaining in the system versus time is presented in Figure 5 for all three cases. The reduction of water table upwelling resulting from simultaneous water and air pumping is shown in Figure 4. The mass removal rate is approximately 15% greater with simultaneous water and gas pumping than gas pumping only for a given mass transfer coefficient, reflecting the greater gas flow rate for the water and gas pumping scenario ($365 \text{ m}^3 \text{ d}^{-1}$)

In the above simulations, nonequilibrium mass transfer is not initiated until after 2.5 days to avoid numerical instabilities. Thus, the results are identical up to 2.5 days for all three partitioning coefficients. Total PER mass in the soil shows a small increase ($\sim 2.5\%$) during the first day, which reflects a numerical mass balance error before the solution stabilizes and mass removal rates become nearly constant

Table 1. Input parameters for PER spill problem.

<i>Soil properties:</i>	<i>Bulk fluid properties:</i>
$K_{swx} = 5.0 \text{ m d}^{-1}$	$\beta_{\alpha o} = 2.3$ $\beta_{ow} = 1.77$
$K_{swz} = 2.0 \text{ m d}^{-1}$	$\eta_{ro} = 0.9$ $\rho_{ro} = 1.62$
$\phi = 0.4$	<i>Component properties (PER):</i>
$S_m = 0.1$	$D_{\alpha w}^o = 0.85 \times 10^{-4} \text{ m}^2 \text{ d}^{-1}$
$S_{or} = 0.2$	$D_{\alpha o}^o = 0.95 \times 10^{-4} \text{ m}^2 \text{ d}^{-1}$
$\alpha = 3.0 \text{ m}^{-1}$	$D_{\alpha a}^o = 0.65 \text{ m}^2 \text{ d}^{-1}$
$n = 2.8$	$\Gamma_{\alpha o} = 10,800.$
$A_L = 0.1 \text{ m}$	$\Gamma_{\alpha o a} = 0.35$
$A_T = 0.02 \text{ m}$	$\rho_{\alpha} = 1.62 \times 10^6 \text{ g m}^{-3}$

CONCLUSIONS

Nonequilibrium effects were incorporated in a multiphase flow and transport model. A first order kinetic model was employed with a phased-summed transport model using the concept of apparent partition coefficients. The model was tested for two different scenarios to study the removal efficiency during soil venting. Efficiency clearly decreases as the mass transfer coefficients decrease due to the increasing degree of nonequilibrium. Removal efficiency can be enhanced with simultaneous pumping of air and water as the latter enables control of water table upwelling which increases the gas flow rate and the volume of NAPL exposed to gas flow.

At high velocities or low oil saturations, mass transfer coefficients may diminish sufficiently to result in nonequilibrium behavior. Furthermore, in heterogeneous formations, apparent nonequilibrium behavior may arise due to diffusive mass transfer limitations between high and low permeability zones. At the present time, the kinetics of mass transfer in heterogeneous media is not well understood. Future efforts are needed to better understand the efficiency of in situ gas venting systems.

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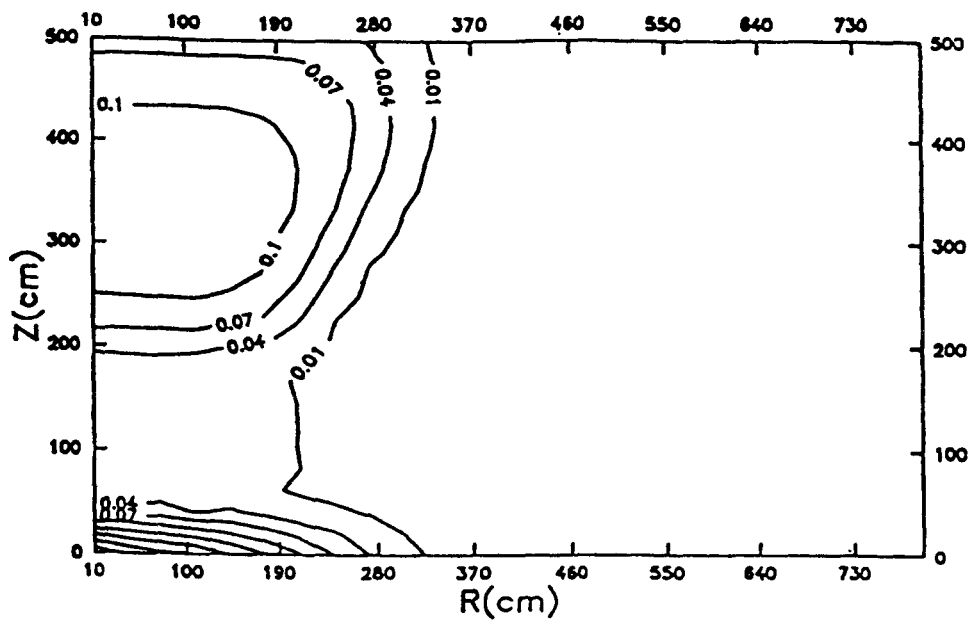


Figure 1. Oil saturation contours at the end of Stage 2.

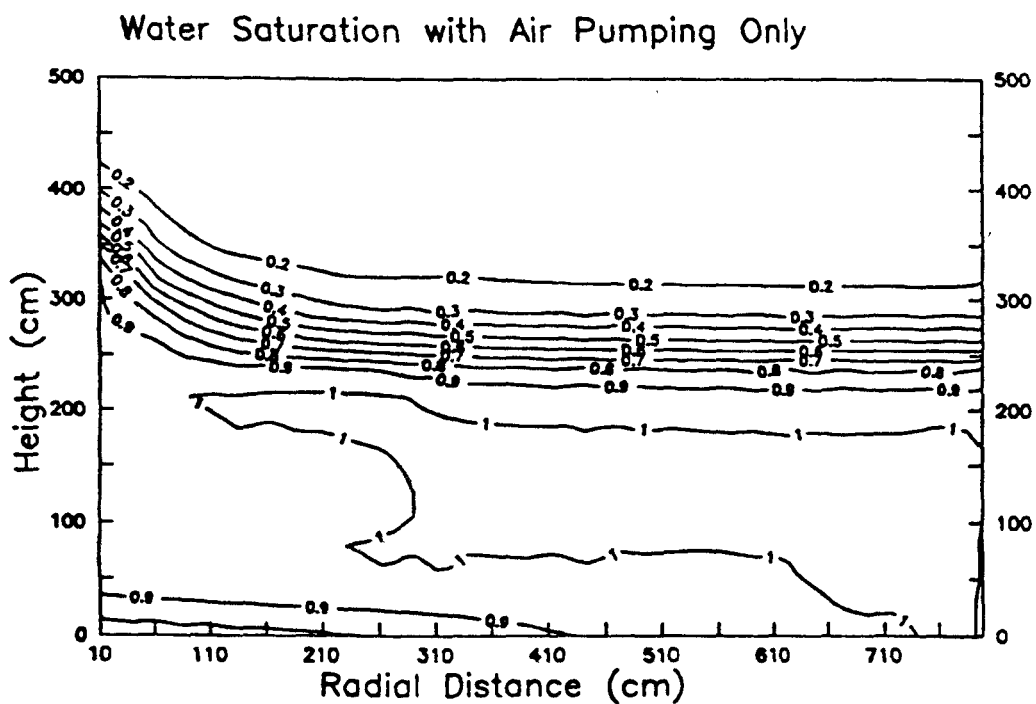


Figure 2. Water saturation profiles at the end of Stage 3 with air pumping only.

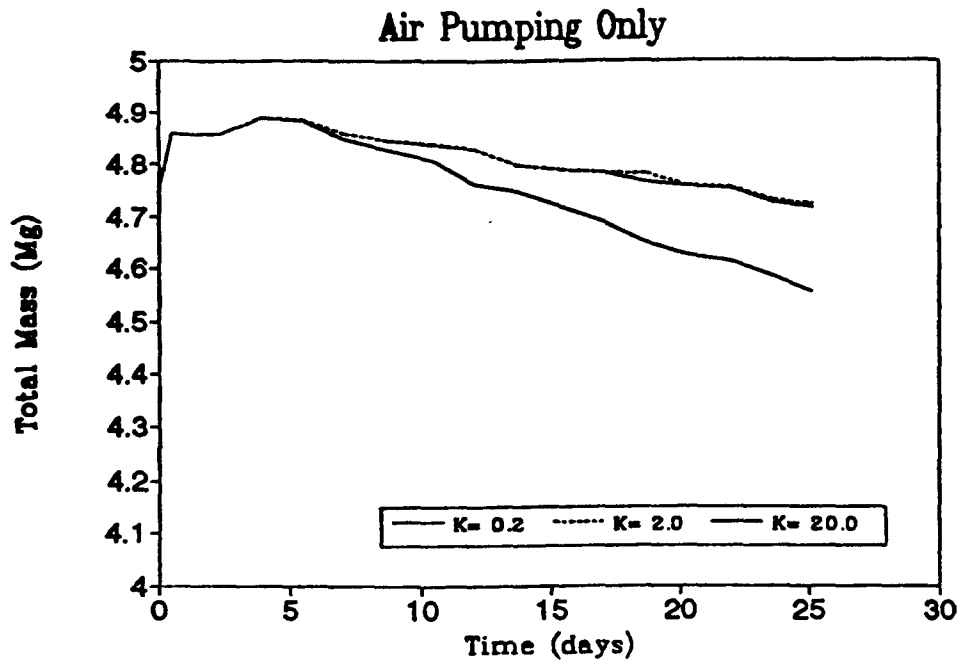


Figure 3. PER mass in the system at the end of Stage 3 with air pumping only.

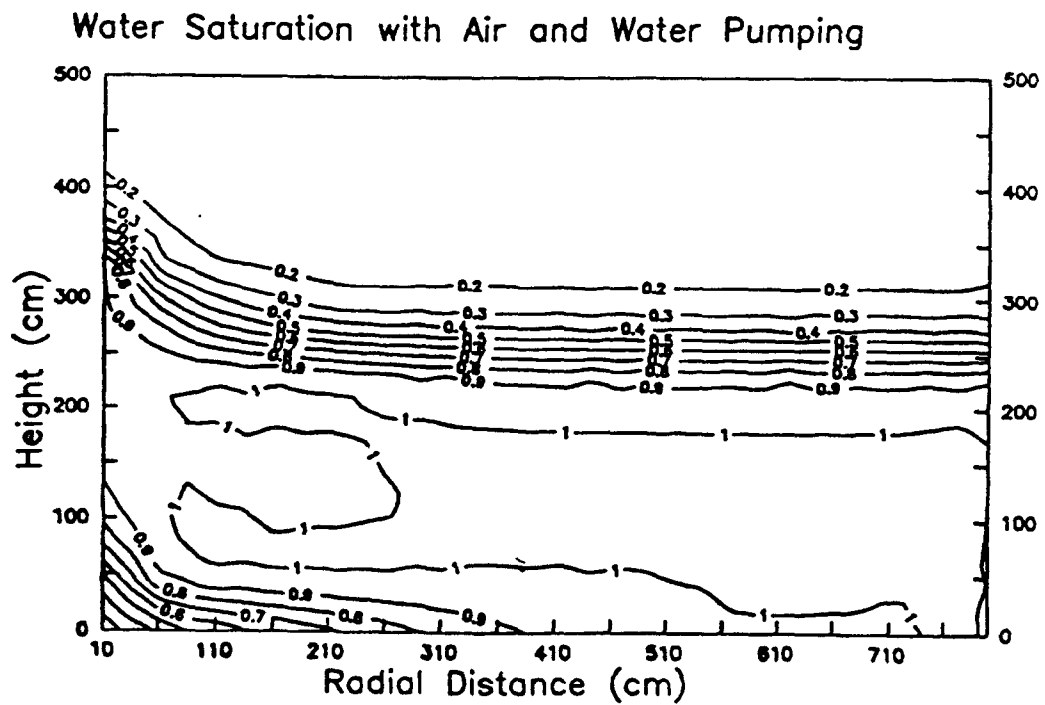


Figure 4. Water saturation profiles at the end of Stage 3 with air and water pumping.

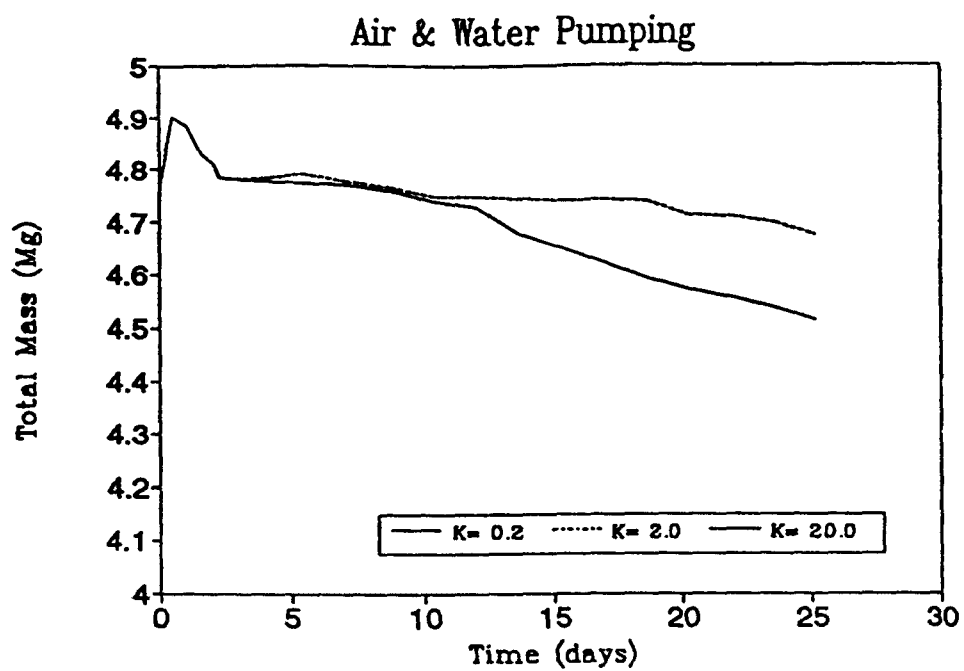


Figure 5. PER mass remaining in the system at the end of Stage 3 with air and water pumping.

APPLYING COMPUTER SIMULATION MODELS TO DESIGN LARGE-SCALE SOIL VENTING AND BIOREMEDIATION SYSTEMS

J. C. WALTON, R. G. BACA, J. B. SISSON, A. J. SONDRUP, AND S. O. MAGNUSON

Idaho National Engineering Laboratory

Geosciences Group

P.O. Box 1625

Idaho Falls, Idaho 83415

ABSTRACT

Computer models have been developed to simulate the generation, release, transport, and cleanup of organic contaminants from waste sites. The models for generation and release of organic vapors consider processes such as deposition rates, surface coverage, container corrosion, and temperature and mixing effects upon contaminant fugacity. Subsequent to release from source waste zones, contaminants move into the environment in liquid, vapor, and/or aqueous solution form. Computer models have also been developed to simulate subsurface migration of contaminants and *in situ* site remediation methods such as soil venting and bioremediation. This paper discusses model theory and recent applications of the models to the design of a large-scale soil venting system at the Idaho National Engineering Laboratory.

INTRODUCTION

Migration of organic contaminants from hazardous waste disposal sites is a significant environmental concern. Organic contaminants, particularly in the vapor phase, can pose a health hazard to workers in the vicinity of the disposal site and contaminate the underlying aquifer. Volatile organic compounds such as carbon tetrachloride, chloroform, and trichloroethylene are frequently encountered at waste sites. These chlorinated hydrocarbons are relatively common chemicals and widely used as industrial solvents.

Organic vapor plumes have been noted at waste disposal sites at a number of U. S. Department of Energy (DOE) facilities. At the Idaho National Engineering Laboratory, for example, chlorinated solvent vapors have been found at the Radioactive Waste Management Complex (RWMC). The primary source of the solvents is thought to be drums of mixed waste from DOE's Rocky Flats Plant near Golden, Colorado that were buried during the approximate period 1966 to 1971. The waste consists of plutonium-contaminated chlorinated solvents including carbon tetrachloride mixed with machining oil and solidified with a commercial absorbent. Over time the integrity of the drums has been lost from crushing and corrosion, and the vapors have migrated downwards through the vadose zone toward the underlying aquifer and upwards towards the atmosphere.

As a result of past disposal practices at the RWMC, significant amounts of organic vapors have moved through the vadose zone. Organic compounds have been detected at low levels in the Snake Plain Aquifer, a major water source for Southeastern Idaho and the primary source of drinking water at the RWMC. In addition to being used for irrigation, water from the aquifer is used to culture a large portion of the trout grown commercially in the U.S. Because of concern for water quality, soil venting is being considered as a means of removing volatile organic compounds from the vadose zone and reducing further contamination of the Snake Plain Aquifer.

HISTORY

Low-level, transuranic, and hazardous wastes have been disposed of at the RWMC since the mid-1950s. While the majority of the waste was buried in trenches, pits, and vaults, unspecified amounts of liquid wastes were discharged into open pits. A significant portion of the waste (i.e., the portion from Rocky Flats) was packaged in 208 liter (55 gal) drums and placed in pits and trenches dug in the surficial sediments. The drums were randomly dumped into the pits or stacked. The pits were then backfilled and the soil compacted. This past disposal practice may have lead to early failure and release of contaminants from a significant number of drums.

Disposal records indicate that approximately 3.4×10^5 l (88,000 gal) of organic waste from the Rocky Flats Plant were disposed at the SDA from 1966 to 1971. These wastes are particularly significant because they consisted of approximately 9×10^4 l (24,000 gal) of carbon tetrachloride, 9.5×10^4 l (25,000 gal) of miscellaneous organics consisting of chloroform, trichloroethylene, trichloroethane, and tetrachloroethylene, and 1.5×10^5 l (39,000 gal) of Texaco Regal machining oil. These solvents, after being solidified with a commercial absorbent, were placed and sealed in 208-l (55-gal) drums.

Organic chemicals were first detected in the groundwater at the RWMC in September 1987 as the result of sampling conducted by the U. S. Geological Survey. Analysis of samples from wells in the vicinity of the RWMC showed concentrations above detection limits for a number of organic compounds (2). All groundwater samples but one, however, were below the U.S. Environmental Protection Agency maximum of 5 ppb for drinking water standards. Organic vapors were later detected during well drilling operations at the RWMC.

A soil-gas survey, performed by Golder Associates, was conducted to identify the types and sources of organic vapors near the surface of the RWMC. Gas samples were taken on a 40 x 30 grid on 61-m (200-ft) centers. Holes were augured to a depth of 0.76 m (2.5 ft) at each grid point and a carbon steel pipe was driven in the hole for gas extraction. Four chlorinated hydrocarbons were detected: carbon tetrachloride, trichloroethylene, trichloroethane, and tetrachloroethylene.

GEOLOGY

The RWMC is located on a thin layer of alluvial and eolian sediments of Quaternary age. Beneath the surface alluvium is a thick sequence of basalt lava flows and sedimentary interbeds that extend to a depth of approximately 610 m (2000 ft). Sedimentary interbeds are generally considered to represent quiescent periods between volcanic episodes, when the top most lava flow was covered by accumulations of eolian and alluvial sediments. A schematic geologic cross section through the RWMC is presented in Figure 1.

The Snake Plain Aquifer is considered to be unconfined, and the depth to water is about 180 m (580 ft). Permeability of the Snake Plain Aquifer is controlled by the distribution of highly fractured basalt flow tops and interflow zones; some permeability is contributed by fractures, vesicles, and intergranular pore spaces. The variety and degree of interconnected water bearing zones complicates the direction of groundwater movement locally throughout the aquifer. Sedimentary interbeds generally have lower permeability than the surrounding basalt flows and impede the movement of groundwater. Small regions of perched water have been encountered above major sedimentary interbeds during drilling activities at the RWMC. The perched water zones are not continuous below the RWMC and appear to be associated with local infiltration phenomena.

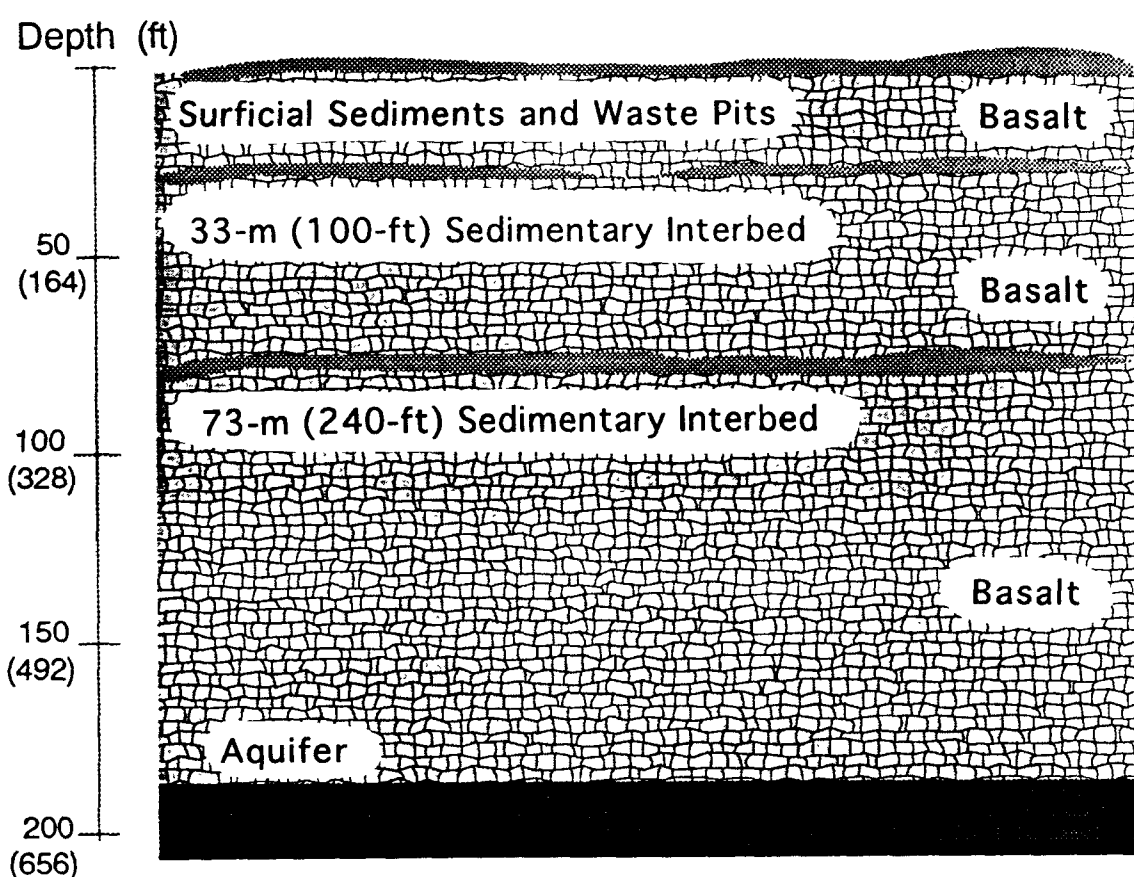


Figure 1. Schematic diagram of geology beneath the Radioactive Waste Management Complex (RWMC). Of major significance are the sedimentary interbeds and the depth to the water table.

The clean-up of the site by soil venting will be complicated by the complex geology. In particular, perched water zones and moist sediments are expected to respond poorly to induced airflow. The impermeable (to air) nature of the moist regions will greatly slow contaminant removal rates. Vapor/liquid partitioning will cause the moist regions to act as secondary sources of contaminants as constituents dissolved in the aqueous phase are volatilized.

INITIAL MODELING WORK

Role of Modeling Analysis

The vadose zone plume of chlorinated solvents extends vertically to the aquifer at a depth of 180 m (591 ft) and laterally over an area of greater than 60 ha (150 acres). The large size of the RWMC, combined with the difficulty and expense of drilling through fractured, contaminated basalt rock, have led to the use of mathematical models to assist with site characterization and remediation.

The modeling analyses are a means of better understanding and interpreting the available data. Through applying numerical models it is hoped that fewer wells will be required to characterize the extent of contamination and a more cost effective cleanup strategy can be planned. Modeling is not an exact predictive tool or a replacement for monitoring data.

Four separate computer simulations or submodels have been developed and applied to the RWMC organics problem: 1) source term (release rate from waste pits); 2) plume growth in the vadose zone and release into the aquifer; 3) transport in the Snake River Plain aquifer; and 4) cleanup of the vadose zone plume by soil venting. Additionally a model for bioremediation has been developed but not applied at the RWMC. Output from the source term and plume growth models serves as input for the aquifer and soil venting calculations. The source term, plume growth, soil venting, and bioremediation submodels are summarized below.

Source Term

The source term submodel covers the release of contaminants from waste drums and migration from the disposal pits. This submodel is discussed in detail in Walton *et al* (1989). A major conclusion from the source term model was that the long-term release rate of highly volatile constituents (e.g., carbon tetrachloride) is controlled by drum failure rates. This conclusion was used to simplify the source term model to analytical equations for the release of contaminants from waste drums. Other processes that exerted minor controls on the release rate from the waste pits were ignored. The analytical solution provides a time variant source term for the plume growth model that describes contaminant release to the vadose zone. The source term code also gave strong evidence, based upon the physics of the problem, that liquid wastes would not migrate significant distances from the disposal pits (3). Transport away from the pits is considered to be vapor dominated.

Retrieval studies at the RWMC were used to obtain estimates of drum failure rates. The Rocky Flats Plant wastes were assumed to be disposed of at a uniform rate during the period 1966 to 1971. Quantitative estimates of other amounts of chlorinated solvents disposed of at the RWMC were unavailable and assumed to be zero.

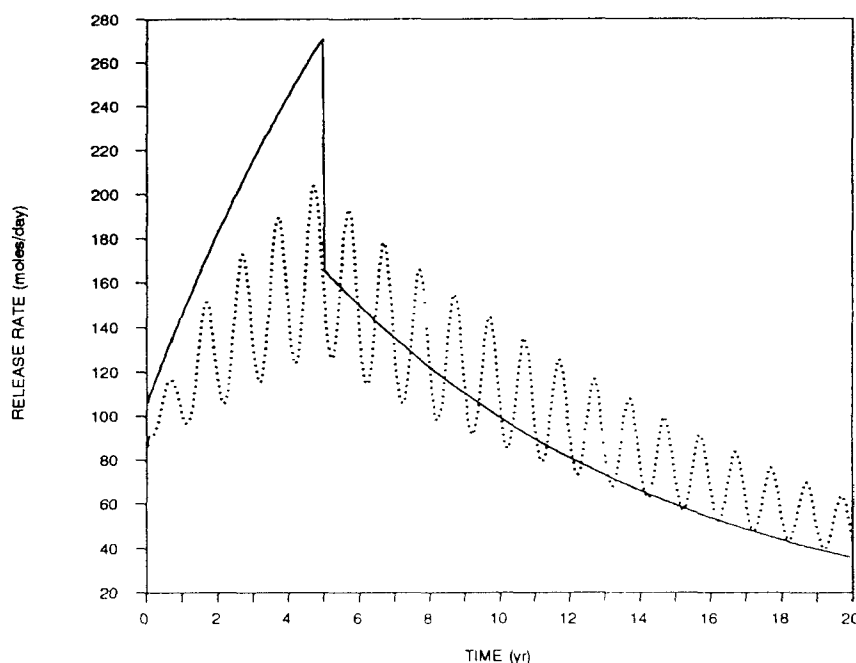


Figure 2. Simulated release rate of carbon tetrachloride from the waste disposal pits. The solid line represents a simplified analytical solution and the dotted line represents the full numerical solution. The annual cycle is related to seasonal variations in soil temperature.

The source term evaluation is based upon limited data. All of the input data are highly uncertain and the basic simplifying assumptions remain unvalidated and untested. Although a sensitivity analysis could be performed, no quantitative basis exists for estimating total uncertainty. The only validation data is the shape of the current subsurface plume which exists greatest concentrations around the 110-foot interbed. The source term code predicts the peak subsurface concentrations in this area. Mathematically the phenomenon results from a declining or dying release rate from the waste pits.

If a decision is made to leave the waste in place, then validation of the source term model would be warranted. This could be accomplished by evaluating important processes and the actual inventory in the waste pits, not a simple task. If the source is removed or destroyed by *in situ* vitrification then validation of the source term model will not be necessary.

Plume Growth

The second submodel is the growth of the vadose zone plume. The plume growth model results are dependent upon the source term calculations and geologic transport properties. As stated previously, the analytic

simplification of the source term model is discretized to form a time variant source zone in the transport code. The governing equations are solved in three dimensions with the finite difference flow and transport code PORFLO (4).

The geologic setting and its geometry are defined for the model in terms of the strata type, thickness, and textural characteristics. Available geologic information for the vadose zone beneath the RWMC has been used to estimate the primary geologic parameters. In many cases important parameters, such as the effective diffusion coefficient, were initially set with engineering judgment. As more data have become available, some of the original simplifying assumptions have been reevaluated.

The contaminants of concern are highly volatile and only sparingly soluble. The dominant mode of mass transport for these compounds in the vadose zone is vapor diffusion. Sinking of the plume caused by density differences between the contaminant plume and uncontaminated soil air was initially thought to be unimportant in the overall plume because of the relatively low concentrations of the contaminants, relative to the permeability of the geologic media. However this simplifying assumption is currently being reevaluated because experience with the soil venting equipment has demonstrated that air permeabilities in the system are 1 to 2 orders of magnitude higher than initial estimates. For this reason, it is likely that density effects are more important than previously thought.

The original simplifying assumptions were designed to simulate organic vapor transport in computer codes designed for simulating of saturated groundwater flow and transport in geologic media. Transport modes considered are diffusion/dispersion of organic vapors, advection of vapors dissolved in soil moisture, and advection in soil air. The flux is expressed by diffusion in the vapor phase, advection in the vapor phase, and advection in the liquid phase. Diffusion/dispersion in the liquid phase is not considered. Monitoring data gathered to date on the nature and extent of the subsurface plume are qualitatively consistent with model predictions of plume size and extent.

The most significant prediction of the plume growth model is that releases to the Snake Plain Aquifer will increase if no remedial action is taken. This prediction is consistent with the shape of the measured subsurface plume, but monitoring data from the aquifer are currently inadequate to either support or reject the prediction. Mathematically, the prediction of increased release to the aquifer results from transport time lag. The leading edge of the diffusional plume is just now beginning to reach the aquifer.

Because of gross simplifying assumptions in the source term and plume growth models, it is preferable to calibrate the plume growth model using monitoring data from the vadose zone plume. The calibrated results from the plume growth model can serve as initial conditions for modeling cleanup of the vadose zone plume. Currently, six wells are instrumented with gas sampling ports. Gas samples are being taken from these wells and analyzed for organic vapor concentrations. When the data collection is complete and quality assurance requirements have been satisfied, the plume growth model will be calibrated to represent the current subsurface plume, lessening the importance of information obtained from the source term submodel.

Bioremediation Modeling

The Geosciences Group at the Idaho National Engineering Laboratory has developed a computer code for use in design and optimization of bioremediation systems. The code is primarily intended for use with *in situ*

bioremediation activities, but it is equally applicable to optimizing operation of bioreactors. The model considers fluid flow with allowances for a number of injection or extraction areas. A number of contaminants, nutrients, and microbial populations can be considered. Microbial kinetics are isolated in a separate subroutine which can be modified to reflect different forms of kinetic equations. The simultaneous equations are solved in a two dimensional domain using the alternating direction implicit method. The finite difference grid allows for variable node spacing. The current code is limited to simulating a single fluid phase (presumably water, but air flow could be simulated) and is still in the format of a research code with no published user's guide, independent verification, or benchmark testing.

ADDITIONAL DATA GATHERED AND EXPERIENCE

While this paper focuses on remediating the present subsurface organic vapor plume, data from and modeling of the RWMC indicate that vapors are migrating directly from the source pits down to the Snake Plain Aquifer. Because contaminant concentrations in the aquifer are below drinking water standards, the cleanup strategy focuses on stopping further contamination of the aquifer. If the source of contaminants to the aquifer is removed, remediation of the aquifer will not be necessary.

Soil Venting Strategy

One widely used method for remediating a site with organic vapor problems is soil venting. Potential application of soil venting to the RWMC has been evaluated in a preliminary computer modeling study (1). The effectiveness of two distinct pumping configurations were evaluated in the modeling study. These were: (1) single well soil-gas pumping and (2) multiple well pumping with an impermeable cover placed on the soil surface. Results of the preliminary study indicated that both configurations could be very effective in removing a significant portion of the subsurface vapor plume. The rate of cleanup, however, depends greatly on the average permeability and ratio of vertical to horizontal permeability (anisotropy) of the basalt, which is currently uncertain because of lack of site specific data. Another large source of uncertainty comes from vapor migration out of relatively impermeable zones which remain stagnant even with pumping.

A field demonstration of soil venting was conducted at the RWMC in the spring of 1990. The soil venting demonstration consisted of a single extraction well that was pumped for a 4 month period and six monitoring wells for gas pressure and contaminant concentration measurement. The extraction well was open between the 110-ft and 240-ft interbeds, where the greatest level of contamination occurs. Before pumping, baseline data were obtained at each sampling port for at least 5 weeks. Because of the variable nature of field gas chromatograph results obtained to date, a long baseline period was required to differentiate analytical uncertainties from actual changes in the subsurface plume.

The objectives of the field demonstration were two-fold: (1) to collect sufficient field data for use in calibrating the organic vapor transport model and (2) to provide an interim remedial action and evaluate its effectiveness. In addition, the soil venting demonstration was intended to provide a field-based method for evaluating the potential effectiveness of a longer term soil venting program. During the 4 month test the soil venting system operated for 2090 hours. 65 x 10⁶ ft³ of gas was extracted which contained 430 kg of carbon tetrachloride and 160 kg of trichloroethylene.

Reconsidering Initial Modeling Assumptions

Although sophisticated three-dimensional models provide impressive graphic images and illusions of knowledge, realistic understanding and prediction of large and complex subsurface phenomena is much more difficult. In particular, several problems with the initial predictions were discovered as a result of the 4-month extraction test.

The first revelation was that initial predictions of the permeability of the fractured basalt layers were approximately 1 or 2 orders of magnitude too low. This is actually favorable for an extraction program and reflects an initial desire to make conservative projections concerning the likely success of vapor extraction efforts. The increased permeability means that the extraction blower was undersized and could not provide sufficient drawdowns. The small pressure drops at the extraction well did not produce measurable pressure changes at the monitoring ports in the monitoring wells. Thus the test did not provide information on important parameters such as the ratio of vertical to horizontal permeability in the fractured basalt.

The higher permeability also has implications for plume growth. Initial calculations (based upon the erroneous initial estimates of basalt permeability) suggested that density-related vapor migration was not of great significance for growth and migration of the organic vapor plume and that density effects were only important in pockets of high vapor concentration. The increased permeability may indicate an increased importance for density driven vapor migration during plume growth. Unfortunately because the extraction test did not provide data on vertical versus horizontal permeability in the basalts, the likely importance of density driven flow cannot yet be resolved with certainty.

Approximately 50% of the soil gas extracted from the production well originated from a basalt rubble zone at a depth of 58 m (190 ft). The presence of the rubble zone increased the effective radius of the extraction well by producing a more vertical soil gas movement pattern. Thus, the rubble zone at 190 feet will be an important consideration in the design of future systems.

Diffusion from Stagnant Zones

Any modeling analysis of a complex system has a limited capability to deal with (a) geologic heterogeneities in the subsurface and (b) complexities of multicomponent transport with non-ideal solutions, non-linear sorption, poorly understood container failure, and multiple, unknown chemical reactions. These uncertainties lead some analysts to conclude that computer modeling is a meaningless exercise. The usefulness of the modeling program will be determined by how uncertainties are dealt with in the modeling exercises.

One factor that slows cleanup is the rate of vapor migration out of stagnant zones in the subsurface. Regions of massive basalt with few fractures are sometimes found in the basalt flows of the Snake River Group. These regions have lower permeability and may remain relatively stagnant during the soil venting. Cleanup times for stagnant zones will be controlled by diffusion rates out of the blocks. Perched water is also found at several locations in the subsurface beneath the RWMC. Because it is not feasible to characterize the entire area of the site it is important to examine the potential importance of stagnant zones at least parametrically. Water contained in the stagnant zones will slow the diffusion rates and serve as a secondary source of vapors because of vapor/liquid partitioning. The diffusion time above assumes that vapor phase diffusion is dominant. In perched water zones, liquid diffusion will predominate.

The actual impact on stagnant zone diffusion at the RWMC may never be known in detail. Site characterization at this scale is simply not practical. The potential importance of stagnant zone diffusion is examined with a set of calculations which estimate under what conditions stagnant zone diffusion will control cleanup times.

An estimate of the potential impact of stagnant area diffusion at the RWMC is given in Figures 3 and 4. The extraction flow rate is taken as 0.47 m³/s (1,000 cfm) over a thickness of 40 m (130 ft). The 40 m thickness represents the distance between the two major sedimentary interbeds (Figure 1). The ratio of diffusion out of stagnant zones is plotted relative to travel time to the well as a function of stagnant zone size and well spacing. When the ratio exceeds one diffusion will control cleanup times. As long as diffusion out of stagnant zones controls cleanup times, adding additional extraction wells and/or pumping at a higher rate will have a limited effect on ultimate cleanup time. The calculations illustrate that, in the presence of great uncertainty, a simple dimensional analysis of the situation may provide as much useful information as more sophisticated models and large computer codes.

Stagnant Zone Diffusion Vapor Dominated Blocks

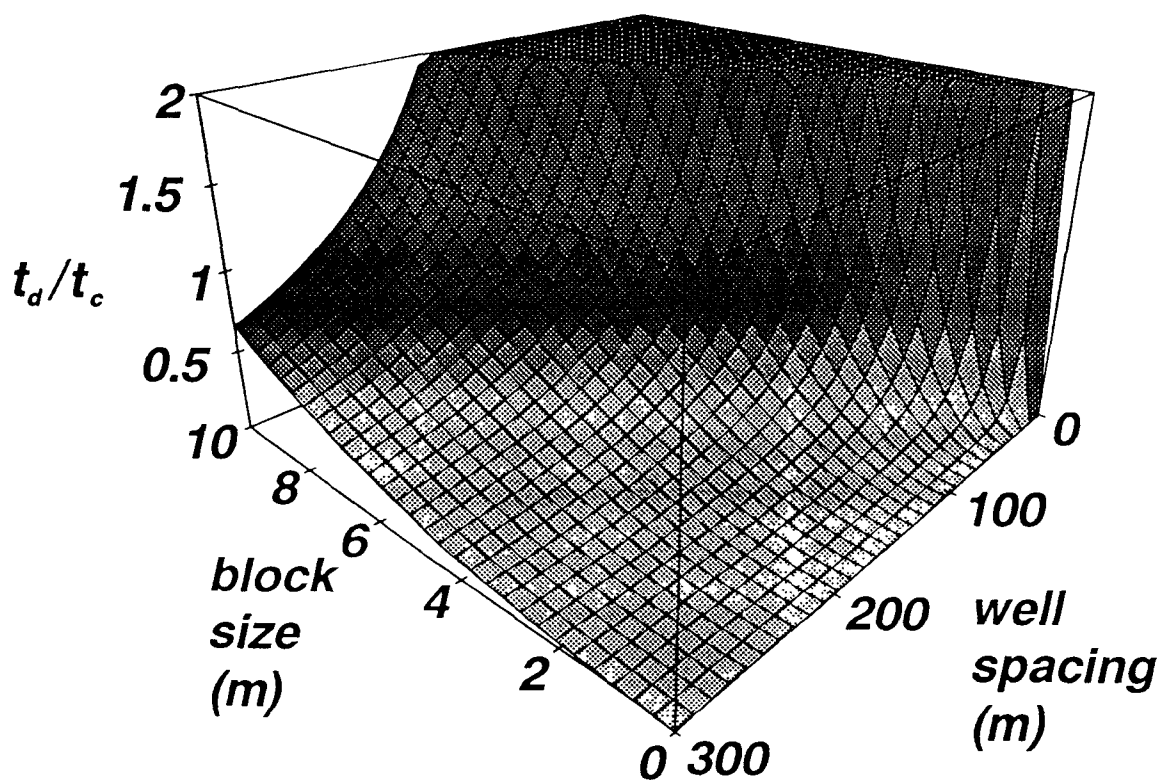


Figure 3. Dimensionless time for diffusion of organic vapors out of large stagnant blocks of basalt as a function of well spacing and block size. When the dimensionless time moves above 1.0 then diffusion from blocks will control cleanup times, not travel time to a well. In this situation, closer well spacing and/or greater pumping rates do little to speed ultimate cleanup of the site. Note that the graph is truncated at a dimensionless time of 2.

Stagnant Zone Diffusion from Perched Water Locations

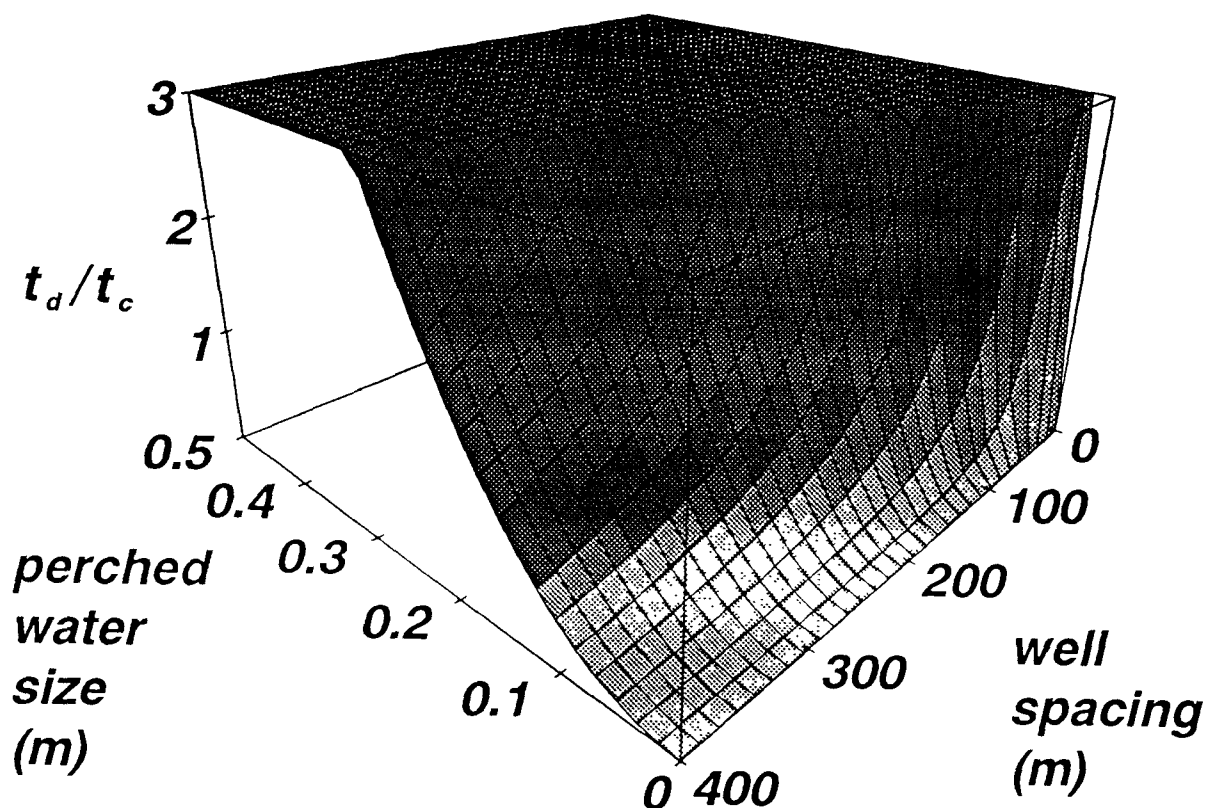


Figure 4. Ratio of diffusion time out of perched water zones relative to travel time to well. Numbers greater than 1.0 indicate that diffusion will control ultimate cleanup time. The graph is truncated at a dimensionless time of 3.

Although diffusion is likely to control cleanup time at well close well spacings, diffusion out of the vapor dominated stagnant zones is relatively rapid compared to perched water zones.

Perched water zones are potentially the greatest source of problems and may take very long times for removal of contaminants. Evaluations of the potential nature and extent of perched water may be required. The total mass of contaminants in the perched water may be considered *de minimus*. Because most of the other organic solvents have a lower Henry's Law constant than carbon tetrachloride their characteristic time for removal will be longer. The increased difficulty in removal of the other contaminants is compensated by the much lower concentrations in the subsurface and generally lower toxicity.

SUMMARY

Modeling has been a useful tool for understanding the site and for design of potential cleanup strategies at the Radioactive Waste Management Complex (RWMC). Models have been developed for all stages of the problem including release rate of contaminants from the source, contaminant migration in the vadose and saturated zones, and cleanup by soil venting. The usefulness of the modeling work is limited by the complexity of the site and limited availability of characterization data. Despite several years of work on the organic vapor problem, design and implementation of a final remediation system has not been accomplished to date.

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VOC CLEANUP BY IN SITU SOIL VAPOR EXTRACTION-- SOME RECENT DEVELOPMENTS IN MODELING

**EPA SOIL VAPOR EXTRACTION WORKSHOP,
HOUSTON, TX, APRIL 29 - MAY 1, 1991**

JOSE M. RODRIGUEZ-MAROTO, CESAR GOMEZ-LAHOZ*,
AND DAVID J. WILSON*

Departments of Chemistry and of Civil and
Environmental Engineering
Vanderbilt University
Nashville, TN 37235 (615) 322-2633

*Present address Depto. de Ingenieria Quimica, Universidad de Malaga, 29071, Malaga, Spain

INTRODUCTION

There are both field results and laboratory work indicating the importance, at some sites, of diffusion and/or desorption kinetics limitations to soil vacuum extraction (SVE) (3, 4, 11), although the assumption that the vapor and stationary phases are at local equilibrium with respect to volatile organic compound (VOC) transport appears to be an adequate approximation at other sites (1, 3). DiGiulio et al. (1990) have described a field technique for ascertaining the extent to which diffusion/desorption kinetics may be operative. Hutzler et al. (1989) have developed a lab column model which includes kinetics limitation. Wilson (1990) and Oma et al. (1990) have published lab column and field vapor stripping well models which include kinetics limitation. A major practical problem has been the large amount of computer time which these required. A way around this difficulty was recently discovered in which a diffusion-limited SVE model required virtually no more computer time per run than a typical local equilibrium model.

HIGH SPEED MODELING OF DIFFUSION KINETICS

For reasons of mathematical simplicity and usually for want of an adequate data base on a site, models for SVE have generally assumed that the pneumatic permeability of the soil is constant and isotropic in the domain of interest. However this is generally not the case. One usually finds strata of very different permeabilities, clay lenses of quite low permeability, and other heterogeneities in the soil which may have significant impact on the time required for cleanup. The first law of SVE application is that you must be able to draw air through all of the contaminated soil. If well logs indicate that the soil permeability is likely to be highly variable, models should be able to explore at least qualitatively the impact this may have on SVE cleanup times, and should provide some sort of estimate as to the uncertainty in the calculated cleanup times which this heterogeneity causes. We have extended a model for SVE with horizontal slotted lateral pipes to include the possibility of low-permeability lenses, as well as strata of different permeabilities. Results with these models suggest ways in which boring log data can be used to design an SVE system for a particular site which is minimally affected by such heterogeneities.

Our two-dimensional model for diffusion-limited SVE well operation makes use of a lumped parameter approximation to handle diffusion kinetics and can be run on a microcomputer (12). Although the results of the model appear quite reasonable, it suffers from the fact that one must use very small values of the time increment when doing the numerical integrations required by the model. Mechanical engineers would say that the differential equations used in the modeling are quite stiff. When the model is used on a 20 MHz PC-AT clone microcomputer with a math coprocessor, times required for physically realistic simulations are typically 60 hours or more per run. This severely limits the usefulness of that model for the simulation of SVE operations which are diffusion controlled; one would like to have a model which ran at least ten times faster than our first attempt. One of the principal reasons to do modeling is so that you can explore quickly and cheaply a large number of designs and options. Obviously this cannot be done if each simulation takes 60 hours.

EFFECTS OF VARIABLE PERMEABILITIES AND SYSTEM GEOMETRY ON THE TIME REQUIRED FOR SVE CLEANUPS

Here we present models for soil vapor stripping in lab columns and by means of field vapor extraction wells which include diffusion/desorption limited kinetics and which utilize a steady state approximation similar to that used in chemical kinetics to simplify the rate equations arising in that field.

In the following models we make the steady state approximation for the vapor phase VOC concentrations. That is, we assume that the vapor phase concentrations are sufficiently small that the mass of contaminant VOC in the vapor phase is an almost negligible fraction of the total mass of VOC present in the system. If this is the case, then the net rates of change with time of the vapor phase VOC concentrations with time will be extremely small in comparison to their rates of change by diffusion (replenishment) and their rates of change by advection (removal). The steady state approximation consists in setting these very small net rates of change of VOC concentrations in the vapor phase equal to zero. This type of approximation is very commonly used to simplify the analysis of the kinetic mechanisms of complex chemical reactions; one sets the net rates of change of highly active intermediate species present at extremely low concentrations (atoms, free radicals, etc.) equal to zero. In chemical kinetics the approximation is well understood and well established; our use of it in this new context will require justification by comparison with the results of calculations in which it is not made.

One-Dimensional Lab Column Model

Our model for SVE in a lab column with diffusion kinetics is diagrammed in Figure 1, which also includes notation. We use SI units throughout. As with our previous diffusion-controlled model, we use a lumped parameter method for approximating diffusion and desorption kinetics; estimation of the rate parameter for diffusion has been discussed earlier (12). The lumped parameter approach assumes that diffusion into and out of the blocks of low-permeability porous medium is governed by Equation (1).

$$\frac{dc_1^s}{dt} = \lambda \left[\frac{c_1^y}{K_H} - c_1^s \right] \quad [1]$$

Included here is the assumption that partitioning of VOC between the vapor and stationary phases is linear—that the system obeys Henry's Law, with an effective Henry's constant which typically is substantially smaller than the Henry's constant for the VOC in aqueous solution.

If we focus only on diffusion transport between the stationary and vapor phases in the i th compartment (a conservative process), we have Equation (2), which, together with Equation (1), gives Equation (3).

$$vA\Delta x \left(\frac{dc_i^v}{dt} \right)_{\text{diff}} + wA\Delta x \frac{dc_i^s}{dt} = 0 \quad [2]$$

$$vA\Delta x \left(\frac{dc_i^v}{dt} \right)_{\text{diff}} = -\lambda wA\Delta x \left(\frac{c_i^v}{K_H} - c_i^s \right) \quad [3]$$

A mass balance on the vapor phase in the i th compartment gives Equation (4) for the rate of change of vapor concentration in the i th compartment with time.

$$vA\Delta x \left(\frac{dc_i^v}{dt} \right) = v_{i-1/2} vA c_{i-1}^v - v_{i+1/2} vA c_i^v - wA\Delta x \lambda \left(\frac{c_i^v}{K_H} - c_i^s \right) \quad [4]$$

This is set equal to zero by virtue of the steady state approximation for the vapor phase concentrations.

Solving Equation (4) for the vapor phase concentrations then yields Equations (5).

$$c_i^v = \frac{\frac{w\lambda}{v} c_i^s}{\left(\frac{v_{1/2}}{\Delta x} + \frac{w\lambda}{K_H} \right)}, i = 1 \quad [5]$$

$$c_i^v = \frac{\left(\frac{v_{i-1/2}}{\Delta x} c_{i-1}^v + \frac{w\lambda}{v} c_i^s \right)}{\left(\frac{v_{i+1/2}}{\Delta x} + \frac{w\lambda}{vK_H} \right)}, i = 2, 3, \dots$$

Equation (1) is then integrated forward in time, with the vapor phase concentrations c_i^v being calculated at every step from Equation (5). This can either be done by a standard predictor-corrector method or one can rearrange Equations (1) to Equation (6), assuming that the c_i^v remains essentially constant during the time increment in the integration, Δt . This yields Equations (7).

$$\frac{dc_i^s}{dt} + \lambda c_i^s = \frac{\lambda c_i^v}{K_H} \quad [6]$$

$$c_i^s(\Delta t) = c_i^s(o) \exp(-\lambda \Delta t) + \frac{c_i^y(o) [1 - \exp(-\lambda \Delta t)]}{K_H} \quad [7]$$

We are now in position to carry out the calculation. The gas velocity within the column is given by Equation (8), and the initial VOC concentrations in the pore liquid are given by Equation (9).

$$v_x = \frac{K_D (P_{in}^2 - P_{out}^2)}{2L} \left(P_{in}^2 - \frac{P_{in}^2 - P_{out}^2}{L} \right)^{1/2} \quad [8]$$

$$c_i^s(0) = 10^{-3} \rho \frac{c}{w} \quad [9]$$

A somewhat lengthy but straightforward analysis shows that this steady state model, in the limit as the diffusion rate parameter approaches infinity, gives removal rates which differ from the local equilibrium model results by a factor of $1 + vK_H/w$. Typically the air-filled porosity v is roughly 0.3, the specific moisture content w is about 0.2, and K_H is of the order of 0.005 (dimensionless), so that our factor is smaller than 1.0075. It therefore appears that the steady state approximation can be expected to lead to errors in cleanup time estimation of less than 1%.

Two-Dimensional Model for a Field Vapor Stripping Well

The analysis for a cylindrically symmetrical model for a field vapor stripping well is rather similar to that for the lab column. One calculates the soil gas pressure distribution by the over-relaxation method since this permits us to include the effect of strata of varying permeabilities. Use of the steady state approximation for the vapor phase VOC concentrations yields a system of mixed differential and algebraic equations for the movement of VOC's with the lab column model. This system can then be integrated forward in time to simulate the behavior of the soil vapor extraction well.

Computer programs were written in TurboBASIC to implement the diffusion-limited models of SVE in lab columns and by means of vapor extraction wells. The lab column model, which runs very rapidly, was used for testing approximations and algorithms. It is unlikely to be particularly useful, however, since the very process of collecting soil samples and packing them into lab columns disrupts the soil inhomogeneities which are a major cause of diffusion-limited behavior in SVE. We therefore focus on results obtained with the field SVE well model. The runs were made on microcomputers with math coprocessors and running at 12 or 20 MHz. A typical run required between 2 and 3 hours. This compares very favorably with the run times of 2-4 days which were required for similar runs carried to similar levels of cleanup made with our earlier model, and is not significantly longer than the computation times required to run similar systems for similar times with our local equilibrium models.

The standard parameter set used is given in Table I. These parameters were used in all the runs except as noted on the figures or in the captions to the figures.

A set of runs was made to explore the validity of the steady state approximation used in this model for diffusion-limited SVE and to see the effect of varying the rate constant for diffusion from the porous domains

of low permeability. The parameters for these runs were given in Table 1; only the diffusion rate constant was varied. A calculation was made using our local equilibrium model for comparison purposes. Three calculations were made for each of the values of λ shown in Figure 2. These were (1) a calculation using our earlier "exact" model (i.e., without the steady state approximation); (2) a calculation in which the predictor-corrector method was used for the numerical integration, and (3) a calculation in which the integrated form of the differential equations was used for the numerical integration. All three models which included diffusion gave results which are virtually identical; plots at the scale of Figure 2 are completely indistinguishable. These numerical results are in agreement with our analysis above of the lab column model, which showed excellent agreement between the steady-state diffusion model with a very large diffusion rate constant and the local equilibrium model. It was found that the value of $2\Delta t$ must be 0.01 or less if reliable results are to be obtained with the steady state models; Δt was set equal to 100 sec for the runs with $\lambda = 10^{-4} \text{ sec}^{-1}$.

For this system and at this gas flow rate the local equilibrium results were indistinguishable from those obtained when $\lambda = 10^{-4} \text{ sec}^{-1}$. As λ decreases below 10^{-5} sec^{-1} , however, the rate of VOC removal becomes progressively slower.

Another set of runs was made in which the effective Henry's constant K_H was reduced from 10^{-2} to a value of 10^{-3} ; these are shown in Figure 3. (Note the change in scale of the time axis between Figures 2 and 3.) We found that, if all of the system parameters except λ and K_H are held constant and that K_H is varied proportional to λ , then the cleanup time is proportional to λ^{-1} . A comparison of Figures 2 and 3 also shows that the damaging effects of a small effective Henry's constant are not limited to local equilibrium and near-local equilibrium conditions.

In Figures 4 and 5 the effects of overlying impermeable caps are investigated for a range of values of the diffusion rate constant. Figure 4 compares runs having no cap with runs having a cap of radius 6 m. We see that a cap results in greatest percentage reduction in cleanup time (to, say, the 99.9% level) if the diffusion rate constant is large; for slow diffusion rates the cap has a negligible effect. Figure 5 compares runs made with caps of 4 and 8 m radius for systems having a range of diffusion rate constants. The larger caps give shorter cleanup times, but, as in Figure 4, the differences decrease as the diffusion rate constant becomes smaller. These results are as one would intuitively expect, since the effect of a cap is to increase the efficiency of the gas flow pattern by increasing gas flow rates in the relatively stagnant portions of the domain out near the periphery of the cylinder; however, the efficiency of the gas flow pattern in advection becomes less and less important as diffusion rates become more and more limiting.

The effects of the presence of a set of passive vent wells located around the periphery of the domain of interest and screened along their entire length are shown in Figures 6 and 7. No impermeable cap is present in these runs. For this particular geometry, the passive wells result in relatively little changes in removal efficiencies; with the local equilibrium run and the run with the largest diffusion rate constant (10^{-5} sec^{-1}) the presence of passive wells may actually reduce efficiency toward the end of the run. As the diffusion rate constant becomes very small, the effect of the passive wells on cleanup time is seen to decrease on a percentage basis, as one would expect.

The situation is rather different if these passive wells are combined with overlying impermeable caps. In Figure 8 runs were made with or without impermeable caps of radius 10 m and passive vent wells screened

along their entire lengths. The combination of caps and passive wells results in significant increases in removal rates for diffusion rate constants of $5 \times 10^{-7} \text{ sec}^{-1}$ and larger. As before, as diffusion becomes slower it overpowers the effects of anything one can do to the gas flow pattern.

In Figure 9 runs were made with and without caps and passive wells screened along their entire lengths; the radius of the impermeable cap is 8 m. In this configuration the passive wells are highly beneficial, more than doubling the rate of removal for the local equilibrium model, and resulting in very substantial increases in removal rates for diffusion rate constants greater than $5 \times 10^{-7} \text{ sec}^{-1}$. If one is under some pressure to meet a rather short deadline for cleanup of a site, these results suggest that money might well be spent on a configuration involving both caps and passive wells.

The effects of gas flow rate are shown in Figures 10 and 11. In Figure 10 we see that cleanup rates for the local equilibrium model are directly proportional to the soil gas flow rate, exactly as one would anticipate. As diffusion processes become more limiting, however, the payoff achieved by increasing the gas flow rate becomes less and less. In Figure 11 it is apparent that doubling the gas flow rate from 2.75 to 5.5 mol/sec results in only a 20% increase in cleanup rate if the diffusion rate constant is 10^{-6} sec^{-1} . If this parameter is 10^{-7} sec^{-1} , increasing the gas flow rate from 2.75 to 5.5 mol/sec results in a negligible increase in removal rate. One concludes that diffusion limitations should be explored in some depth during the pilot phase of a SVE feasibility study as suggested by DiGiulio et al. (1990).

EFFECTS OF VARIABLE PERMEABILITIES AND HORIZONTAL WELLS ON THE TIME REQUIRED FOR SVE CLEANUPS

In this section, the results obtained with a two-dimensional local equilibrium model for SVE with horizontal lateral slotted pipes is presented. It is assumed that the horizontal laterals are long in comparison to the spacing between them, so that we can use a two-dimensional Cartesian coordinate representation and ignore end effects. We assume that the permeability is anisotropic and is a function of position, so the calculation of soil gas pressures and velocities in the domain of interest must be done numerically; we use an over-relaxation method which has done well for us previously (9). The model assumes a linear, Henry's Law type isotherm. The details of the model will be published shortly (5).

The molar gas flow rate per unit length of slotted pipe is given by Equation (10).

$$Q = \frac{Kv\Delta(P^2)}{RT} \pi r \quad [10]$$

Soil gas streamlines and their transit times are very helpful in quickly identifying regions in the domain of interest which will clean up slowly. The streamlines are calculated by numerical integration of Equations (11) and (12), where the pressure derivatives are calculated by use of finite differences and Taylor series representations.

$$\frac{dx}{dt} = -K_x(x,y) \frac{\partial P}{\partial x} \quad [11]$$

$$\frac{dy}{dt} = -K_y(x,y) \frac{\partial P}{\partial y} \quad [12]$$

The movement of VOCs is given by numerical integration of Equation (13).

$$\frac{\partial m}{\partial t} = - \frac{\nabla v m}{v + w/K_H} \quad [13]$$

This equation contains no dispersion term; this is represented by the effects of numerical dispersion in the finite difference mesh used for the numerical integration.

Eight runs were made to explore the effects of a single low permeability domain on the soil gas streamlines. The permeability function used to represent m such domains is given in Equation (14).

$$K_x(x,y) = K_{x0} - \sum_{i=1}^m A_i \exp \left\{ - \left[\left(\frac{x - x_i}{r_i} \right)^2 + \left(\frac{y - y_i}{s_i} \right)^2 \right]^n \right\} \quad [14]$$

The standard parameter set is given in Table 2. Figure 12 shows the streamlines and gas transit times (in thousands of seconds) for the soil gas to move from the surface of the ground to the horizontal vacuum pipe for run number 1, for which no low-permeability lenses were present. Figure 13, run no. 2, shows streamlines and transit times for a case where the lens is centered over the extraction well and a short distance above it. The transit times are markedly different from those obtained in the absence of a lens (Figure 12), but none are appreciably larger than the maximum time seen in Figure 12, nor is there any part of the domain from which gas flow is excluded. We therefore expect that the presence of a lens in this position will have little effect on the overall rate of cleanup. Shortly we shall see that this is in fact the case.

Run 3, shown in Figure 14, shows the effect of a low-permeability lens above the well and somewhat to the left. The somewhat increased gas transit times on the left side indicate that the cleanup time for Run 3 will be somewhat longer than those for Runs 1 and 2.

Run 4, in Figure 15, illustrates poor placement of a vacuum well relative to a low-permeability lens. The lens, far on the left side of the domain of influence, has markedly reduced the flow of soil gas through the lower left portion of the domain, as indicated both by the long transit time of the leftmost streamline and the shapes of the streamlines. We therefore expect a substantial decrease in cleanup rate for this run.

Run 5, shown in Figure 16, represents total disaster in the placement of a vapor stripping well. The well is screened right in the middle of the low permeability lens. This has reduced the molar gas flow rate from a value of 0.218 mol/sec (no lens) to a value of 0.0265 mol/sec, one-eighth of the reference flow rate. The transit times of the soil gas have been correspondingly increased, and we expect a greatly reduced rate of cleanup.

Figure 17 shows plots of \log_{10} (total contaminant mass) versus time for runs 1 through 5. We see that, as expected, the lens in run 2 (Figure 13) has had little effect on the rate of cleanup of this system. The off-center lens in run 3 (Figure 14) has slowed down the rate of cleanup slightly. In run 4 (Figure 15), the lens which was located far on the left side of the domain has very markedly reduced the rate of cleanup; the slope of the plot for run 1 is 2.25 times the slope of the plot for run 4 in the linear sections of the plots. The plot of \log_{10} contaminant mass versus time for run 5 shows that the effect of screening the well in the middle of the low permeability lens was indeed disastrous, due principally to the decreased gas flow rate through the well in run 5 as compared to run 1. 99% cleanup in run 1 required 15.9 days; in run 5 it required 85 days.

Runs 6, 7, and 8 were made with two low permeability lenses located out toward the sides of the domain of influence of the well; these were placed low-low, low-high, and high-high. As seen in Figure 18, the rates of cleanup in these runs are rather similar; all are substantially lower than the rate of cleanup of the system without any low permeability lenses.

Another series of runs were made with the model parameters specified in Table 3. The parameters describing the low permeability lenses are given in Table 4. The locations of the centers of the lenses are shown in Figure 19.

The main point of interest with these runs is the spread in the rates of cleanup which result from the various locations of the lenses. This is shown in Figures 20 and 21. Again we find that lenses near the middle of the domain cause relatively little decrease in cleanup rate, while lenses out at the edges are fairly damaging. Run 17, in which the lens is located directly underneath the vapor stripping well, has the smallest cleanup rate of the set. The differences in the positions of the lenses in these runs result in a variation in 99.9% cleanup time from a low of about 700 hours to a high of about 1200 hours with these parameters. Runs 10, 14, and 16 show cleanup rates which are slightly greater than the cleanup rate of run 9, which has no lenses at all.

These runs indicate a measure of the uncertainty in cleanup times which may be associated with variations in the soil permeability; the lenses have permeabilities which may be as little as 5% of the permeability of the surrounding matrix. These typically cause variations of the order of - 10 to + 50% in cleanup times, and may, in particularly unfavorable cases, may cause increases in cleanup times by as much as 500%.

The runs also indicate the advantages to be gained by taking into account the inhomogeneities in the permeability when designing a soil vapor extraction system, provided that the necessary data are available. Qualitative data of the sort needed might readily be obtained from boring logs, cone penetrometer tests, etc. The runs show that the damaging effects of such low permeability domains can often be reduced to an acceptable level by proper placement and design of the well system. Low permeability lenses centered near the border separating the zones of influence of two adjacent wells are likely to be damaging. The screening of a well within or over a region of low permeability is likely to be very damaging, and should be avoided if at all possible. The other configurations studied yielded cleanup rates only slightly different from the cleanup rate found for a homogeneous domain of influence.

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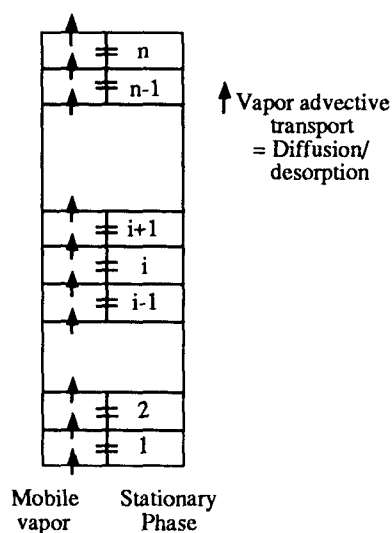


Figure 1. Model for soil vapor stripping in a laboratory column; mathematical partitioning.

- A = cross-sectional area of column
- v = soil air-filled porosity
- w = soil volumetric moisture content
- $v_{i+1/2}$ = linear gas velocity between the i th and $(i + 1)$ th compartments into which the column is mathematically partitioned
- C_i^v = vapor phase VOC concentration in the i th compartment
- C_i^s = stationary phase(s) VOC concentration in the i th compartment

Table 1. Standard parameter set for simulations of a soil vapor stripping well

<i>Parameter</i>	<i>Value</i>
Radius of domain of influence	10 m
Depth of water table	8 m
Depth of well	6 m
Radius of impermeable cap	0 m
Gravel-Packed radius of well	0.12 m
Wellhead pressure	0.866 atm
Temperature	12° C
Gas-filled porosity	0.2
Water-filled porosity	0.2
Pneumatic permeability, K_z	0.6206 m ² /atm sec
Pneumatic permeability, K_r	0.6206 m ² /atm sec
Effective Henry's constant	0.01 (dimensionless)
Initial contaminant concentration	10 mg/kg
Soil density	1.7 gm/cm ³
Molar gas flow rate	1.102 mol/sec
Volumetric gas flow rate	0.02579 m ³ /sec

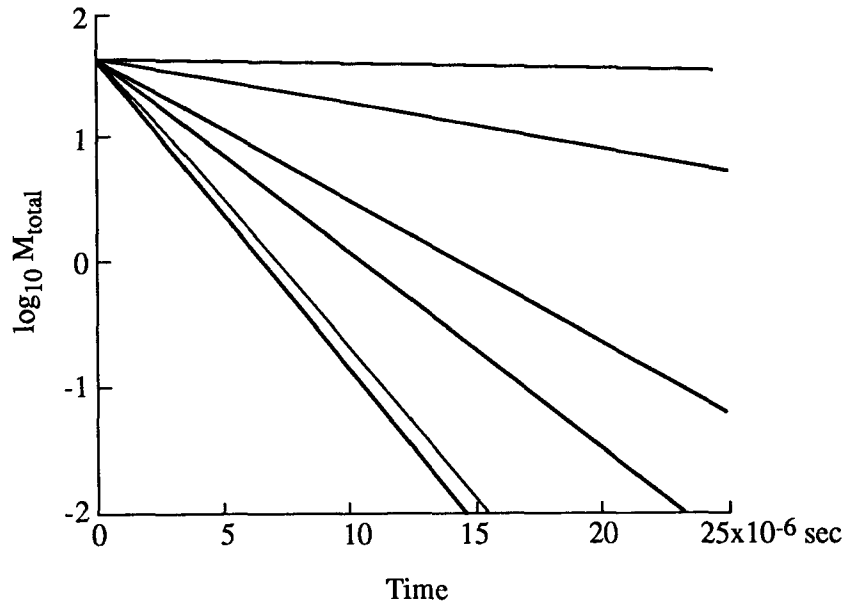


Figure 2. Plots of \log_{10} total contaminant mass versus time; effect of diffusion rate constant λ . From the top down, values of λ are 10^{-8} , 10^{-7} , 5×10^{-7} , 10^{-6} , 10^{-5} , and 10^{-4} sec^{-1} . The plot with $\lambda = 10^{-4} \text{ sec}^{-1}$ is indistinguishable at this scale from a plot with $\lambda = \infty$ (the local equilibrium model). Other system parameters are given in Table 1. No passive wells or impermeable caps are present.

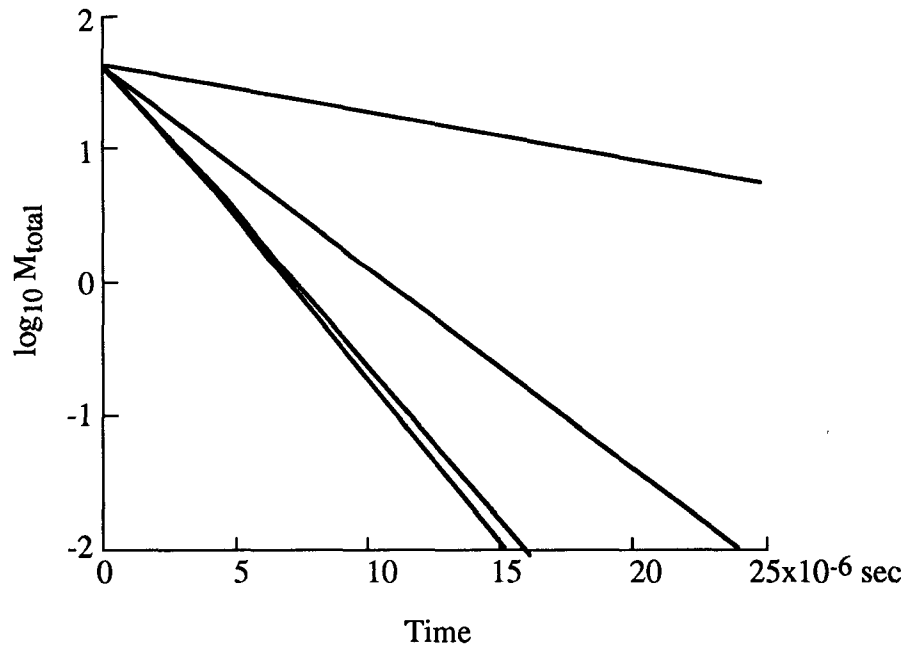


Figure 3. Plots of $\log_{10} M_{\text{total}}$ versus time; effect of diffusion rate constant λ . K_H for these runs has been reduced to 0.001. From the top down, values of λ are 10^{-8} , 10^{-7} , 10^{-6} , 10^{-5} sec^{-1} and (local equilibrium).

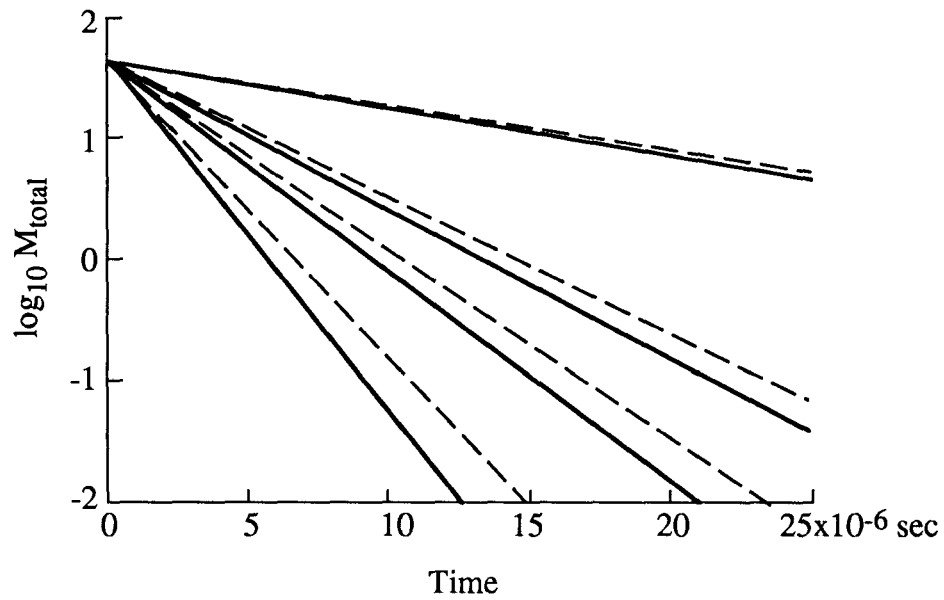


Figure 4. Plots of $\log_{10} M_{\text{total}}$ versus time; effect of an impermeable cap of 6 m radius. Runs made without a cap are indicated with dashed lines. From the top down, values of λ are 10^{-7} , 5×10^{-7} , 10^{-6} sec^{-1} , and ∞ (local equilibrium).

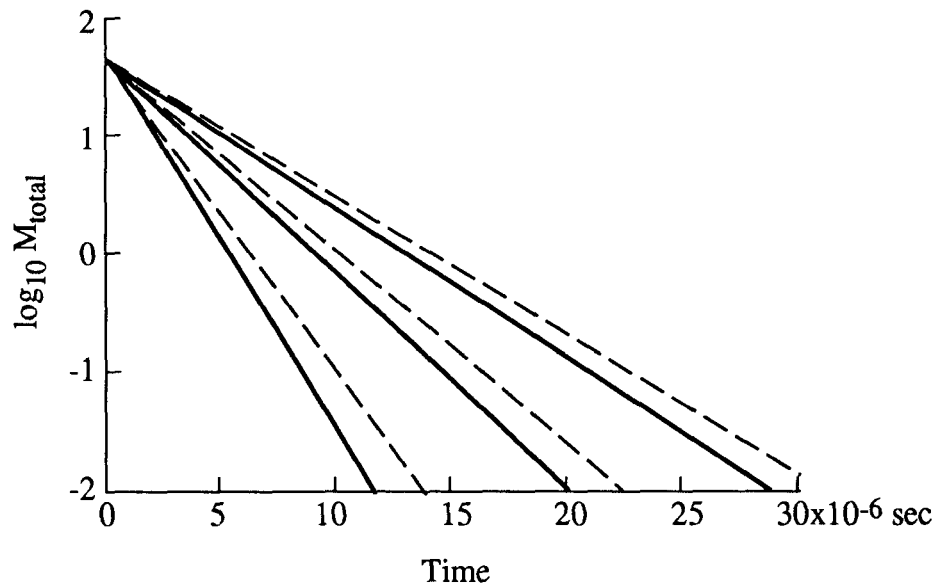


Figure 5. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of impermeable caps of 4 m radius (dashed lines) and 8 m radius (solid lines). Values of λ are 5×10^{-7} , 10^{-6} sec^{-1} , and ∞ (local equilibrium).

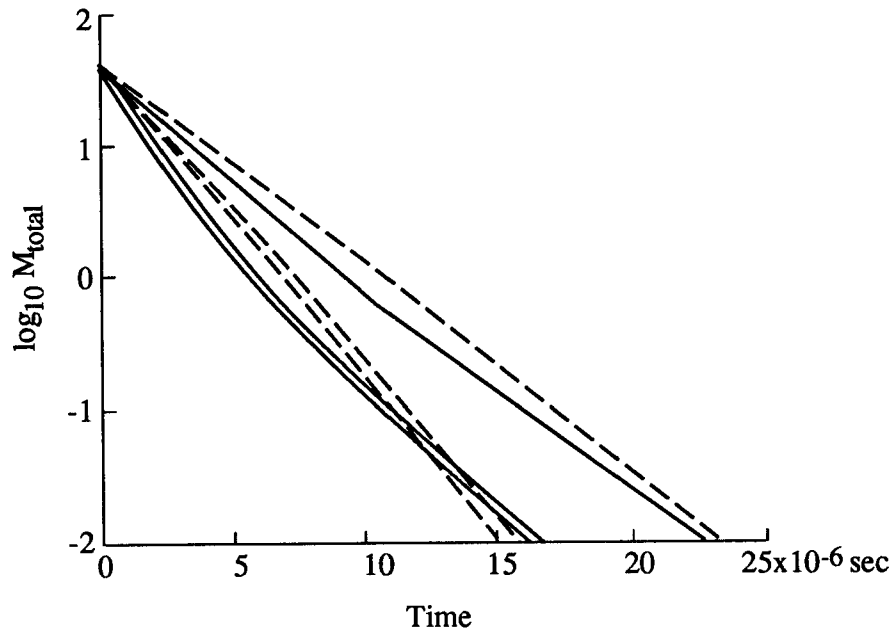


Figure 6. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells screened along their entire length and located around the periphery of the domain. Runs made with passive wells present (solid lines) and absent (dashed lines) have values of λ of 10^{-6} , 10^{-5} sec^{-1} and ∞ from the top down.

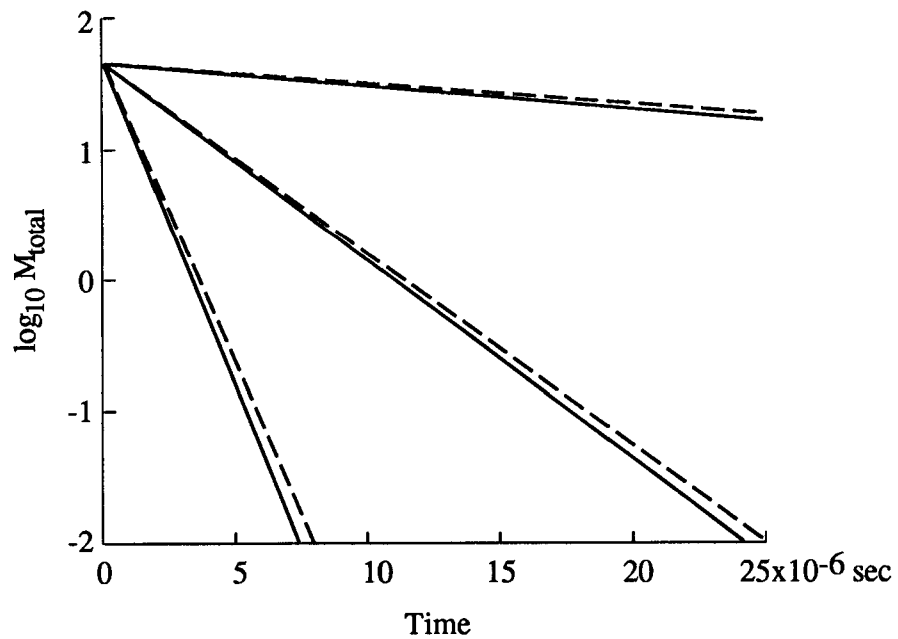


Figure 7. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells. Runs with passive wells present (solid lines) and absent (dashed lines) have values of λ of 10^{-8} , 10^{-7} and 10^{-5} sec^{-1} .

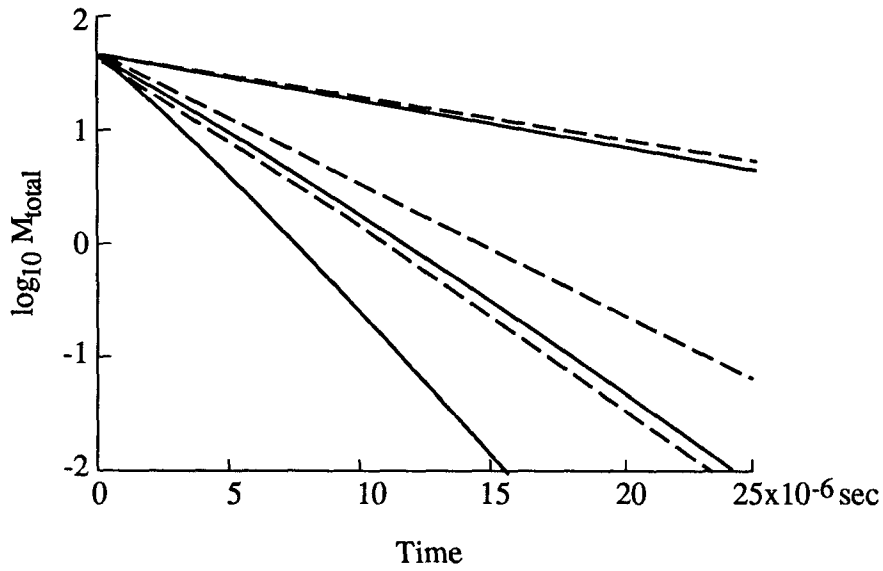


Figure 8. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells combined with a 10 m impermeable cap. Runs with passive wells and caps present are indicated with solid lines; runs without wells and caps are shown with dashed lines. Values of λ are 10^{-7} , $5 \times 10^{-7} \text{ sec}^{-1}$, and 10^{-6} sec^{-1} from the top down.

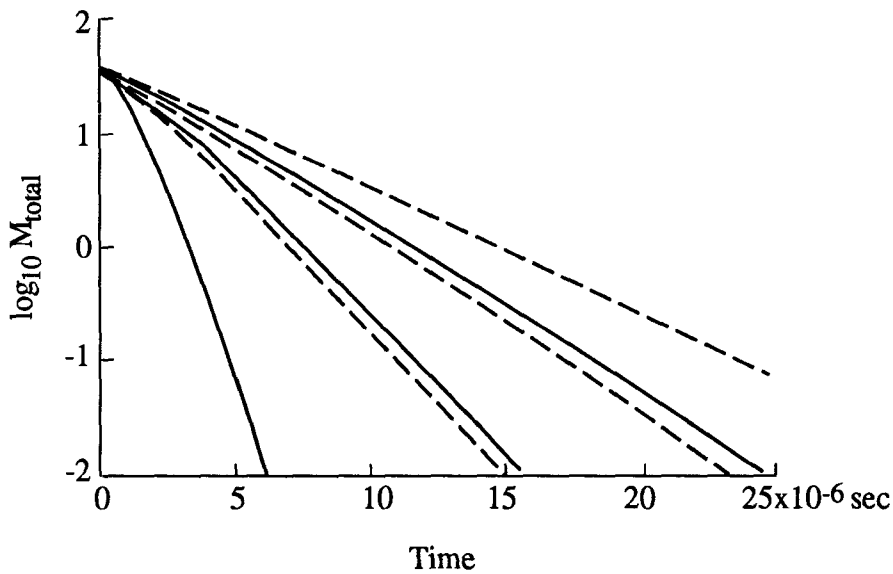


Figure 9. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of passive wells combined with an 8 m impermeable cap. Runs with passive wells and caps present are shown with solid lines; runs without wells and caps are shown with dashed lines. Values of λ are 5×10^{-7} , 10^{-6} sec^{-1} and ∞ (local equilibrium) from the top down.

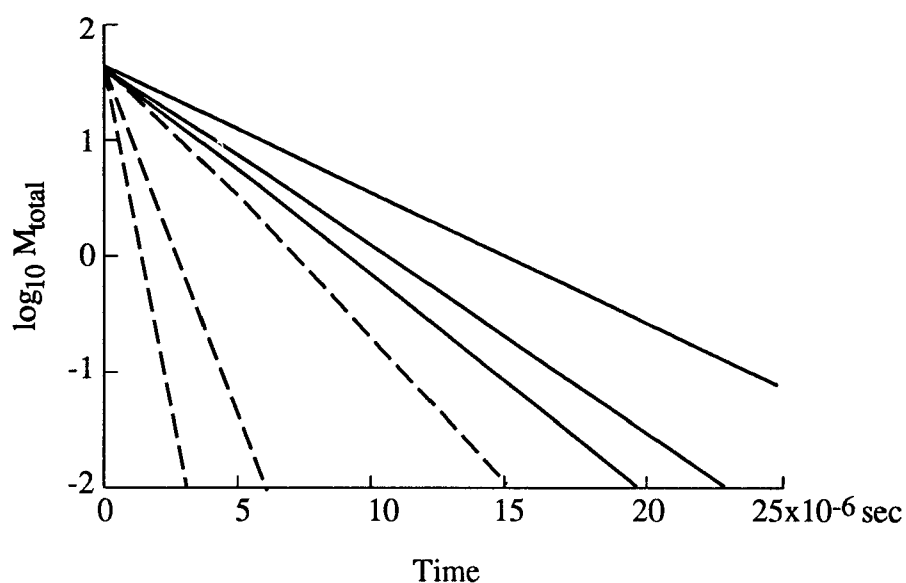


Figure 10. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of gas flow rate. No passive wells or caps are present. Runs made with the local equilibrium assumption are shown with dashed lines. Runs having $\lambda = 5 \times 10^{-7} \text{ sec}^{-1}$, are shown with solid lines. Gas flow rates in each of the two sets of runs are 1.05, 2.75, and 5.5 mol/sec from the top down.

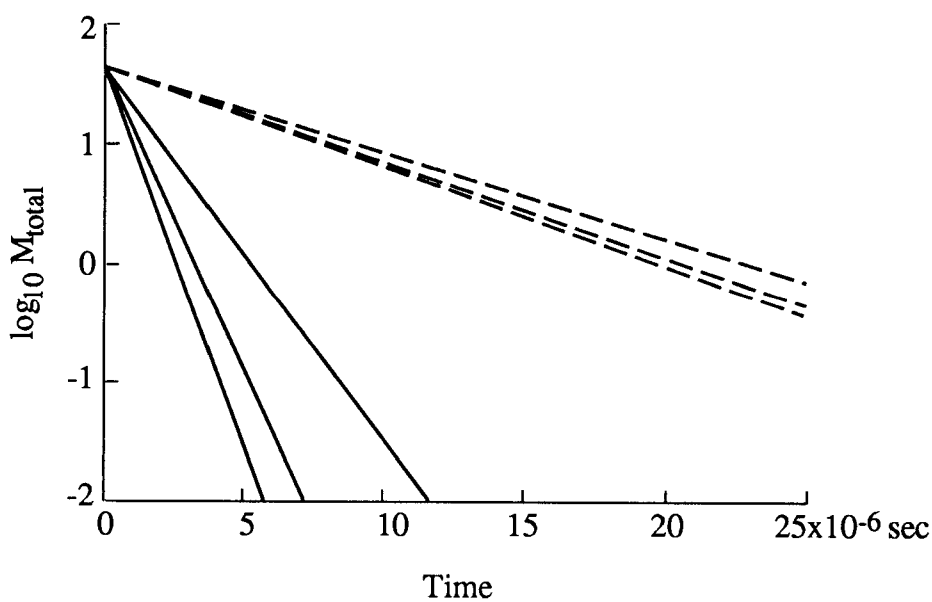


Figure 11. Plots of $\log_{10} M_{\text{total}}$ versus time; effects of gas flow rate. No passive wells or caps are present. Runs made with $\lambda = 10^{-7} \text{ sec}^{-1}$ are shown with dashed lines; runs made with $\lambda = 10^{-6} \text{ sec}^{-1}$ are shown with solid lines. Gas flow rates are 1.05, 2.75, and 5.5 mol/sec from the top down in each set.

Table 2. Standard Parameter Set for the Runs shown in Figures 12-21

Domain length	13 m
Domain depth	8 m
dx, dy'	1 m
Location of well	x = 6.5 m, y = 0.5 m
Packed radius of well	0.2 m
Wellhead pressure	0.85 atm
Temperature	14°C
Soil gas-filled porosity	0.3
K_r, K_z	1.100 m ² /atm • s
Initial soil contaminant concentration	100 mg/kg
Soil density	1.7 g/mL
Specific moisture content	0.2
Effective Henry's constant	0.005

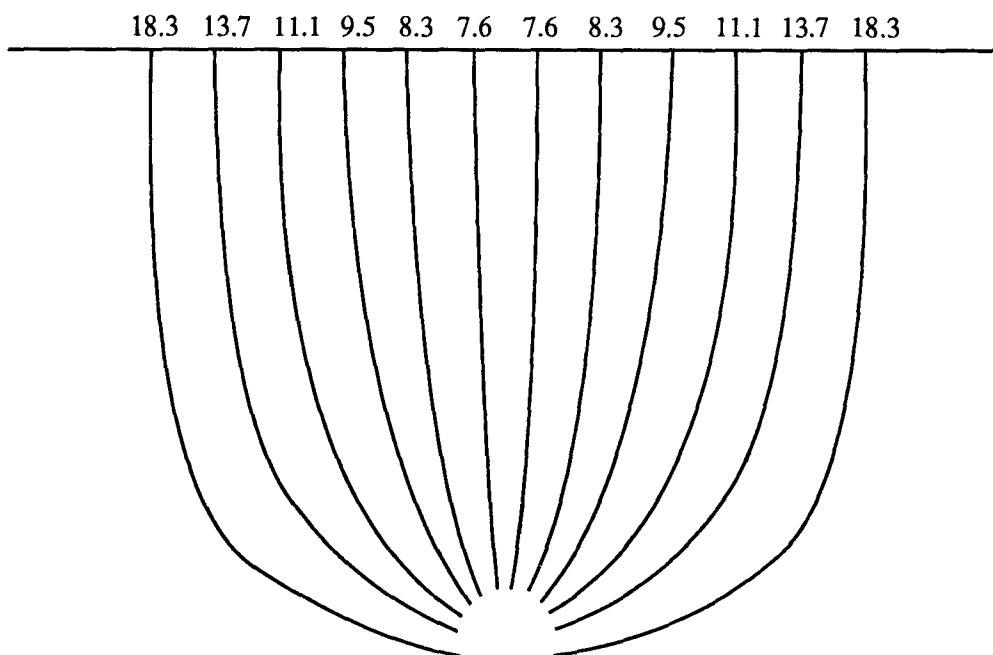


Figure 12. Streamlines in the absence of low permeability lenses (Run 1). The numbers at the top of the streamlines are the gas transit times in units of 1000 s. See Table 2 for model parameters for Runs 1-8.

18.7 14.7 12.7 12.2 13.1 17.2 17.2 13.1 12.2 12.7 14.6 18.6

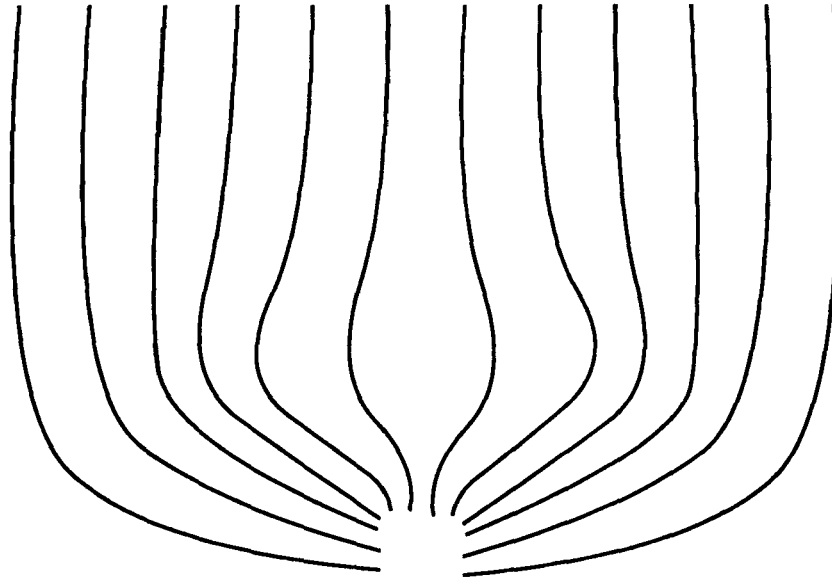


Figure 13. Streamlines in the presence of a lens centered over the vapor extraction well. The lens is centered at the point (6.6, 3). $A = B = 0.095 \text{ m}^2/\text{atm s}$, $r = 3 \text{ m}$, $s = 1 \text{ m}$, $n = 2$. Run 2.

21.5 22.5 25.6 14.1 9.5 7.5 7.2 7.6 8.8 10.4 12.9 17.3

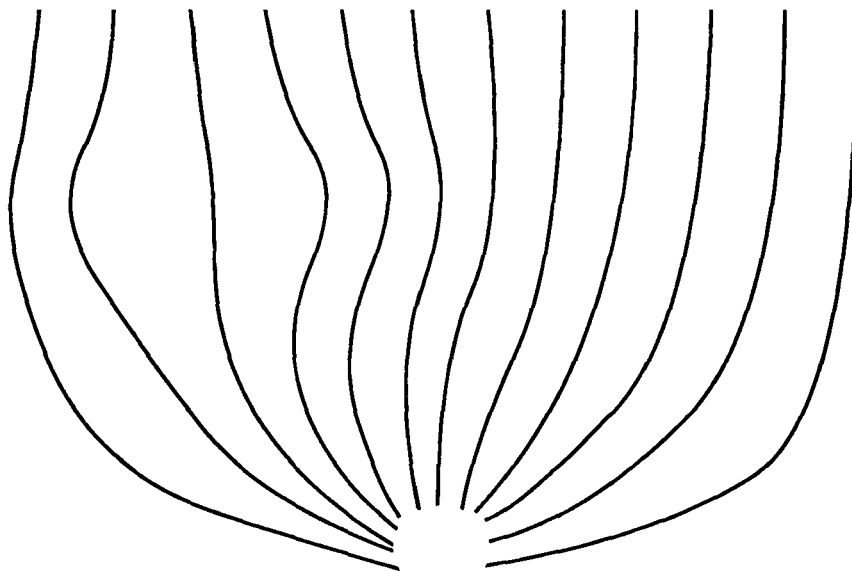


Figure 14. Streamlines in the presence of a lens in the upper left portion of the domain, centered at (3, 5). Other lens parameters are in Figure 13. Run 3.

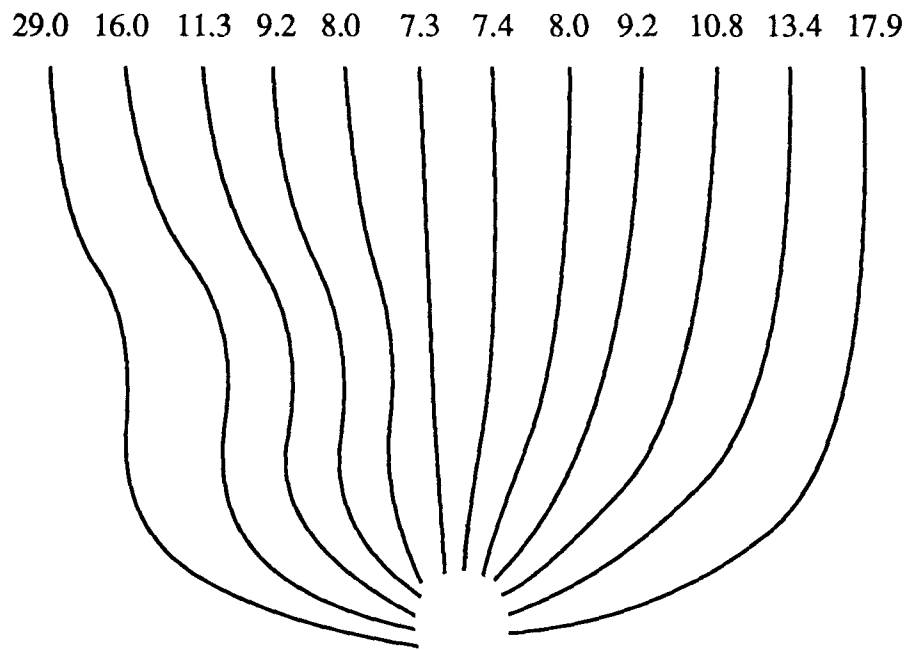


Figure 15. Streamlines in the presence of a lens in the far left portion of the domain, centered at (1, 4). $r_1 = 4$, $s_1 = 1$ m, other parameters as in Figure 13. Run 4.

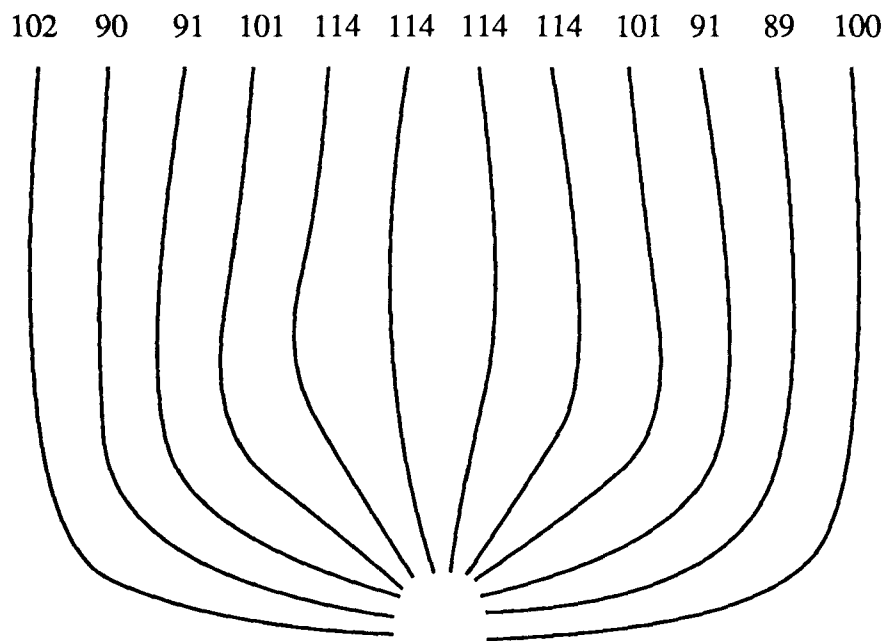


Figure 16. Streamlines in the presence of a lens surrounding the screened section of the well, centered at (6.5, 2). $r_1 = s_1 = 4$ m, other parameters as in Figure 13. Run 5.

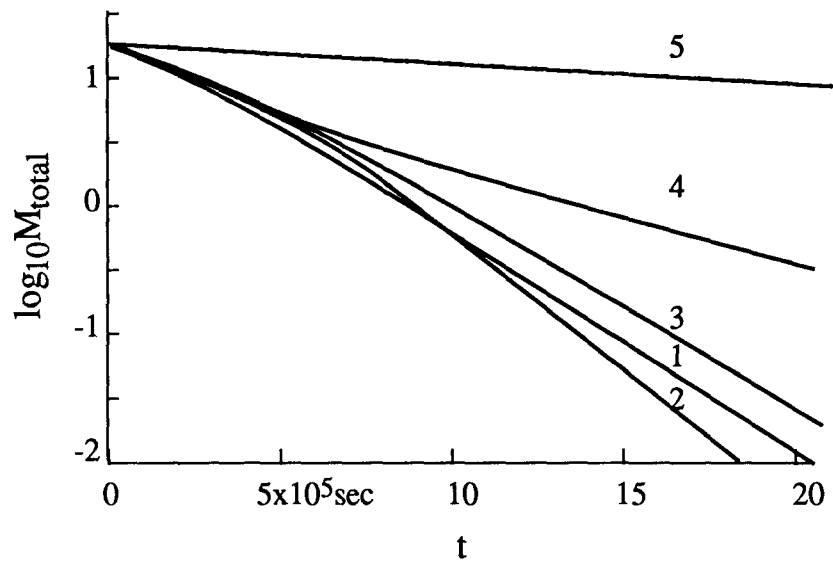


Figure 17. Plots of \log_{10} (total contaminant mass, M_{total}) versus time for Runs 1 through 4.

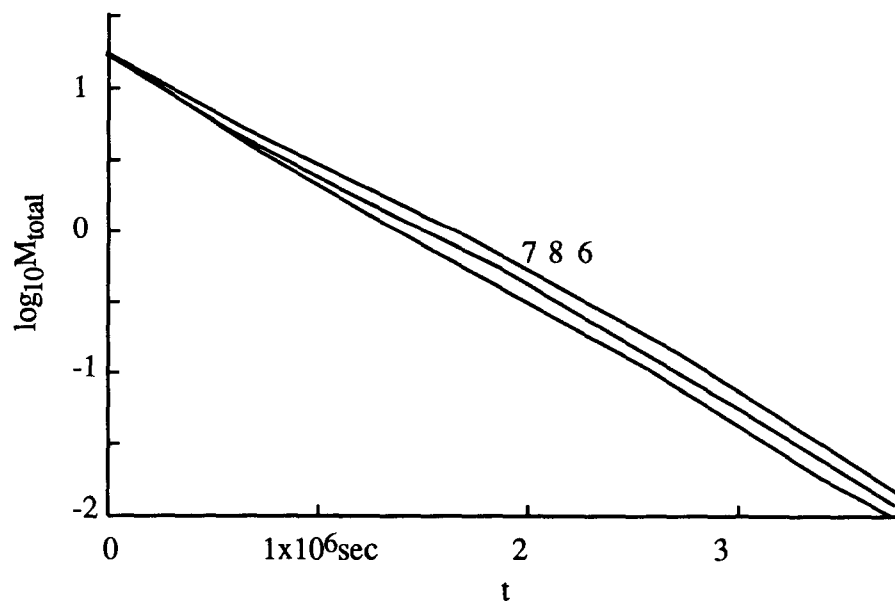


Figure 18. Plots of \log_{10} (M_{total}) versus t for Runs 6, 7, 8.

Table 3. Geometrical and Physical Parameters for the Model, Runs 9 - 17.

Depth of domain	12 m
Width of domain	25 m
dx	1 m
dy	0.6 m
Wellhead pressure	0.75 atm
Height of bottom of screened well section above the water table	1.2 m
Height of top of screened well section above the water table	3.0 m
Effective Henry's constant	0.001
Initial total contaminant mass	10 kg
Permeabilities K_{x_0} and K_{y_0}	0.1 m ² /atm • s
Temperature	25°C

Table 4. Parameters Describing the Lenses, Runs 9-17

A	0.095 m ² /atm • s
B	0.095 m ² /atm • s
r_i	6.0 m
s_i	1.5 m
n	1

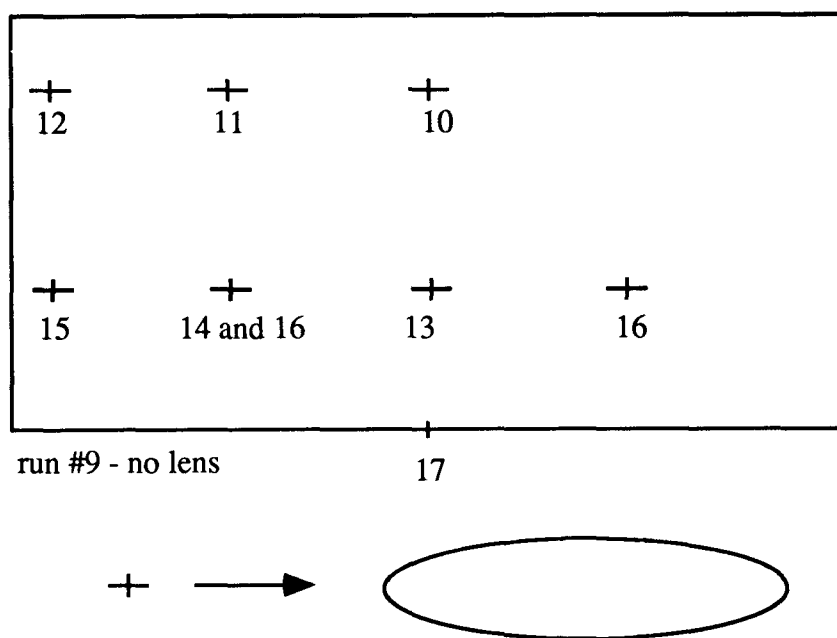


Figure 19. Positions of the centers of the low permeability lenses for Runs 10-16. Run 9, the reference run, has no lenses. See Tables 3 and 4 for parameter values.

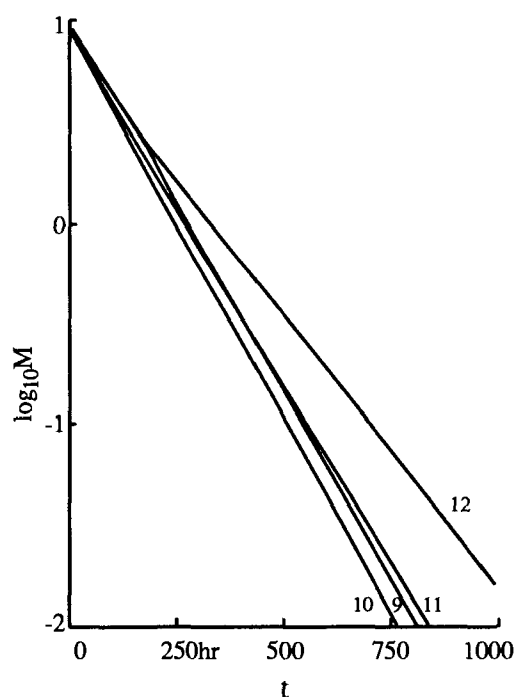


Figure 20. Plots of $\log_{10} (M_{\text{total}})$ versus t for Runs 9-12, as indicated by the numbers by the plots. See Figure 19 and Tables 3 and 4 for parameter values.

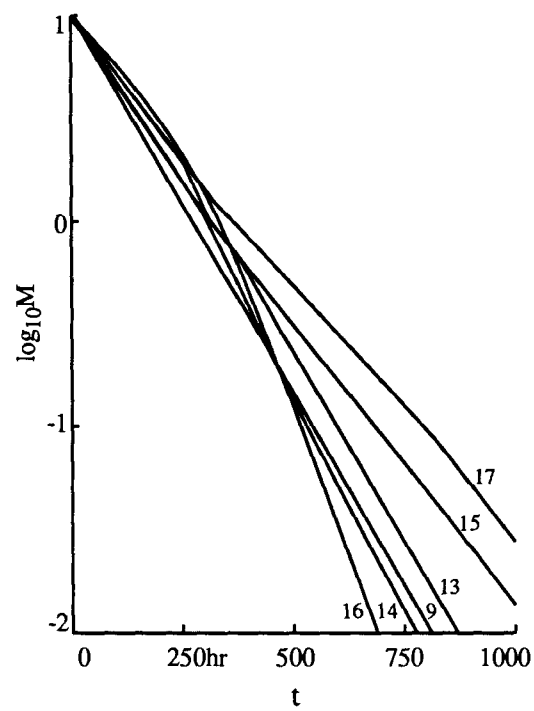


Figure 21. Plots of $\log_{10}(M_{\text{total}})$ versus t for Runs 9 and 13-17 as indicated by the numbers by the plots. See Figure 19 and Tables 3 and 4 for parameter values.

DEVELOPMENT AND APPLICATION OF A THREE DIMENSIONAL AIR FLOW MODEL IN THE DESIGN OF A VAPOR EXTRACTION SYSTEM

MICHAEL C. MARLEY

*Vapex Environmental Technologies, Inc.
Canton, Massachusetts*

ABSTRACT

The long term environmental and public health threats posed at sites with contaminated vadose zone soils are only now attaining the attention required. Innovative technologies are being developed to aid remediation of these contaminated soils. Vapor extraction (soil venting) of volatile and semi-volatile petroleum hydrocarbons is rapidly being recognized as a technically sound and economical remediation alternative.

To date, the majority of vapor extraction system designs have been based on long term pilot studies or non-engineered, less economical installations based largely on the principle of trial and error. Engineered system design depends on knowledge of the site soil properties in relation to air flow. The relevant soil properties includes the relative intrinsic permeabilities of each geologic unit and of the confining unit(s) within the soil system.

This paper presents the development of a three dimensional compressible fluid (air) flow model, the utilization of the model in the evaluation of a site's soil properties in relation to air flow using the data collected during the conduct of a short term field test, and the application of the model in the design of an optimal, cost effective, full scale vapor extraction system. The model provides management with a scientifically based decision making and design tool.

INTRODUCTION

The fate and transport of volatile, semi-volatile, and gaseous contaminants released into the subsurface environment has become a subject of primary concern the past two decades. It has been estimated that up to 20 percent of the approximately 2 million federally regulated underground storage tanks in the United States may be leaking (15). Spilled product migrates through the unsaturated soil zone, under the influence of gravitational and capillary forces, to the water table. Corrective action generally includes an effort to physically remove the product by bailing and pumping as well as pumping and treating contaminated ground water. The product retained in the unsaturated zone, however, can be a significant portion of the total spill. For example, Hoag and Marley (1986) determined residual saturations of a commercial gasoline to be 26 and 44 grams per kilogram of medium and fine sand, respectively, at field moisture conditions. Baehr (1987), Sleep and Sykes (1989) have developed natural transport models and demonstrated the potential for long-

term ground water contamination due to vapor and solute transport emanating from the trapped immiscible plume in soils above the ground water table.

In the past few years, the need to remediate these contaminated unsaturated soils as part of a comprehensive and cost effective site clean-up has been emphasized. There are a number of methodologies commonly utilized in the remediation of contaminated unsaturated soils including:

- excavation and off-site disposal
- excavation and on-site treatment
- biodegradation
- in-situ soil washing
- in-situ vapor extraction (soil venting, air stripping, enhanced volatilization)

In general, it is recognized that where applicable, vapor extraction is the most cost effective alternative.

Vapor extraction entails the induction of an advective air phase through contaminated vadose zone soils. In the unsaturated zone, the optimal air flow field can be established with combinations of withdrawal and injection (if required) wells and/or trenches. The advective air flow induces intraphase transfer of the contaminants from the immiscible and water phases into the air phase. Air laden with contaminant vapors moves along induced flow paths toward the withdrawing system where it is analyzed, treated, and/or released to the atmosphere. The success of the method depends on the rate of contaminant transfer from the immiscible and water phases into the air phase, and in particular, the ability to establish an air flow field that intersects the distributed contaminants.

The cost effectiveness of utilizing vapor extraction has been diminished by less than optimal employment of the technology. Often, vapor extraction systems have been designed and implemented based on less than a full understanding of the physical/chemical principles governing the process. The design of a vapor extraction system is comparable to the design of a ground water resource or ground water extraction and treatment system. Industry has learned that mathematical models are essential tools in the design of ground water extraction and treatment systems. This is also the case in the design of vapor extraction systems. Mathematical equations/models are utilized to approximate the physical conditions that exist in the subsurface environment. They provide a scientific basis - not a black box - upon which design and management decisions can be made.

A SCIENTIFIC DESIGN APPROACH

A general approach to vapor extraction system design follows the pattern where the information obtained from the evaluation of the degree and extent of contamination is utilized to provide assumptions of uniform contamination over a specified soil zone. Intraphase equilibrium is assumed between the contaminants and the air and water phases. Uniform air flow fields are assumed and extrapolations of the remediation process are performed. However, following immiscible fluid flow in porous media, the retained, immobilized, immiscible fluids may exist as a few large globs of liquid, or a large number of smaller globs. The geometry of the fluid distribution depends on the nature of the capillary forces between the fluids, the pore sizes and geometry, and the history of fluid movement in the medium. Although intraphase equilibrium may exist at the pore scale, the heterogeneous distribution of the immobilized immiscible organics within the pores may

make the overall equilibrium assumptions inappropriate. Marley (1985) and Baehr, Hoag and Marley (1989) demonstrated that where a relatively uniform distribution of residual contamination does exist, the assumption of a dynamic equilibrium between the advective air phase and the immiscible contaminant provides a good approximation of the governing physical/chemical processes. More generally, the intraphase transfer of contaminants should be considered in terms of mass transfer limitations. At this time, few transport models which consider potential mass transfer limitations exist.

Of greater importance than the potential mass transfer limitations or equilibrium assumptions is the capability to control the airflow pathways in the vadose zone to optimize contact with the contaminants. Without the aid of air flow models, it would be difficult to evaluate the airflow pathways for all but the most simplistic of cases (homogeneous, isotropic, dry sands, impermeable surface boundary, with no subsurface structures within the extraction system zone of vacuum influence).

AIR PERMEABILITY AND AIR FLOW MODELING

Compressible flow in porous media has been a subject of investigation for many years in petroleum reservoir engineering. Mathematical models of air movement in unsaturated porous media have been calibrated with air pressure data in previous investigations to provide determinations of in-situ air permeability. Muskat and Botset (1931) developed a one-dimensional (radial) air flow model to evaluate the horizontal permeability of gas reservoirs. Boardman and Skrove (1966) injected air into packed-off sections of drill holes and observed radial pressure distributions to obtain horizontal fracture permeability of a granitic rock mass. Stallman and Weeks (1969) and Weeks (1977) describe the use of depth dependent air pressure to calculate vertical air permeability in the unsaturated zone. Rozsa and others (1975) document an application of this technique to determine vertical air permeabilities of nuclear chimneys at the Nevada Test Site. As another historical note, soil scientists (6, 9, 19) have utilized injected air and pressure measurements to evaluate soil permeability but these techniques provide estimates over small regions of soil and are not directly applicable for unsaturated zone evaluation.

The application of such models to aid in the design of a vapor extraction system is exactly analogous and can be thought of in two steps:

1. Evaluate, in-situ, the air permeability tensor of the contaminated unsaturated zone soils by calibrating a steady-state air flow model with pressure measurements obtained during short-term air pump tests; and,
2. utilize the air permeability values and air-flow models to determine the well spacings, screened intervals of wells in the unsaturated zone, and the size and type of pumps required to generate the desired air movement.

An in-situ determination of the air-phase permeability tensor is preferred over laboratory determinations to account for variations in prevailing soil-water conditions, the presence of the immiscible organic liquid, and anisotropy and heterogeneity in air phase permeability. Further, permeability evaluations are sensitive to the soils bulk density and structure, these properties are generally altered in soil samples taken for laboratory analysis.

The governing equation defining conservation of mass for compressible flow is given as:

$$\frac{\partial (\rho_a \theta_a)}{\partial t} + \nabla \cdot (\rho_a q_a) = 0 \quad (1)$$

where,

ρ_a	=	air density
θ_a	=	air filled porosity
q_a	=	specific discharge vector

expressing density as a function of pressure in accordance with the ideal gas law and q_a by Darcy's law:

$$\rho_a = \frac{P_a W_a}{RT} \quad (2)$$

$$q_a = -\frac{k_a}{\mu_a} \nabla P_a \quad (3)$$

where,

P_a	=	air pressure
W_a	=	molecular weight of air
R	=	universal gas constant
T	=	temperature
k_a	=	intrinsic permeability tensor
μ_a	=	air viscosity

yields a partial differential equation in terms of air phase pressure. The selection of a coordinate system and appropriate boundary conditions, together with equation (1) defines the air-flow model. The steady state air flow model is given by the following partial differential equation:

$$\nabla \cdot (k_a \nabla P_a^2) = 0 \quad (4)$$

Commonly, hydraulic conductivity values are available from ground water studies performed prior to the vapor extraction feasibility study, where applicable (e.g., uniform, dry, medium-coarse sands), these values may provide a relatively accurate evaluation of the intrinsic horizontal air permeability that could be used in the design process. However, in the majority of cases, this assumption is invalid for one or more of the following reasons:

- gas slippage is ignored (Klinkenberg (1961))
- anisotropy is neglected,
- swelling soils are present,
- the variable water saturation in the unsaturated zone is ignored,

- the presence of an oil phase is ignored,
- the groundwater test may be in a different strata,
- the scale of the ground water test may invalidate the parameter evaluations.

To determine air phase permeability, a radially symmetric region with a single well (Figure 1) is assumed. This implies that the principal axes for the air-permeability tensor are in the radial (r) and vertical (z) directions. Air is injected or withdrawn through the well screen. The unscreened portion of the well is a no flow boundary. Referring to Figure 1 the boundary conditions at $r = r_o$ (well diameter) are:

$$P = P_s \text{ for } r = r_o \quad (5)$$

and

$$\frac{\partial P}{\partial r} = 0 \text{ for } r = r_o \quad (6)$$

where P_s is the steady state pressure along the well screen, located between elevations z_{w1} and z_{w2} . The boundary at $r = r_f$ (far radius of influence) can be chosen to be unaffected by the well:

$$P = P_{atm} \text{ for } r = r_f \quad (7)$$

where P_{atm} is atmospheric pressure. Pressure measurements (if available) can be used to define the boundary condition at $r = r_f$. The lower boundary, formed by the water table, is impervious to air flow, and is as follows:

$$\frac{\partial P}{\partial z} = 0 \text{ for } z = z_{wat} \text{ and all } r \quad (8)$$

The land surface may be open to the atmosphere or impervious to air flow to simulate paved surfaces. This boundary is:

$$\begin{aligned} \frac{\partial P}{\partial r} &= 0 \text{ for } z = z_{surf} \text{ and } r < r_{imp} \\ P &= P_{atm} \text{ for } z = z_{surf} \text{ and } r_{imp} < r < r_f \end{aligned} \quad (9)$$

where r_{imp} is the radius of the impervious portion of the land surface.

Solutions to eq.(2) subject to boundary conditions (5) - (9) were developed. For the special case of radial flow that is induced by fully screening the well in the unsaturated zone beneath an entirely impervious ground

surface, the analytical solution to equation (1) presented by Muskat and Botset (1931) can be used to obtain a horizontal air-phase permeability, averaged over the entire depth of the unsaturated zone. The solutions derived for 2, however, can simulate flow to a partially screened well, and thus, allow for a determination of vertical and horizontal air phase permeabilities, averaged over portions of the unsaturated zone. Further, the solutions allow for evaluating heterogeneous unsaturated zones.

During the conducted field air pump test, the system is operated at a minimum of two air flow rates; this allows for both the initial calibration of the model (i.e., parameter evaluations using the collected field data at the primary air flow rate) and verification of the model (i.e., the model is set to simulate the system for the secondary air flow rates using the parameters established in the calibration mode and comparison is made between the predicted air flow rates and pressure distributions at the well/probes by the model, and the actual pressure data measured at the well/probes at the secondary air flow rates), Figures 2 and 3.

After determining air-phase permeability, multi-dimensional air flow models based on eq. (3) are used to determine the well/trench spacings, screen intervals, air flow rates, (injection and/or withdrawal) and system equipment requirements.

MODEL APPLICATIONS

The following sections present applications of numerical and analytical solutions to the two-dimensional (radially symmetric) and a numerical solution to the three-dimensional (cartesian coordinate) forms of equation (3).

Figure 4 presents a plan for a gasoline spill site in Massachusetts. The three-dimensional air flow model was used to predict the pressure distribution at several depths in the subsurface soils using the field permeabilities as calculated. Figures 5 and 6 display a plan view and 3-Dimensional perspective on the observed pressure distribution in the soil system and the pressure distribution predicted by the calibrated model respectively. The close correlation observed between the model predictions and the observed field data validates the air flow modelling approach.

Figure 7 and 8 present an application of the three dimensional (cartesian coordinate) air flow model in the evaluation of a proposed full scale soil vapor extraction system design. The design consists the simultaneous operation of two vapor extraction wells and a vapor extraction trench. Figure 7 shows the vacuum isopleths (in atmospheres) across the site under full scale operation. Figure 8 presents a perspective view of the zone of vacuum influence associated with the system design. Further model simulations are performed to attain a site-specific optimal vapor extraction system design.

SUMMARY

To date, the majority of vapor extraction system designs have been based on long term pilot studies of non-engineered, less economical installations based largely on the principle of trial and error. Engineered system design requires the evaluation of the site's soil properties in relation to air flow. The relevant soil properties include the relative intrinsic permeabilities of each geologic unit and of surface and sub-surface confining unit(s). Laboratory evaluation of these parameters is difficult, time consuming, costly and subject to the errors associated with extrapolation of data from discrete soil samples.

The relative intrinsic permeability is the fundamental design parameter required to predict the air-flow field. An in-situ determination of this parameter can be obtained by calibration of an air-flow model with air flow rate and pressure distribution data collected during the conduct of a short term pilot test.

Analytical and numerical air flow models have been developed to evaluate the relevant soil properties. Following calibration and verification from field air pump test data, the models can be utilized to size vacuum pumps and to define flow rates, subsurface air pressures, and the flow fields associated with alternate vapor extraction system configurations. The simulations performed allow for evaluation of the most effective and economical system design.

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Typical Subsurface Test Configuration

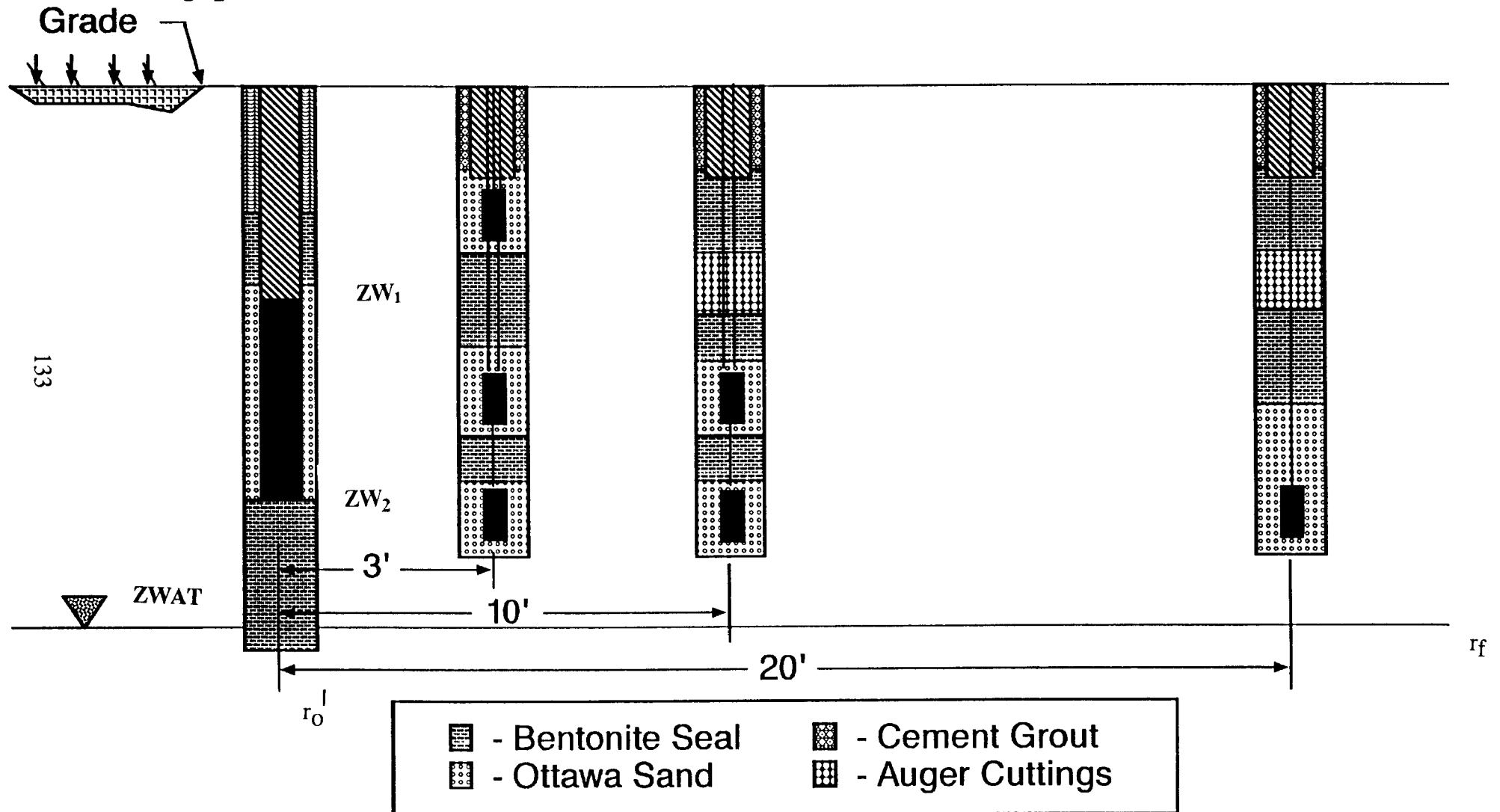


FIGURE 1

VW1 @ 10.1 CFM - 3D Model Calibration

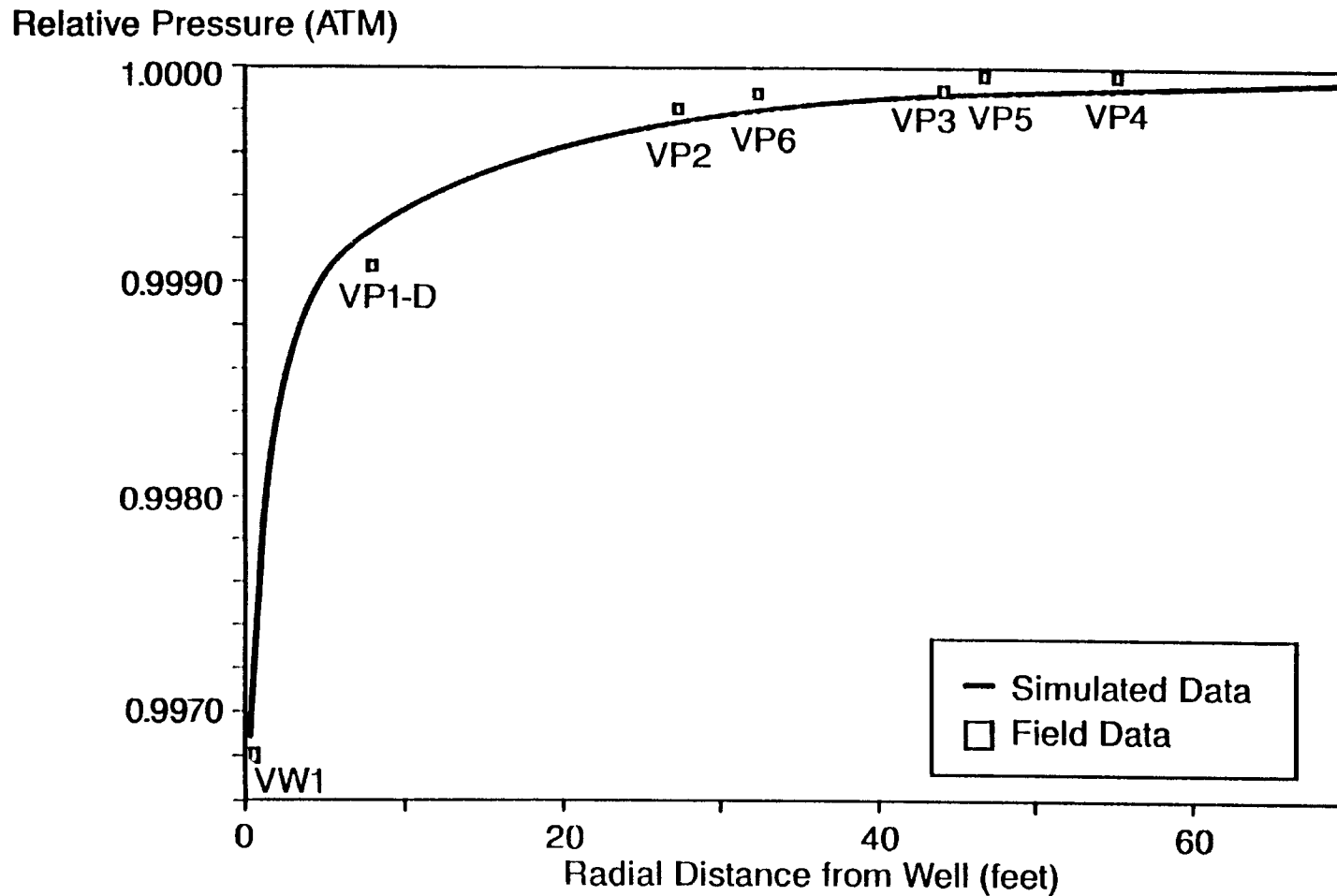


FIGURE 2

VW1 @ 23 CFM - Model Verification

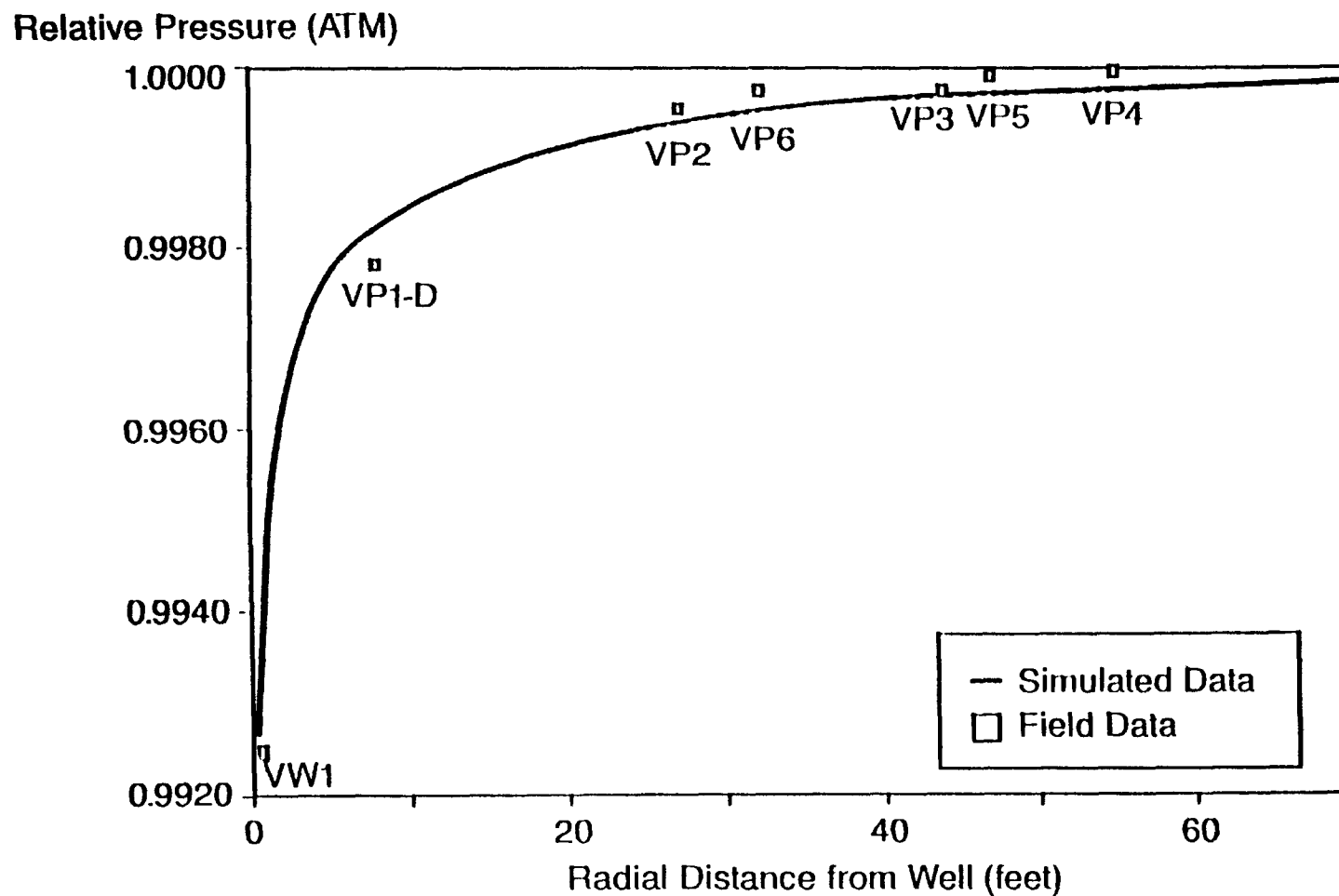


FIGURE 3

Site Plan

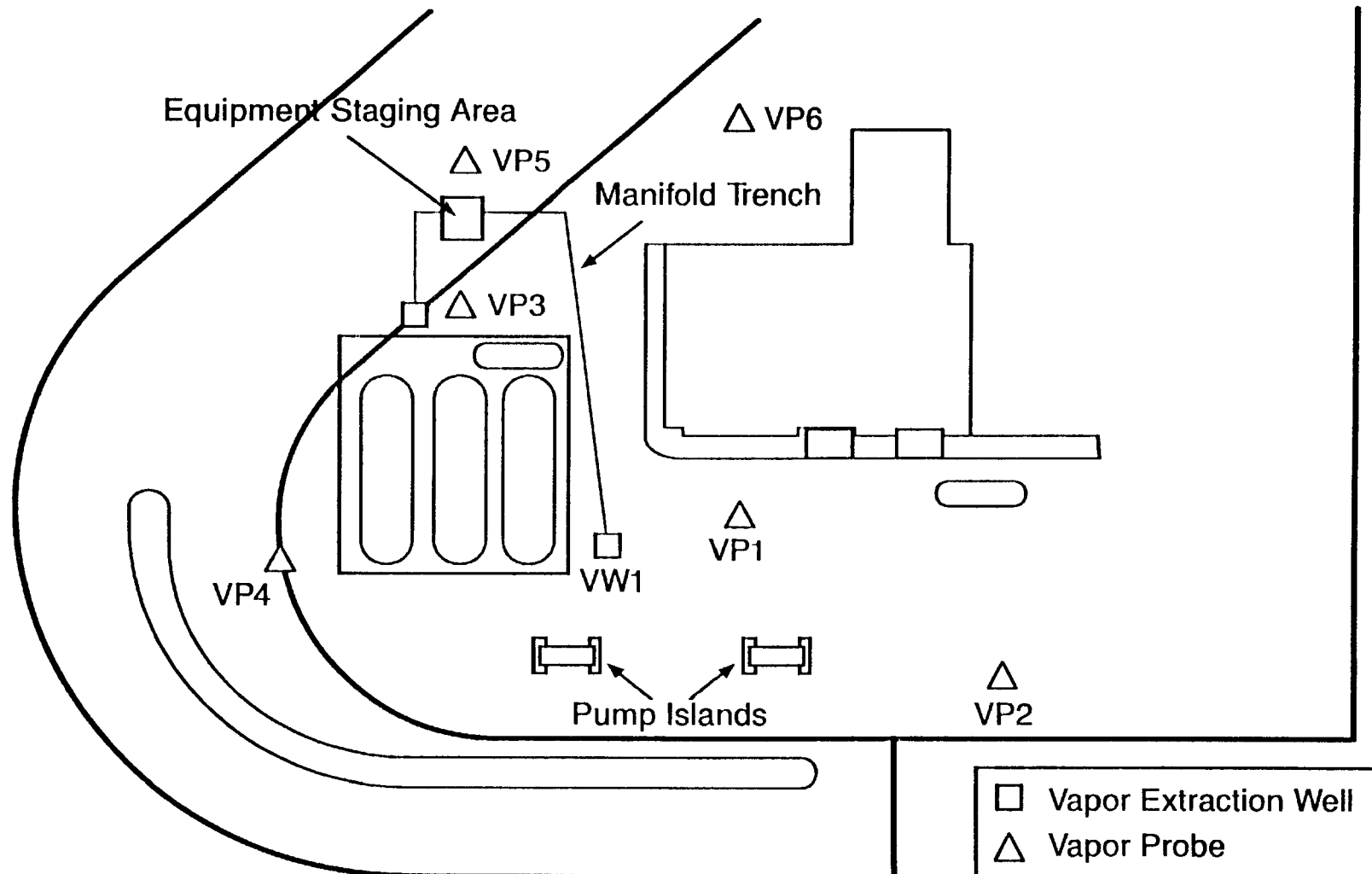


FIGURE 4

FULL SCALE SVES: 2 WELL SYSTEM; YARMOUTH, MA.

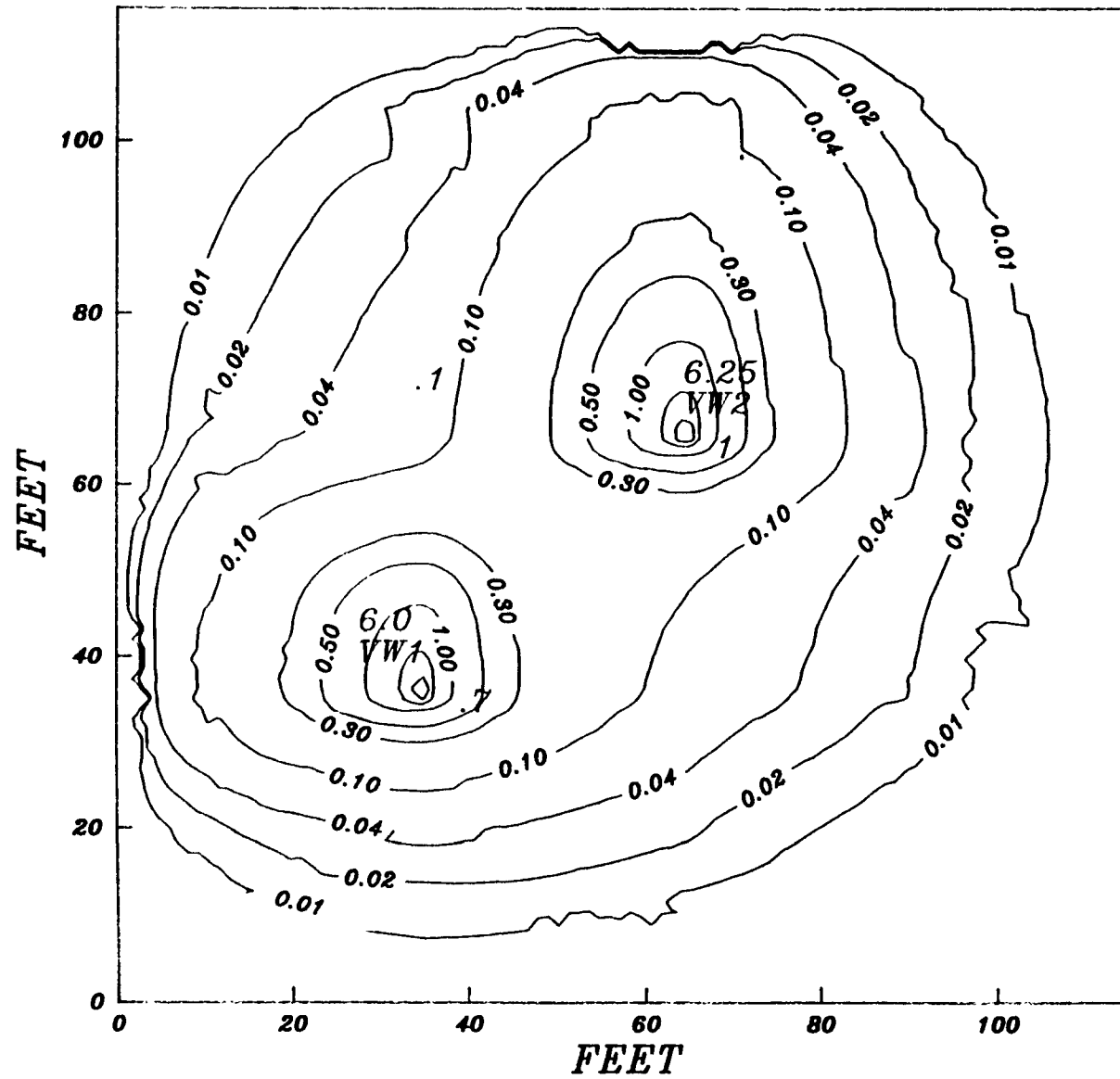


FIGURE 5: VACUUM ISOPLETHS

FULL SCALE SVES: 2 WELLS; YARMOUTH, MA.

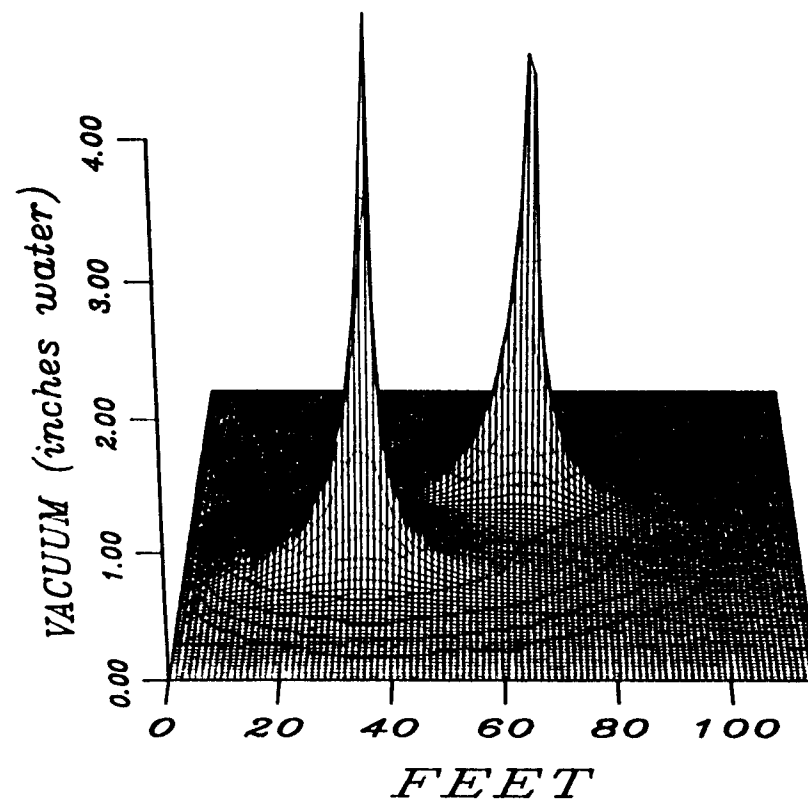


FIGURE 6: VACUUM PERSPECTIVE

FULL SCALE SVES: MAIN St. ORANGE, CT.

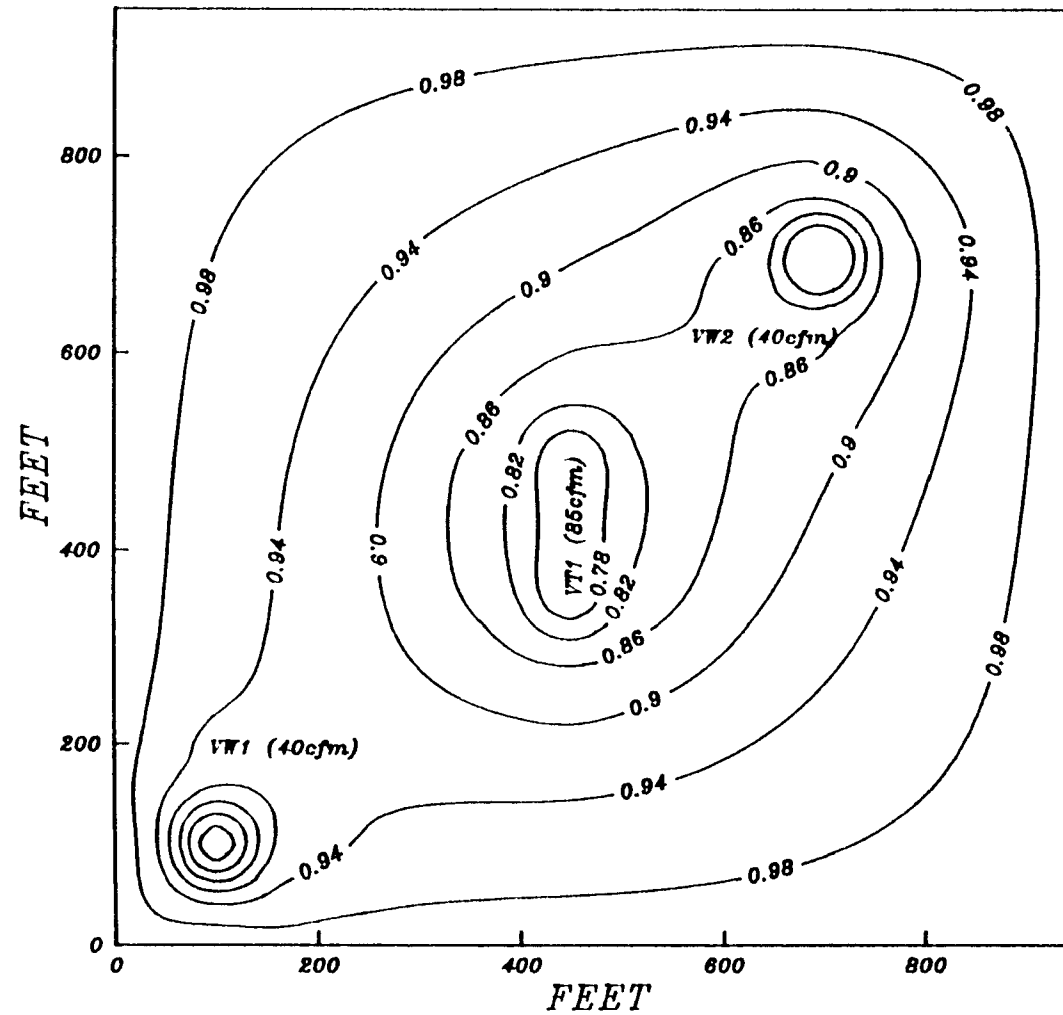


FIGURE 7: VACUUM ISOPLETHS

FULL SCALE SVES: MAIN ST. ORANGE, CT.

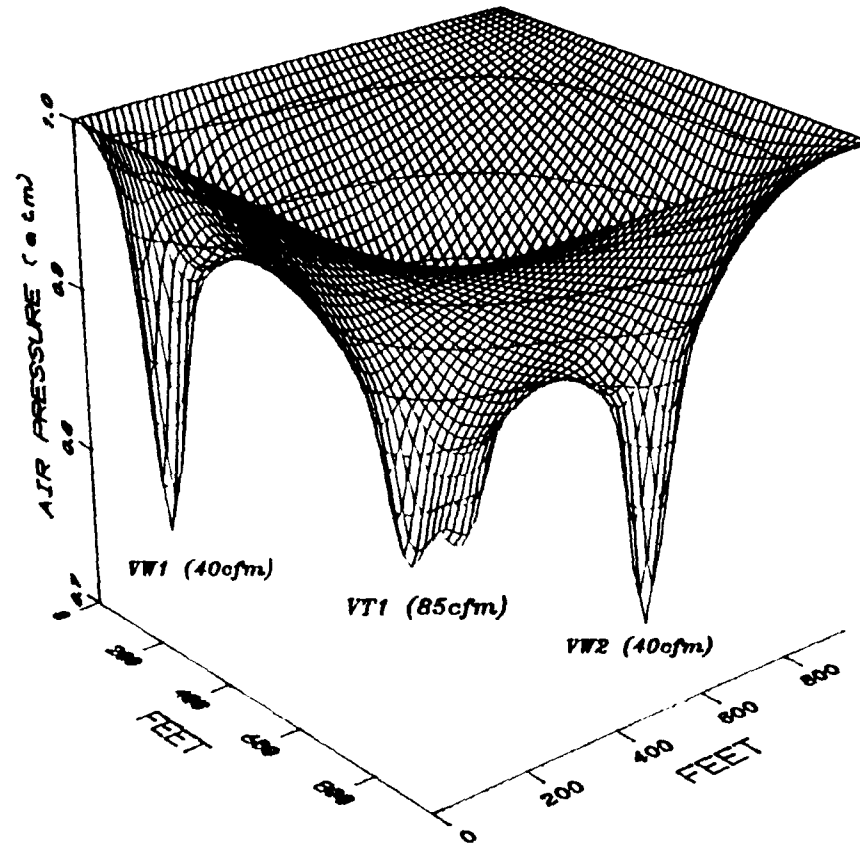


FIGURE 8: VACUUM PERSPECTIVE

MODELING IN-SITU BIODEGRADATION IN UNSATURATED AND SATURATED SOILS

HAROLD W. BENTLEY

HydroGeoChem, Inc.

BYRAN TRAVIS

Los Alamos National Laboratory

ABSTRACT

In-situ biodegradation of subsurface organic contamination requires delivering the chemical constituents necessary for the biodegradation reactions to the contaminated zone and the removal of toxic or inhibitory components produced either by the biodegradation process or present because of the contamination event. Modeling these chemical and physical processes requires numerical simulation of multi-component transport and reaction in the gas, liquid, and solid phases.

TRACR3D is a finite difference code capable of simulating gas and liquid flow, and multi-component solute transport under saturated and unsaturated conditions in three dimensions. We have now modified TRACR3D (and renamed it) TRAMP to include microbial reaction kinetics. The microbial reactions are based on Michaelis-Menten kinetic equations whereby the rates of organic substrate decay vary from zero order when nutrients, electron acceptors, and substrate are in abundance to first order when the concentration of a necessary component becomes rate limiting. These equations also include inhibition terms that limit the rate when the concentration of a toxic or inhibitive component becomes excessive. The equations are balanced according to stoichiometry and reaction yield. These coupled equations are solved with an iterative numerical algorithm. Both aerobic and anaerobic biodegradation can be simulated. Lag time, the poorly understood acclimation time before the biodegradation reactions are initiated, is not accounted for in the model.

TRAMP is capable of simulating such processes as soil venting, the effect of introducing cometabolites into the contaminated zone, co-oxidation processes such as methanotrophic oxidation of chlorinated ethenes, the enhancement of biodegradation by nutrient addition, and the effects of toxin removal on in-situ bioremediation.

Practical examples presented include a one-dimensional simulation of the biodegradation of benzene introduced into an aerobic ground water system, simulations of the effect of changes in water saturation on rates of SVE/biodegradation, and a two-dimensional simulation of SVE/biodegradation of soils containing volatile and non-volatile organics leaking from a contaminated perched mound.

CHARACTERIZING PERMEABILITY TO GAS IN THE VADOSE ZONE

MICHAEL SULLY

Department of Hydrology and Water Resources
University of Arizona

ABSTRACT

The permeability of the vadose zone is a key parameter in predicting the rate of vapor transport in partially saturated media. It is highly relevant to the successful design of a soil venting system to recover volatile hydrocarbon compounds. The permeability of soil to gas is dependent upon the portion of the soil void space which is occupied by liquid. In this paper we review the theory of permeability measurement, the state of the art in field and laboratory testing, and gaps in current technology. We also present indirect methods to determine permeability such as through particle size analysis, as well as methods to determine the moisture content which is associated with the permeability measurement. A case study will be presented in which two different field methods to characterize air permeability were composed.

USE OF SOIL GAS MEASUREMENTS IN THE DESIGN OF SOIL VAPOR EXTRACTION SYSTEMS

GARY R. WALTER AND HAROLD W. BENTLEY

HydroGeoChem, Inc.

ABSTRACT

The design of a soil vapor extraction (SVE) system requires a knowledge of the mass and spatial distribution of the contaminants, their concentrations in the soil vapor phase, the rates at which air can be circulated through the soil, and the air flow patterns which will result from a particular extraction system design. The measurements required to design an SVE system are exactly analogous to those needed to design a ground water pump and treat system. Given the premise that sampling for remedial design should target the mobile phase of the media being removed, soil gas sampling and analysis represents the appropriate technology for SVE design investigations.

Because soil cleanup standards are defined in terms of total soil concentrations, the standard approach to soil remedial design has been to collect and analyze soil samples directly. Direct soil analyses are generally regarded as being more accurate than soil gas analyses. In principle, however, soil gas analyses are no less accurate than other methods for measuring contaminant concentrations in environmental media. The results of soil analyses are well known to be subject to high variability and to suffer from contaminant losses during storage and processing. The variability of soil analyses also increases the cost of investigations because large numbers of samples are required to define contaminant distributions.

Soil gas samples represent a superior method for quantitatively defining contaminant distribution in the vadose zone because they are repeatable, represent relatively large volumes of soil, and have minimal processing losses. Soil gas samples can also be analyzed relatively easily and accurately in a close support laboratory environment to provide rapid guidance to the sampling team and to greatly reduce analytical costs. Given measurements of total organic carbon, moisture content and porosity, soil gas concentrations can be converted into total soil concentrations.

An additional benefit of soil gas sampling is that the same tools used to collect the soil gas samples can be used to perform in situ measurements of soil air permeability. Such measurements are essential for successfully designing the physical air circulation equipment for the site.

The practical application of these approaches is presented based on the remedial design investigation for an SVE system at the Seymour Superfund site.

ASSESSING THE PERFORMANCE OF INSITU SOIL VENTING SYSTEMS BY SOIL SAMPLING AND VOLATILE ORGANIC COMPOUND MEASUREMENTS

ROBERT L. SIEGRIST

Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

Soil contamination by volatile organic compounds (VOCs) is often remediated by in situ soil venting systems. Assessing the performance of these systems requires measurements of the soil VOC concentrations present. VOC measurements in soil systems are subject to many sources of error. Random errors can normally be effectively managed through statistical techniques, but systematic error or bias is far more elusive. While positive bias (e.g. cross-contamination of samples) can be managed through quality assurance provisions (e.g. trip and field blanks), negative bias is more difficult to delineate and control. Negative bias in VOC measurements (i.e. measured value < true value) can be caused by diverse factors including: 1) volatilization losses during soil surface exposure and sample removal from the soil profile, 2) volatilization losses from the sample container during pre-analytical holding, 3) chemical and biochemical transformation during pre-analytical holding, and 4) volatilization losses during subsampling from laboratory analysis.

There are currently no standardized procedures for sampling soils for VOC analyses. Instead, a wide variety of methods have been used, in some cases without regard for the serious sampling errors associated with them.

Until recently little effort has been expended to understand the errors associated with sample collection methods and to develop appropriate quality assurance techniques. In 1989 at the Institute for Georesources and Pollution Research in Norway, this author directed one of the first controlled experiments to study negative sampling bias associated with VOC measurements in contaminated soils. The effects of sample disturbance, container headspace volume, container integrity and in field methanol preservation on VOC concentrations measured were investigated in solvent contaminated soil. This research revealed that sampling method effects can be substantial and significant.

For soil samples containerized in Teflon sealed jars, the lack of in field immersion in methanol contributed the greatest negative bias (up to 81%). High headspace volume and disturbance contributed considerably less bias (up to 17%). The negative bias observed was comparatively less for VOCs with lower solubilities and volatilities. Collection of disturbed soil samples in plastic bags yielded non-detectable levels of VOCs or essentially 100% negative bias.

Research is continuing at Oak Ridge National Laboratory and at other laboratories in the USA. This laboratory and field research is directed at evaluating different sampling devices (e.g. Shelby tube; standard split-spoon), sample preservation conditions (e.g. preservation temperature; holding time), and analytical techniques (e.g. field vs. lab).

Based on this research, it is clear that soil VOC measurements must account for the special properties and behavior of these compounds. This paper presents a discussion of the research conducted by this author as well as a synopsis of selected other work ongoing in the USA. The application and implications of the findings to performance assessments of in situ soil venting systems will be discussed.

A FIELD TECHNIQUE FOR DETERMINING UNSATURATED ZONE AIR PERMEABILITY

CRAIG J. JOSS

Drexel University
Dept. of Civil Engineering
32nd & Chestnut Street
Philadelphia PA 19104

ARTHUR L. BAEHR

JEFFERY M. FISCHER

US Geological Survey
810 Bear Tavern Road
West Trenton, NJ 08628

ABSTRACT

A field technique for determining air-phase permeability in the unsaturated zone has been developed to provide a method for obtaining site specific data for use in models that simulate air flow induced by vapor extraction systems. The apparatus used includes a pneumatic pump, a length of stainless steel tubing, a flow meter, a water manometer, a thermometer, and a barometer. One end of the tubing is modified to form a pressure probe by drilling holes to form a screen. The screened end of the probe is set approximately mid-depth in a lithologic unit. The test consists of withdrawing (or injecting) air from (or into) the unit through the probe at various flow rates and measuring the corresponding air pressure at the probe. This information is used to calibrate a mathematical model of radially symmetric steady state air flow. This model is coupled with a model of air flow through a tube to account for pressure losses not due to the porous media. Applications of the technique at a research site in Galloway Township, New Jersey, are presented.

1.0 INTRODUCTION

Recent research into the behavior of volatile organic chemicals in the unsaturated zone has resulted in the development of a number of models which include advective transport in the vapor phase. For example, models describing the movement of organic vapors in the unsaturated zone have been presented by Sleep and Sykes, (1989), Mendoza and Frind, (1989), Falta et al., (1989), Thorstenson and Pollock, (1989), Baehr and Bruell, (1990). Models that simulate air flow in the unsaturated zone induced by vapor extraction systems are also emerging, for example Baehr et al. (1989). With these increasingly sophisticated models, the need to obtain values for the parameters of these models has been defined.

A key parameter in the vapor phase transport equations, is the air-phase permeability. The air-phase permeability varies with the degree of moisture saturation of the porous medium. Thus, in order to obtain values of permeability that reflect prevailing field conditions, some form of in-situ measurement is required. Also because changes in unsaturated zone lithology can occur over small intervals, it is important to develop measurement techniques over relevant spatial scales. Variation in air permeability as a function of unsaturated zone lithology is an important consideration in the design of induced venting systems.

The test procedure involves injecting or withdrawing air through a probe located in the unsaturated zone. The induced air flow is resisted by the porous media surrounding the probe. Pressure response in the domain at different flow rates is measured using water manometers or pressure transducers attached to observation probes surrounding the extraction probe. The test may also be performed using a single probe which acts as both an extraction probe and an observation probe. In such instances, the pressure at the probe is determined by correcting the surface pressure measurements for pressure losses due to flow in the tube. Air flow rates in the tube connecting the probe to the land surface are measured using a rotometer. Atmospheric pressure, temperature and sub-surface temperatures are measured for standardization purposes. Knowing the pressure at the probe(s) and the mass flow rate at steady state, an estimate of the air permeability is obtained by calibrating the model of radially symmetric air flow.

The number of observation probes used in the test defines the information that is generated on the air phase permeability. If a single observation probe is used to record pressure response in the domain under different flow rates, calibration of the model will only provide estimates of an averaged air permeability (k) of the particular lithologic unit in which the probe is located. If however, multiple probes are used to measure pressure response, calibration of the model will provide estimates of the radial (k_r) and vertical permeabilities (k_z) of the domain. The procedure employing results from a single vapor probe is referred to as a small-scale or mini-permeability test while the procedure using measurements from multiple probes is called a full-scale permeability test.

2.0 FIELD METHODS

2.1 Equipment

Figure 1 gives a general schematic of the test equipment used at the Galloway research site. Basic components of the field equipment necessary to perform the permeability evaluations in the unsaturated zone include:

- length(s) of stainless steel tubing;
- a water manometer;
- a condensation chamber;
- a flow meter;
- a pneumatic pump (and power supply);
- a thermometer;
- a barometer.

The probes used in permeability tests at Galloway Township, New Jersey, are stainless steel tubing that extends down from the land surface to the desired depth. The final 15 centimeter (cm) section of the tube

is perforated with a number of small holes wrapped in 100 mesh stainless steel screen to form the probe. The probes are set in hand augured bore holes approximately 7.6 cm in diameter. The annulus between a probe and bore hole wall are filled with coarse 10-20 mesh silica sand. A typical sand pack measures approximately 45 cm in length. Given the high permeability of the sand pack relative to the in situ material, the pressure drop between the probe and the bore hole wall is assumed to be small compared with that attributed to the surrounding porous media. This assumption requires that the dimensions of the sand pack be used in place of the dimensions of the actual probe in the analytical model. For example, input for the well radius should reflect the radius of the sand pack (equivalent to the bore-hole radius). Similarly, the screen length should be approximated by the length of the sand pack. To prevent vertical air flow through the bore hole, a bentonite layer was installed at each end to seal the sand pack.

The internal tube diameter used in the tests performed at Galloway was 0.396 cm. Small diameter tubing was used to minimize dead space for soil gas determinations, therefore the diameter chosen is not necessarily recommended if the probe is to be used solely to determine air permeability. Tubes were labeled at the surface so that individual probes within a nest of probes could be identified.

A water manometer with a capacity of approximately 50 inches of water was connected to the system. A water trapping device was installed in line before the rotometer to capture any water entering the system. Calibrated rotometers were used to measure air flows rates in the range of 0 through 80 liters per minute. A pneumatic pump was used to induce air flow through the vapor probe.

2.2 Probe Installation

A hand auger, 7.6 cm in diameter, was used to drill the holes for the vapor probes. This hand procedure was selected over power techniques to enable a more detailed log of unsaturated zone stratigraphy. Based on the field logs, distinct geologic strata were identified. Probe locations were then selected to coincide with the mid-depth of each separate lithologic strata. Since one boring typically intersected several distinct strata, the vapor probes were nested in the bore holes. Probe construction is described in Section 2.1. This installation procedure allowed specific strata to be isolated for air-permeability determination.

2.3 Test Procedure

Flexible tygon coated tubing is used to connect the steel tubing at the surface to the pump and pressure and flow measuring devices. Prior to commencing the test a pressure and temperature measurement is made to record the prevailing atmospheric conditions. This information is needed to correct flow readings for non-standard flow conditions and to define the model boundary conditions at land surface. The pneumatic pump is then turned on and adjusted to give the desired air flow rate through the probe. Air flow rates should be selected to allow several data sets to be collected, each set corresponding to a different flow rate. The system should be allowed to reach steady state prior to taking any measurements.

2.4 Test Measurements

Three general types of measurement must be taken during the test. Information is required on the test parameters, equipment and on the domain geometry. A summary of the measurements required to implement the analytical model is presented below.

a. Test Measurements

- air flow rate at steady state (e.g., 10.0 liters/minute);
- air pressure at the surface if a single vapor probe is being used (e.g., 5.0 inches of water), or, air pressure in the observation probes surrounding the extraction probe if a network of probes is being used;
- prevailing atmospheric pressure (e.g., 761 mmHg);
- prevailing atmospheric temperature (e.g., 15 °C).

b. Equipment Measurements

- radius of bore hole (e.g., 3.8 cm);
- internal diameter of steel tube (e.g., 0.396 cm);

c. Domain Geometry

Definition of the domain geometry is based on an interpretation of the boring log. One of two analytical models may then be used to analyze the permeability test data. The first model applies to a domain separated from the atmosphere by a confining unit. The second model applies to a domain open to the atmosphere. Depending on the type of model most suited to the geology at the probe location, various input information must be collected. The following data apply :

- presence or absence of a confining unit;
- thickness of confining unit;
- thickness of domain, namely distance between ground surface (or bottom of confining unit) and water table;
- depth to top of sand pack (screen) from ground surface (or bottom face of confining unit);
- depth to bottom of sand pack (screen) from ground surface (or bottom face of confining unit).

The confining unit permeability should be less than the permeability of the domain for the model solution to apply because the model emulates Hantush's leaky aquifer theory whereby leakage through the confining unit is assumed to be distributed across the domain. For domains with permeabilities that are similar to those in adjacent lithologic units, the unconfined model should be selected.

3.0 AIR FLOW MODELS

Baehr and Hult (1991), present two solutions to the air flow equation assuming a radially symmetric domain. A summary will be presented in this paper for reference purposes.

3.1 Steady State Air Flow Model

The steady state air flow equation describing radially symmetric air flow is as follows :

$$k_r \frac{\partial^2 \phi}{\partial r^2} + k_r \frac{1}{r} \frac{\partial \phi}{\partial r} + k_z \frac{\partial^2 \phi}{\partial z^2} = 0 \quad (1)$$

where, r and z are cylindrical coordinates aligned along the major axes of the permeability k_r and k_z ;
 ϕ = air pressure squared $[(g/cm\text{-}sec^2)^2]$;
 t = time [sec].

3.2 Analytical Solution for Domain Separated from Atmosphere by a Leaky Confining Unit

The domain simulated is sketched in Figure 2. The leaky confining unit can be, for example, a strata less permeable to air than the domain (e.g., a silty-clay unit) or a slightly permeable paved surface. The bottom boundary is formed by the water table which is impervious to air. This solution emulates Hantush's leaky aquifer solution by assuming that leakage from the confining unit is distributed across the domain. The analytical solution from Baehr and Hult (1991), is :

$$\begin{aligned} \phi = & P_{atm}^2 + \frac{aQ^*}{\pi k_r r_w} \left\{ \frac{K_0(M_0 \frac{r}{a})}{b M_0 K_1(M_0 \frac{r}{a w})} \right. \\ & \left. + \frac{2}{\pi (1-d)} \sum_{n=1}^{\infty} \frac{1}{n} \left[\frac{\sin(\frac{n\pi l}{b}) - \sin(\frac{n\pi d}{b})}{M_n K_1(M_n \frac{r}{a w})} \right] K_0(M_n \frac{r}{a}) \cos(\frac{n\pi z}{b}) \right\} \end{aligned} \quad (2)$$

where, ϕ = air pressure squared in domain $[(g/cm\text{-}sec^2)^2]$
 P_{atm} = atmospheric pressure $[g/cm\text{-}sec^2]$
 a = square root of anisotropy ratio $(k_r/k_z)^{1/2}$ $[-]$
 Q^* = $\frac{Q\mu RT}{\omega}$
 Q = mass flow rate $[g/sec]$
 μ = dynamic viscosity of air $[g/cm\text{-}sec]$
 R = universal gas constant $[g\text{-}cm^2/sec^2\text{-}mol\text{-}K]$
 T = absolute temperature $[K]$
 ω = average molecular weight of air phase $[g/mol]$
 r_w = radius of well (to filter/soil interface) $[cm]$
 K_0 = zero order modified Bessel function of the second kind
 K_1 = first order modified Bessel function of the second kind

b	=	vertical thickness of domain	[cm]
d	=	distance from lower confining unit to top of well screen	[cm]
l	=	distance from lower confining unit to bottom of well screen	[cm]
M_n	=	$\left[\left(\frac{n\pi}{b} \right)^2 + \frac{k'}{bb'k_z} \right]^{1/2}$	[1/cm]
k'	=	permeability of confining unit	[cm ²]
b'	=	thickness of confining unit	[cm]

3.3 Analytical Solution for Domain with Land Surface as Upper Boundary

The domain simulated is sketched in Figure 3. In this case, the top of the unsaturated zone is assumed to be in direct connection with land surface. The bottom boundary is formed by the water table. The analytical solution from Baehr and Hult (1991), is :

$$\phi = P_{\text{atm}}^2 + \quad (3)$$

$$\frac{2aQ^*}{\pi^2 k_T (1-d)r_w} \left\{ \sum_{n=1}^{\infty} \frac{1}{m} \left[\frac{\cos\left(\frac{m\pi d}{b}\right) - \cos\left(\frac{m\pi l}{b}\right)}{M_m K_1\left(M_m \frac{r_w}{a}\right)} \right] K_0\left(M_m \frac{r}{a}\right) \sin\left(\frac{m\pi z}{b}\right) \right\}$$

$$\text{where, } m = n - \frac{1}{2} \quad \text{and} \quad M_m = \left(\frac{m\pi}{b}\right)$$

In tests using a single vapor probe, the probe pressure is obtained by correcting surface pressure measurements for pressure losses due to flow in the tube.

3.4 Equation for Pressure Loss Due to Flow in a Tube

In mini-permeability tests, a single probe is used to stress the domain and to determine the pressure response in the vadose zone under the imposed stress. Air is injected into, or withdrawn from, the vapor probe via a length of tubing. Pressure and air flow rates in the tubing are measured at the ground surface during the test. The surface pressure measurement is then used to estimate the pressure in the domain at the probe screen-

soil interface. The probe pressure is the value used to calibrate the air flow model and thereby estimate the air phase permeability.

A pressure differential exists between the surface measurement and that prevailing at the probe due to pressure losses resulting from air flow through the tube. The magnitude of the pressure differential is quantified in equation (4). Equation (4) presents the pressure at the probe as the difference between the measured surface pressure and the pressure losses in the tube due to air flow. Equation (4) is an expression derived from elementary fluid mechanics. Application of equation (4) in mini-permeability tests introduces an additional parameter that is not required in full scale tests, namely the friction factor (f) corresponding to air flow in the tube.

$$\phi = P_1^2 \pm \left[\frac{\left(\frac{f}{D}\right)}{\left(\frac{\beta}{\bar{\phi}}\right) - \left(\frac{\omega}{RT(v_1 \cdot \rho_1)^2}\right)} \right] x \quad (4)$$

where,	+	=	positive for air withdrawal	[-]
	-	=	negative for air injected	[-]
	ϕ	=	square of probe pressure	$[(g/cm\text{-}sec^2)^2]$
	P_1	=	system pressure measured at the surface	$[g/cm\text{-}sec^2]$
		=	$P_{atm} \pm P_{man}$	
	P_{atm}	=	atmospheric pressure	$[g/cm\text{-}sec^2]$
	P_{man}	=	manometer pressure differential between system and atmospheric pressure	$[g/cm\text{-}sec^2]$
	f	=	friction factor along pipe	[-]
	D	=	internal diameter of the pipe	[cm]
	β	=	constant (assumed to be unity)	[-]
	$\bar{\phi}$	=	mean pressure squared estimate for tube	$[g/cm\text{-}sec^2]^2$
	ω	=	average molecular weight of air phase	[g/mol]
	R	=	universal gas constant	$[g\text{-}cm^2/sec^2\text{-}mol\text{-}K]$
	T	=	temperature of air in tube	[K]
	ρ_1	=	density of the air in tube at P_1	$[g/cm^3]$
	v_1	=	velocity of air in tube at P_1	$[cm/sec]$
	x	=	length of tube section between probe and surface measurement	[cm]

The estimate $\bar{\phi}$ is obtained by evaluating equation (4) at $x/2$ and assuming all pressure loss is due to friction (ie. $\beta=0$ for determining $\bar{\phi}$ only). The friction factor is obtained from experimental data (see below) or from theoretical considerations.

3.5 Experimental Determination of Friction Factor

The friction factor (f) as a function of Reynolds Number is determined experimentally by conducting flow experiments on a length of tube with the probe end at atmospheric pressure (P_{atm}), and calibrating equation (5). Equation (5) is obtained by rearranging equation (4) and replacing P_1 with P_{atm} .

$$f = \frac{D}{x} \left[\frac{\beta}{\phi} - \frac{\omega}{RT} \frac{1}{(v_1 \cdot \rho_1)^2} \right] \{ \phi - P_{atm}^2 \} \quad (5)$$

is the pressure in the pipe (squared), after the air has passed through a length x of piping. The Reynolds Number for pipe flow is presented in equation (6).

$$Re = \frac{v_1 \rho_1 D}{\mu} \quad (6)$$

4.0 APPLICATION AT GALLOWAY TOWNSHIP, NEW JERSEY

An investigation of induced venting is being conducted at a site of a gasoline spill from a leaking underground storage tank at Galloway Township, New Jersey. An air flow model is being used to examine the effects of unsaturated zone heterogeneity on induced flow patterns. The field technique described in this paper is being used to estimate the air permeability of distinct lithologic units to provide input for the site air flow model.

Figure 4 provides a description of unsaturated zone lithology at the location of this illustrative pneumatic test. Three probes are located within the sandy unit between the perched water table and the thin clay lens located at 183 cm below land surface as illustrated in Figure 5. Another probe is located in the brown clayey sand unit above the thin clay lens.

One set of tests was conducted on 6/4/1991 by injecting or withdrawing air at probe VW9-7.4 and pressure was measured at probes VW9-6.0 and VW9-8.2. Six tests were conducted in this set, three using air withdrawal and three using air injection. Data collected are summarized in Table 1.

The tests were first analyzed assuming the thin clay lens was pneumatically insignificant and that the brown clayey sand unit above the probes had the same air-permeability as the sand unit in which the probes were located. Under this hypothesis the domain illustrated by Figure 3 applies. Table 2 provides a summary of domain geometry and the best fit air permeability under the conceptualization of the unsaturated zone described above. The best fit air permeabilities indicate an unlikely physical situation, that vertical permeability is roughly an order of magnitude higher than the horizontal permeability. Therefore this conceptualization of the unsaturated zone permeability distribution was abandoned.

A more feasible analysis of the pneumatic tests is obtained by assuming the thin clay lens is significantly less permeable than the underlying sand. Under this hypothesis the domain illustrated in Figure 2 applies. Table 3 provides a summary of domain geometry and the best fit air permeabilities under the conceptualization of the unsaturated zone described above. The horizontal and vertical air permeability estimates are similar in magnitude. The clay lens therefore is a significant air flow barrier which should be considered in designing unsaturated zone remediation. Further, air permeabilities k_r and k_z listed in Table 3 are the best estimates representing the sand unit for input in a sitewide air flow model.

To estimate the permeability of the brown clayey sand unit another set of tests were conducted by withdrawing air from probe VW9-3.0. These tests were conducted at an earlier date, 1/21/91. Probe VW9-3.0 was the only probe available in this unit in the vicinity, therefore the adjustment for pressure loss in the tube, given by equation (4), was particularly important. Further, because only one observation is available, the brown clayey sand unit was assumed to be isotropic ($k_r = k_z$). The top of the clay lens located at $z = 155.4$ cm was assumed to be an impervious unit. The medium white sand unit between the brown clayey sand and the clay lens (Figure 4) was assumed to have the same air permeability as the brown clayey sand. The domain illustrated by Figure 3 applies. Data collected for this set of tests are summarized in Table 4. Table 5 provides a summary of domain geometry and best fit permeability estimates. Comparing these estimates to those obtained for the sand unit (Table 3) indicates that the brown clayey sand unit is about three times less permeable than the sand unit beneath it.

5.0 SUMMARY

A field technique has been developed to obtain air permeability estimates of lithologic units in the unsaturated zone. Two analytical solutions are presented for the equation describing axisymmetric air flow to a partially penetrating well screened in the unsaturated zone. One solution applies to a domain directly in contact with land surface and the other applies to a domain separated from land surface by a confining unit of lower permeability. Analysis of one-dimensional air flow in a cylindrical tube allows for use of the injection/withdrawal well as an observation point as pressure losses in the tube should not be attributed to porous media.

The technique was applied at a field site in Galloway Township, New Jersey. Analysis showed that a thin clay lens was pneumatically significant and would affect site wide flows induced for vapor extraction remediation. Estimates for air permeability for the sand unit between the lens and water table range between $4.3 \times 10^{-8} \text{ cm}^2$ and $8.4 \times 10^{-8} \text{ cm}^2$. Estimates of air permeability for the brown clayey sand unit above the clay lens range between $1.9 \times 10^{-8} \text{ cm}^2$ and $2.1 \times 10^{-8} \text{ cm}^2$.

These estimates for the air permeability of lithologic units in the unsaturated zone will lead to better predictions of flow paths for site venting experiments. The field techniques illustrated here can be applied at other sites to obtain the distribution of air permeability in the unsaturated zone.

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TABLES

Table	Description
1	Pneumatic Test Data Collected 6/4/1991 for Sandy Unit
2	Domain Geometry and Best Fit Air Permeability Under Hypothesis of No Confining Unit Above Sand
3	Domain Geometry and Best Fit Air Permeability Under Hypothesis of Clay Lens Acting as a Confining Unit Above Sand
4	Pneumatic Test Data Collected 1/21/1991 for Brown Clayey Sandy Unit
5	Domain Geometry and Best Fit Air Permeability for Brown Clayey Sand

TABLE 1. Pneumatic Test Data Collected 6/4/1991 For Sandy Unit

Test Number	1	2	3	4	5	6
Injection (I) or Withdrawal(W)	W	W	W	I	I	I
Q, Mass Flow Rate (g/sec)	0.6041	0.4620	0.2623	0.7018	0.5069	0.2533
P_{atm} , Atmospheric Pressure (mmHg)	754	754	754	754	755	755
T_{air} , Air Temperature (°C)	22	22	22	25	23	23
T_{soil} , Soil Temperature at Injection/Withdrawal Depth (°C)	17	17	17	17	17	17
Re, Reynolds Number in Pipe	11,045	8,448	4,796	12,799	9,261	4,627
f, Pipe Friction Factor	0.0167	0.0174	0.0202	0.0163	0.0172	0.0205
P/P_{atm} , Normalized Pressure Measured at the Surface	0.880944	0.923729	0.970856	1.138278	1.076580	1.024493
P/P_{atm} VW9-7.4 ⁽¹⁾	0.985138	0.985166	0.993006	1.019580	1.011210	1.005600
Normalized VW9-6.0	0.999132	0.999380	0.999603	1.000943	1.000620	1.000298
Probe Pressure VW9-8.2	0.999256	0.999479	0.999628	1.000868	1.000546	1.000248

NOTES : (1) Pressure at end of probe adjusted for pressure losses in pipe according to equation (4)

TABLE 2. Domain Geometry and Best Fit Air-Permeability Under Hypothesis of No Confining Unit Above Sand

Well Locations (centimeters)
$d = 210$ $l = 241$ $b = 301$ $r_w = 3.8$

Observation Coordinates (r,z) (centimeters)
VW9-7.4 (3.81,225.0)
VW9-6.0 (50.0,183.0)
VW9-8.2 (50.0,250.0)

Best Fit Air Permeability Estimates		
Test Number	k_r (cm ²)	k_z (cm ²)
1	3.29×10^{-8}	6.54×10^{-7}
2	2.15×10^{-8}	7.46×10^{-7}
3	3.02×10^{-8}	6.02×10^{-7}
4	2.63×10^{-8}	6.97×10^{-7}
5	3.51×10^{-8}	7.65×10^{-7}
6	3.40×10^{-8}	8.36×10^{-7}

TABLE 3. Hypothesis of Clay Lens Acting As a Confining Unit Above Sand

Well Locations (centimeters)
$d = 27$ $l = 58$ $b = 118$ $r_w = 3.8$

Observation Coordinates (r,z) (centimeters)
VW9-7.4 (3.81,42.5)
VW9-6.0 (50.0,1.0)
VW9-8.2 (50.0,67.0)

Best Fit Air Permeability Estimates			
Test Number	k_r (cm ²)	k_z (cm ²)	k'/b' (cm)
1	6.07×10^{-8}	4.70×10^{-8}	3.38×10^{-9}
2	4.26×10^{-8}	4.38×10^{-8}	4.01×10^{-9}
3	5.48×10^{-8}	4.74×10^{-8}	3.16×10^{-9}
4	4.48×10^{-8}	8.36×10^{-8}	3.73×10^{-9}
5	6.81×10^{-8}	4.30×10^{-8}	3.88×10^{-9}
6	6.53×10^{-8}	5.29×10^{-8}	4.32×10^{-9}

TABLE 4. Pneumatic Test Data Collected 1/21/1991 For Brown Clayey Sandy Unit

Test Number	1	2	3
Injection (I) or Withdrawal(W)	W	W	W
Q, Mass Flow Rate (g/sec)	0.3840	0.5107	0.8225
P _{atm} , Atmospheric Pressure (mmHg)	767	767	767
T _{air} , Air Temperature (°C)	9	9	9
T _{soil} , Soil Temperature at Injection/Withdrawal Depth (°C)	5.3	5.3	5.3
Re, Reynolds Number in Pipe	7,144	9,502	15,302
f, Pipe Friction Factor	0.0183	0.0171	0.0157
P ₁ /P _{atm} , Normalized Pressure Measured at the Surface	0.962353	0.942846	0.880218
P/P _{atm} ⁽¹⁾ Normalized Probe Pressure	VW9-3.0 0.978850	0.970685	0.951382

NOTES : (1) Pressure at end of probe adjusted for pressure losses in pipe according to equation (4)

TABLE 5. Domain Geometry and Best Fit Air-Permeability for Brown Clayey Sand

Well Locations (centimeters)
$d = 61$ $l = 107$ $b = 155$ $r_w = 3.8$

Observation Coordinates (r,z) (centimeters)
VW9-3.0 (3.81,84.0)

Best Fit Air Permeability Estimates	
Test Number	$k_r = k_z$ (cm ²)
1	2.06×10^{-8}
2	1.98×10^{-8}
3	1.94×10^{-8}

FIGURES

<i>Figure</i>	<i>Description</i>
1	Mini-Permeability Schematic
2	Domain Separated From Atmosphere by a Leaky Confining Unit
3	Domain with Land Surface as Upper Boundary
4	Description of Unsaturated Zone Lithology at Location VW9 at Galloway Township, New Jersey, Research Site
5	Location of Probes for Pneumatic Tests

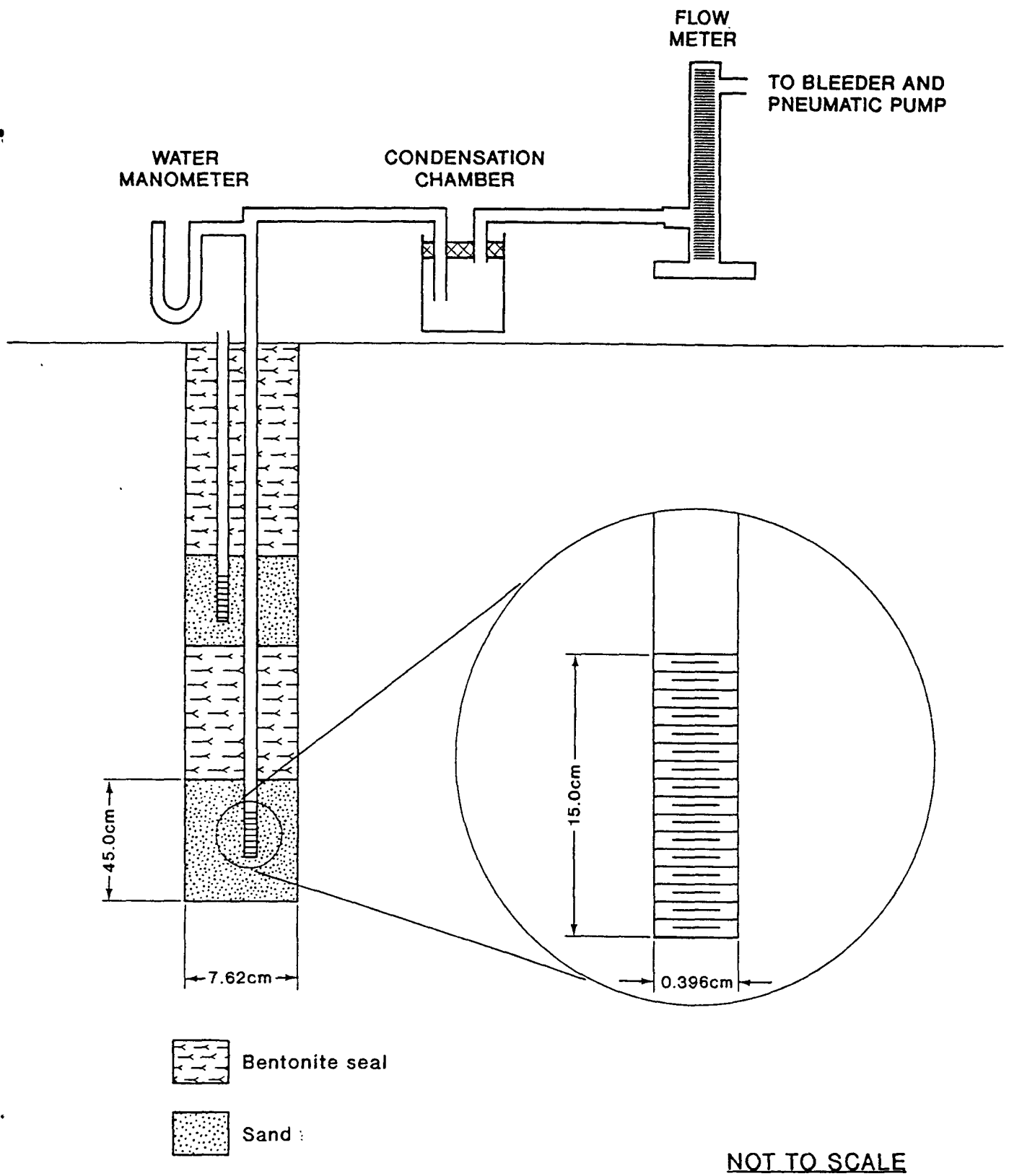


FIGURE 1
Mini-Permeability Schematic

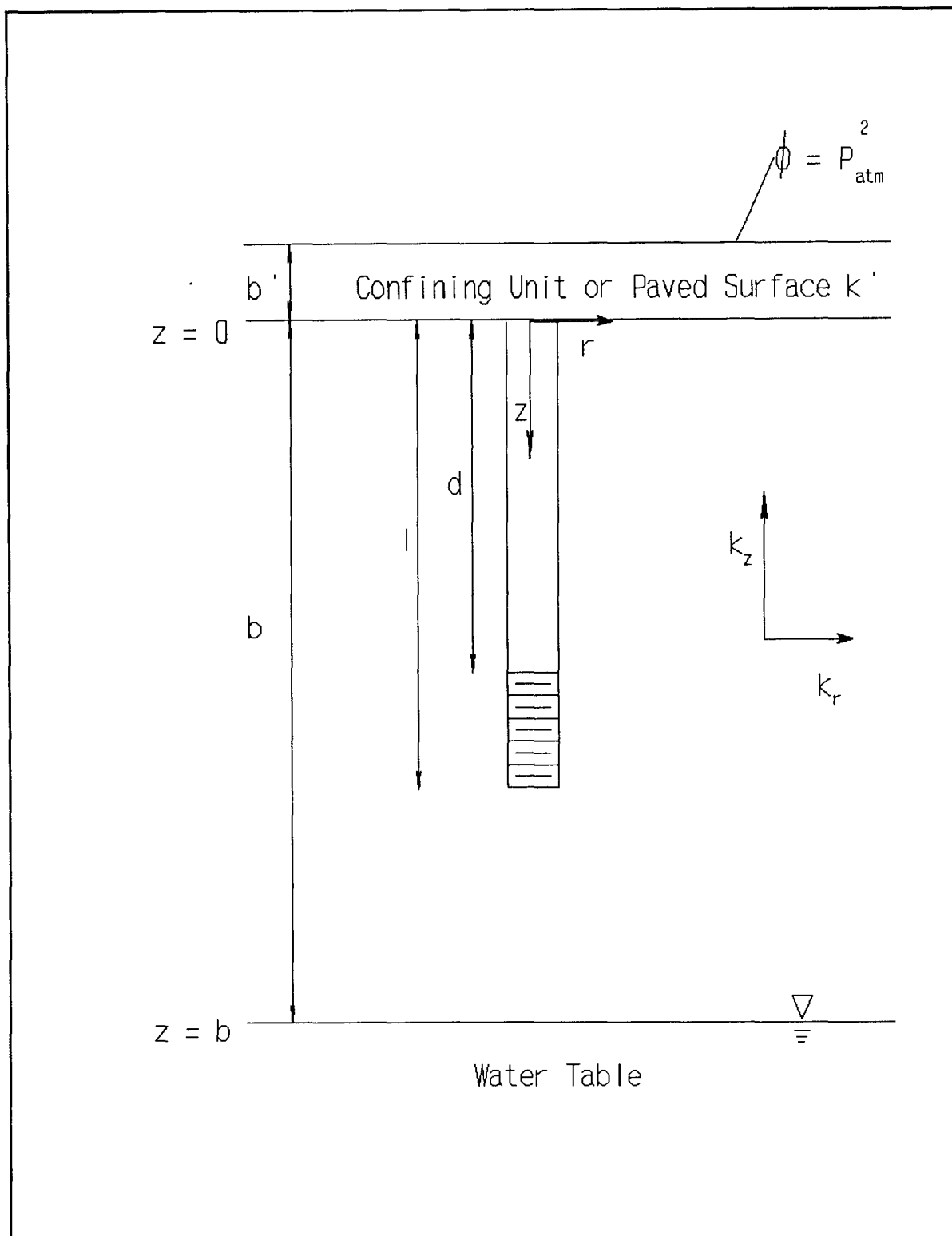


FIGURE 2

Domain Separated From Atmosphere by a
Leaky Confining Unit



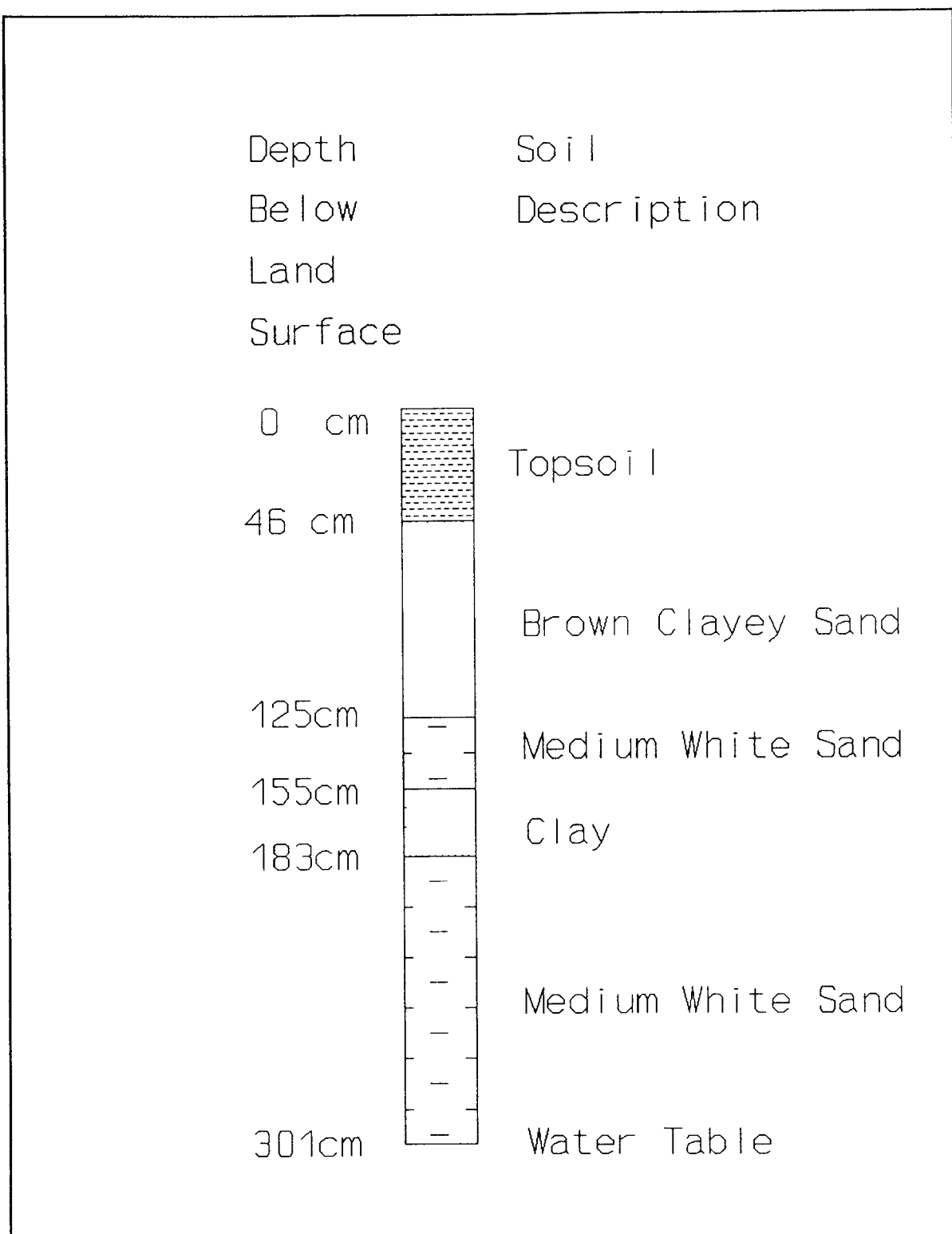


Figure 4

Description of Unsaturated Zone Lithology of Location VW9 at Galloway Township, NJ

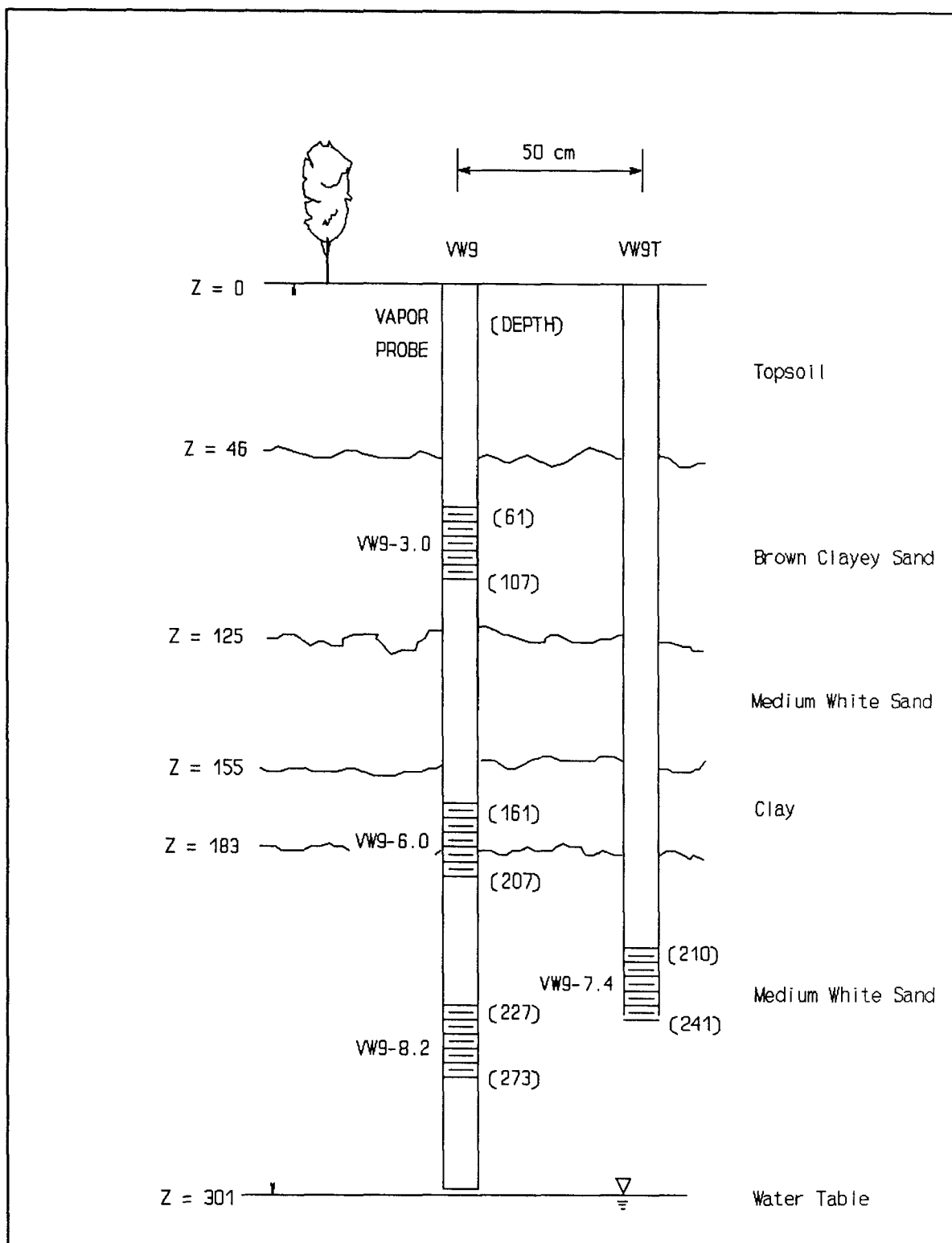


FIGURE 5

Location of Probes for Pneumatic Test

OPTIMIZATION OF THE VAPOR EXTRACTION PROCESS: LARGE PHYSICAL MODEL STUDIES

RICHARD L. JOHNSON
Oregon Graduate Institute
Beaverton, Oregon

ABSTRACT

A series of physical model experiments are currently underway at the Oregon Graduate Institute to evaluate how the efficiency of soil vapor extraction (SVE) can be improved. To accomplish this, gasoline which has "leaked" into a very-large, three-dimensional physical model is being removed by SVE under a variety of well-controlled conditions. Prior to the initiation of each SVE experiment, the distribution of the gasoline within the unsaturated and saturated zones is carefully characterized. For the spill discussed here, the bulk of the gasoline was retained in the unsaturated soil. It was estimated that ~10-20% of the gasoline reached the capillary fringe, and some of that gasoline became trapped below the water table as the result of fluctuations in the ground water level within the aquifer. A series of injection and extraction wells has been installed in the sand aquifer to produce a two-dimensional flow geometry. An impermeable plastic barrier has been placed over the ground surface, and air is being extracted from the system at ~100 scfm. The composition and concentration of hydrocarbon vapors in the extracted air are being monitored to evaluate remediation performance. A three-dimensional array of vapor sampling points are being used to determine the effectiveness of vapor extraction as a function of depth within the system. The sampling points are also being used to monitor pressure within the system, and to conduct tracer tests to directly measure air velocities. Following removal of the gasoline in the unsaturated zone, conditions will be altered to enhance gasoline recovery from near and below the water table. Data from these experiments are being compared to numerical flow and transport models. The combination of detailed sampling and well-characterized subsurface conditions are resulting in a qualitative evaluation of the vapor extraction process.

FIELD TEST OF ENHANCEMENT OF SOIL VENTING BY HEATING

DAVID W. DEPAOLI

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6224

DR. NEIL J. HUTZLER

Department of Civil and Environmental Engineering
Michigan Technological University
Houghton, Michigan 49931-1295

ABSTRACT

An apparent means of contaminant removal enhancement during soil venting is the elevation of contaminant vapor pressures by raising the soil temperature. This paper describes a seven-week test of heated air injection during a full-scale technology demonstration at a JP-4 jet fuel spill site. In this test, heated air from the stack of a catalytic oxidizer emissions control device was pulled into the soil through a passive inlet vent. Soil temperature profiles and hydrocarbon removal rates were monitored during the test. Hydrocarbon removal from the system as a whole during the period of the test was increased by 9% due to heating, while removal was enhanced by 60% within the heated zone. Limited economic projections indicate that the strategy may be advantageous provided that heat can be more evenly distributed throughout contaminated soil zones. Recommendations for future tests and/or implementations are made based upon the results of this study.

1. INTRODUCTION

In situ soil venting, also commonly known as soil vapor extraction, is a rapidly growing technology for remediation of unsaturated zone soils contaminated with volatile chemicals. In this technique the soil is decontaminated in place by pulling air through the soil. The air flow sweeps out the soil gas, disrupting the equilibrium existing between contaminant species in four phases: sorbed on soil particles, dissolved in soil pore water, condensed in a separate liquid phase, and existing as vapor. This causes volatilization of the contaminants and removal in the gas stream. Several well-documented field studies (1,2,3,4,5) and reported site closures (6) have indicated the effectiveness of the technology.

Generally accepted qualitative limits for applicability of the technology are contaminants having a vapor pressure of greater than 0.5 mm Hg (7) (66 Pa) and a soil air permeability of greater than 10^{-10} cm² (8). However, since these limits are based upon the rate of removal of contaminants, the above limits may be extended, and applications well within the limits hastened, if removal rates may be increased by either

shifting equilibrium conditions to higher contaminant vapor concentrations or by accelerating transport rate processes.

One apparent means for enhancing removal rates is elevation of soil temperature. Johnson and Sterrett (3) noted increased removal rates of 1,3-dichloropropene in field conditions with higher ambient temperatures. Higher temperature will affect equilibrium conditions by increasing contaminant vapor pressures and Henry's Law coefficients and by generally causing desorption of contaminants from the soil. Diffusive/convective transport may also be somewhat affected by an increase in diffusivity and by changes in air permeability (mainly due to changes in soil moisture content).

Of these effects, it is expected that the variation of vapor pressure will provide the largest contribution to enhancement by heating. Table 1 shows the profound effect temperature has on the vapor pressure of some selected compounds, as predicted by the Antoine equation (9).

Table 1. Variation of Vapor Pressure (in mm Hg) with Temperature for Selected Compounds

	n-hexane	benzene	toluene	m-xylene	n-octane
50°F	76	46	12	3.2	5.6
75°F	140	90	27	7.8	13
100°F	260	170	53	17	28
Vapor Pressure Ratio					
100°F:50°F	3.4	3.7	4.3	5.3	5.0

This vapor pressure effect could be used to accelerate the timetable of cleanup, as shown in Figure 1. The curves in this figure, displaying the fractional amount of contaminant remaining as a function of cumulative air contacted per mass of initial contaminant present, were derived from a Raoult's Law equilibrium model for removal of JP-4 jet fuel at soil temperatures of 50, 75, and 100°F (10, 24, and 38 °C). For an ideal case of homogeneous air/contaminant contact and equilibrium conditions, 80% removal of JP-4 would be achieved through contact of approximately 50 standard liters of air per gram of JP-4 at a soil temperature of 100°F, while approximately 430 liters of air per gram of JP-4 is necessary for the same removal at 50°F. Therefore, the cleanup using heat enhancement could be performed in 10 percent of the time of the non-heated case. Alternatively, greater than 99% removal could be reached at 100°F in the same time necessary for 80% removal at 50°F.

Due to the potential enhancement of extraction rates with increased temperature, several authors have suggested means for raising soil temperatures. Anastos et al. (2) abandoned plans to heat inlet air by electrical means due to the higher energy requirements for appreciable enhancements. Johnson et al.(10) suggested

radio frequency and conduction heating or injection of exhaust from combustion units. Steam injection has also been mentioned for heating the soil, both in soil venting and in an agitated soil air stripping technique (11). It should be noted that steam injection may be less attractive due to the detrimental effect of moisture in reducing air permeability and the possibility of dissolution and contaminant transport. However, for very dry soil, moisture may enhance desorption of chemicals from the soil particles.

Obstacles to overcome in implementing a heat enhancement strategy include supplying the vast quantity of energy necessary to heat the soils containing the contaminants to the elevated temperature and developing methods for delivering the heat evenly and inexpensively. As an illustration of the magnitude of the heating load required, consider soil having a dry density of 100 lb/ft³ (1600 kg/m³) and heat capacity of 0.2 BTU/lb-°F (837 J/kg-°C). The temperature of a cubic foot (0.028 m³) of dry soil would rise 1°F (0.56 °C) with a heat input of 20 BTU (21,100 J). If the soil contained 5% moisture by weight, the same soil volume would require 25 BTU (26,400 J) for the same temperature rise. One standard cubic foot (0.028 std m³) of air cooling from 1000°F to 68°F (538°C to 20°C) supplies 18.7 BTU (19,700 J), whereas 1 pound (0.454 kg) of steam condensing at 212° (100°C) and cooling to 68°F (20°C) supplies 1115 BTU (1.18 x 10⁶ J).

For the site at which this study was conducted, a contaminated soil volume of approximately 720,000 ft³ (20,400 m³) required treatment, thus, 450 million BTU (4.74 x 10⁹J) would be necessary to raise the entire soil volume 25°F (13.9°C), if there are no heat losses. If this were supplied by air cooling from 1000°F, as described above, air volume is required, which, at a 1000 scfm (0.47 std m³/s) injection rate corresponds to 16.7 days. Steam injection as described above would entail 400,000 lbs (181,000 kg) of steam to raise the soil temperature 25°F (13.9°C). In the process, the average soil moisture content would increase from 5% to 5.5%. However, local moisture levels, particularly in the vicinity of injection points could be much higher, possibly significantly decreasing air permeability. (The effect of permeability on injection flow may be insignificant, however, due to the steam pressures achievable to drive flow.) Also, the additional water would be available for dissolution of hydrocarbons and possible transport by percolation to the saturated zone.

The above rough calculations neglect heat losses, which may be quite substantial. Although considerable energy demands are made, the increased removal rate may make heating of the soil an economical addition to venting systems in many cases. In order to investigate this concept, a test of heat injection was devised and conducted during an Air Force-sponsored full-scale field demonstration of soil venting at a JP-4 jet fuel spill site. The heat source for this study was chosen to be the stack gas of a catalytic oxidation emissions control unit, from which heat was normally wasted to the atmosphere.

2. TEST DESCRIPTION

The *in situ* soil venting field demonstration was conducted at the site of a 102,000 liter (27,000 gallon) JP-4 jet fuel spill at Hill AFB, UT. Site characterization prior to system operation indicated that the hydrocarbon contamination was limited to a soil zone of approximately 36.6 meters x 36.6 meters x 15.2 meters deep (120 x 120 x 50 ft). Total hydrocarbon soil concentration measurements ranged from below detection (20 mg/kg) to 6400 mg/kg. The soil at the site generally consisted of unconsolidated to weakly consolidated sand, with thin lenses of clay. Air permeability measurements ranged from 3 x 10⁻¹² to 6 x 10⁻¹¹ m². Moisture content was generally 3 to 7 weight percent, with higher values (10 to 25 weight percent) associated with clay lenses.

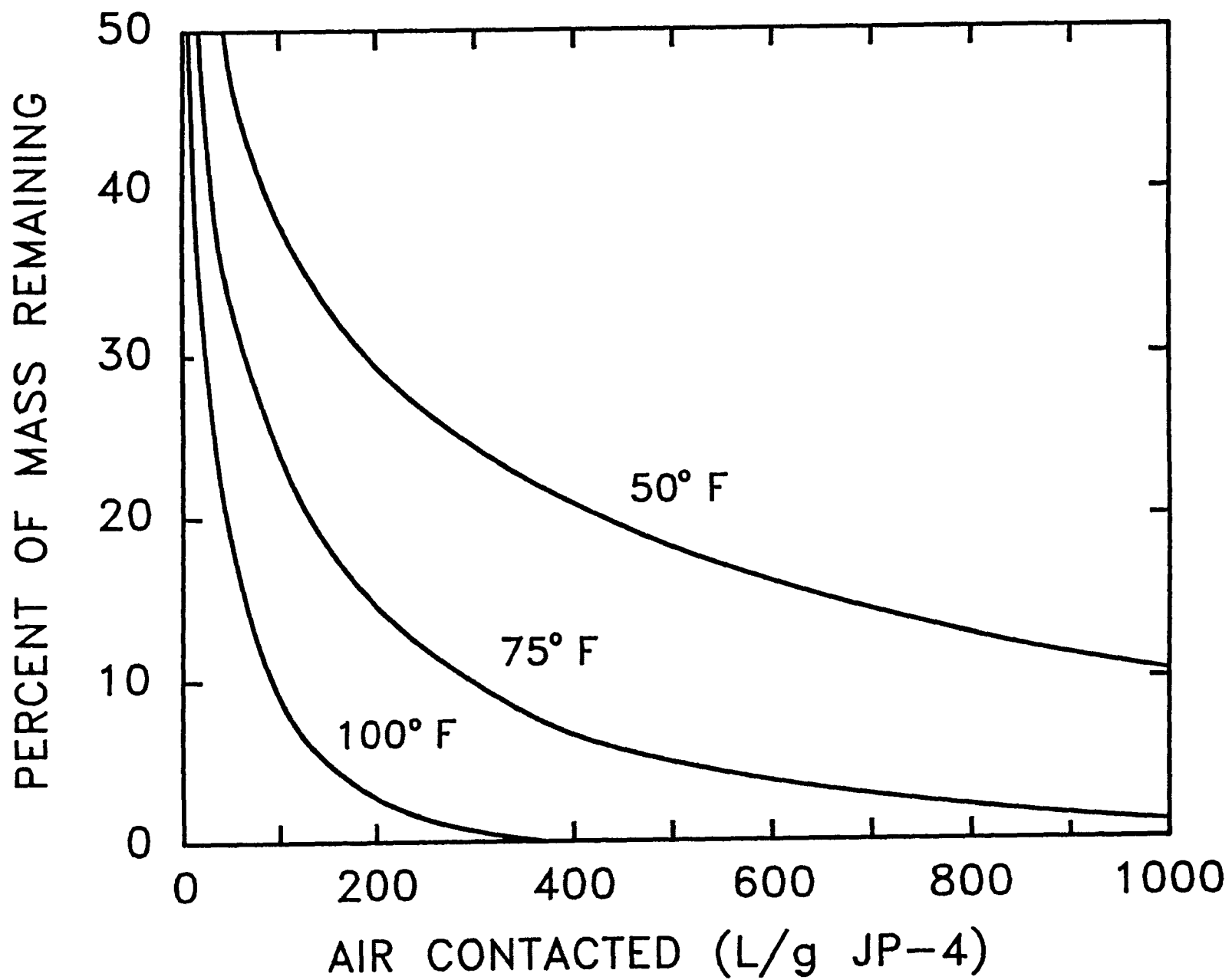


Figure 1. Equilibrium removal curve for JP-4 jet fuel at 50, 75 and 100°F.

The heat injection test system was a small part of the demonstration system which consisted of three subsystems: (1) an array of 15 vertical vents and 31 pressure monitoring wells in the area west of the location of the spill source, (2) a set of six lateral vents and 30 pressure monitoring probes installed under a new concrete pad and dike that were constructed for the tanks after the spill, and (3) a set of lateral vents in the pile of soil that was retained after excavation of the tanks. A common blower/emissions control system was installed for inducing airflow from the three vent arrays and for treating emissions as necessary to meet regulatory requirements of the state of Utah. Two rotary-lobe blowers provided the capability for extraction of up to 0.72 std m³/s (1500 std ft³/min) of gas from the three vent systems at vacuum levels up to approximately 25,000 Pa (100 inches of water). In order to protect against potential hazards presented by combustible gas mixtures, flame arrestors were installed at the inlet to each blower. The blowers were controlled by an automatic shutdown system based on a combustible gas detector. Two propane-fired catalytic oxidation units were used for conversion of the jet fuel hydrocarbons to carbon dioxide and water before discharge into the atmosphere. A vapor/liquid separator, flowmeters, and gas monitors were also included in the system.

Prior to the commencement of the heat injection test, the full scale demonstration system was operated for eight months. During this period, 3.60×10^6 standard cubic meters (127×10^6 standard cubic feet) of gas was pulled through the soil, extracting 45,700 kilograms (101,000 lbs) of hydrocarbons. Concentrations in the extracted gas had decreased from an initial reading of approximately 45,000 ppm_v hexane equivalent as measured by an on-line FID-based total hydrocarbon analyzer (THA) to approximately 700 ppm_v.

The heat injection test system was constructed as shown in Figure 2. The three vents of interest in the test were vertical vents located in the center of the most contaminated soil zone. They formed the eastern end of the central of three vent lines in a grid of 15 vertical vents on a 12.2-m (40-ft) grid spacing, with 6.1-m (20-ft) spacings along the central line. The eastern half of the venting system was covered by a 24 m x 43 m (80 x 140 foot) surface barrier consisting of a 10 mil polyethylene sheet covered by one 6 mil polyethylene sheet and 30.5 cm (12 in) of soil.

Each 11.4-cm (4.5-inch) outside diameter and 10.2-cm (4-inch) inside diameter vent was installed in a 24.4 cm (9-5/8 inch) augured hole. The extraction vents each consisted of a 12.2-m (40-foot) length of flush-joint Schedule 40 PVC screen of slot width 0.51 mm (0.02 inches), installed at a depth of between 3.0 m and 15.2 m (10 feet and 50 feet) below ground surface and capped at the lower end (see Figure 3). Flush-joint Schedule 40 PVC was used for the riser pipe. PVC cement was used to join all PVC fittings. The inlet vent was constructed in a like manner of 4-inch stainless steel well screen and riser pipe, since the PVC was rated to withstand temperatures only up to 60°C (140°F) in the presence of JP-4. Stainless-steel centralizers were installed to maintain the riser pipe in the center of the borehole. Each auger hole was backfilled with dry coarse sand to one foot above the screen, using a tremie tube. A 30.5 cm (12-inch) layer of bentonite pellets was placed on top of the sand, and the hole was grouted to the surface by tremie tube with cement-bentonite (9:1) grout. A concrete collar approximately 0.6 m (2 feet) in diameter was installed to provide mechanical stability for the vent and to divert rainfall from penetrating the backfilled hole. Each vent extended at least 30.5 cm (1 foot) above the concrete collar and was protected with 20-cm (8-inch) diameter steel pipe extending to 7.6 cm (3 inches) below the top of the vent pipe.

A tee was installed on the stack of one of the catalytic incinerators, allowing the diversion of some of the stack gas to the injection vent. Carbon steel tubing of 12.7-cm (5-inch) nominal size was run approximately 107

m (350 feet) to the inlet vent. The tubing was covered with 2.54 cm (1 inch) of high temperature fiberglass insulation protected by aluminum sheet. No blower was installed in the heated gas line; rather, the test was designed to allow vacuum induced in the soil to pull the heated gas into the vent.

Thermocouples were installed in the heads of each of the vents and in the soil in the positions shown in Figure 4. The thermocouples were placed in hand-augered holes at depths ranging from 3.3 to 4.1 m (10.9 to 13.5 ft). Since this depth is near the top of the screened interval of the wells, the temperatures are likely to be less influenced than in the center of the affected zone.

Temperatures and concentrations were read periodically from the thermocouples and the THA as well as continuously recorded on a chart recorder and data logger. Samples were taken periodically in canisters for analysis of the extracted gas by a gas chromatograph (GC). The effects of elevated temperatures upon bioactivity, which had proven to be significant in the earlier portion of the demonstration (5), could not be measured due to the low O₂ and high CO₂ concentration in the inlet gas.

3. RESULTS

Heat injection was begun on 16 August 1989 and continued to 7 October 1989 with a total extraction rate of 0.307 std m³/s (650 scfm), with measured flows of 0.193 std m³/s (410 scfm) from the west extraction vent and 0.113 std m³/s (240 scfm) from the east. In this configuration, a vacuum of 11900 Pa (48 inches of water) was induced under static conditions at the inlet vent. Opening the inlet vent to the heat injection line induced an injection flow rate of 0.044 std m³/s (93 scfm) at 423 Pa (1.7 inches of water) vacuum.

Operationally, the heat injection system ran quite well. However, due to heat losses in the piping, the inlet gas temperature was decreased from over 316°C (600°F) at the incinerator stack to between 93 and 102°C (200 and 215°F) at the inlet vent. Water uptake in the extraction piping was also noted to be increased during the test in comparison to earlier operation, due to a combination of greater vacuum levels at the extraction vents (approximately 14900 Pa - 60 inches of water) and to moisture content of the heated input air. No major changes in the flow rates or vacuum required were noted despite the increased moisture.

The results of temperature measurements from each of the thermocouples are presented graphically in Figure 5 as a function of time of the test. The temperature at each of the points in the soil appears to have reached steady state during the test. Thermocouples farther from the injection vent reached steady state slower than those closer to the injection vent, and reached a lower steady state temperature. This may be seen most clearly by comparison of temperatures at thermocouples 2, 3, and 4, which were placed 1/4, 1/2, and 3/4 of the distance along the line from the inlet vent, to the west extraction vent. TC2 reached a steady state temperature of 36.7 to 37.8°C (98 to 100°F) in about 15 days, TC3 reached steady state temperature of approximately (32.8°C) 91°F in about 23 days and TC4 reached a steady state temperature of about 31.1°C (88°F) in 30 days. The progression of the temperature profile is also shown in the three frames of Figure 6, displaying the temperature (in °F) at the thermocouple positions at the start of the test, after 13 days, and after 36 days. It should be noted that all points except those corresponding to the vents indicate soil temperature, whereas the vent points (those points labeled with temperature values of 207°F at the inlet and 73°F at the west extraction vent in the bottom frame) indicate gas temperature.

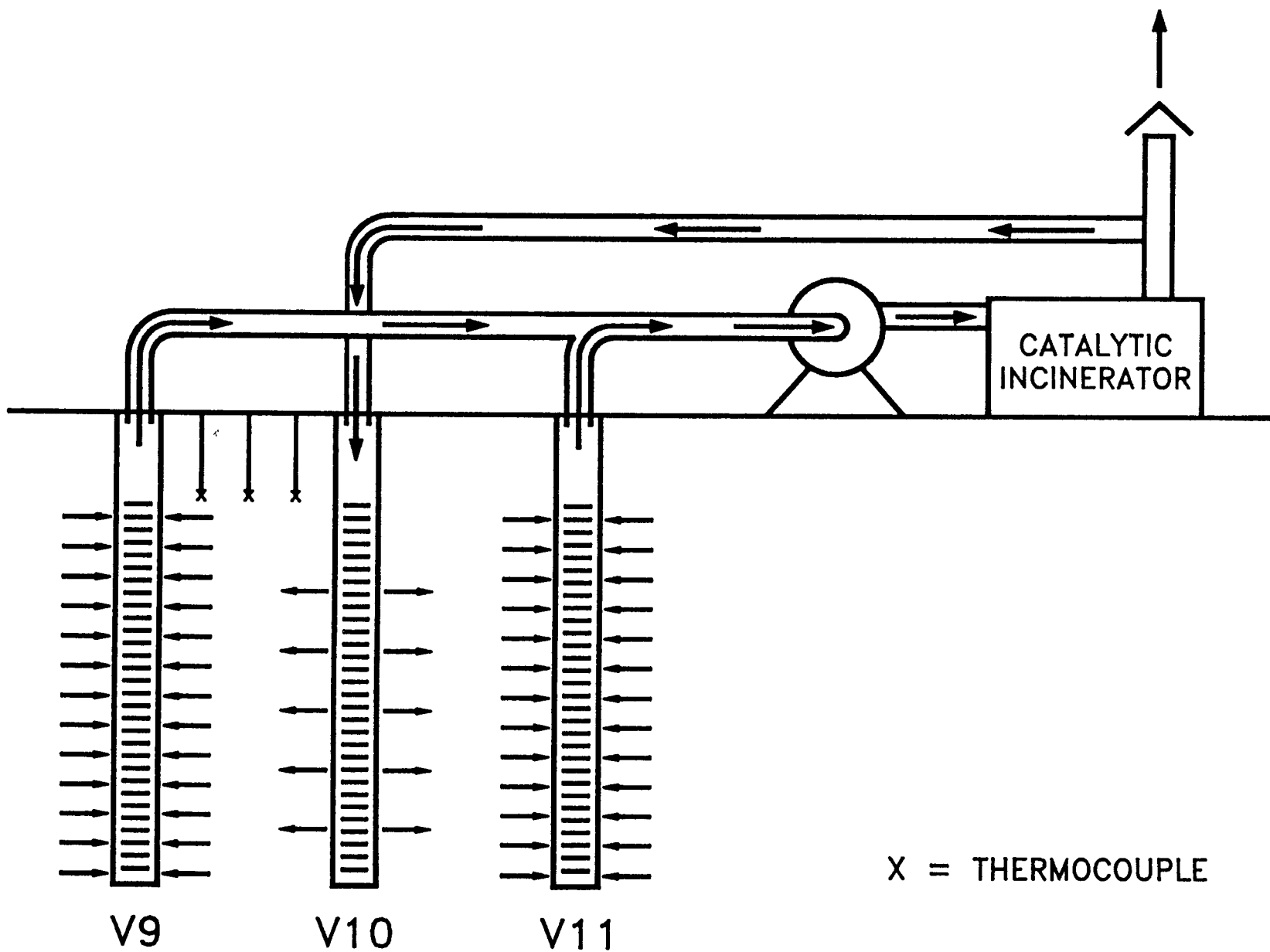


Figure 2. Schematic drawing of Hill AFB heat injection test system.

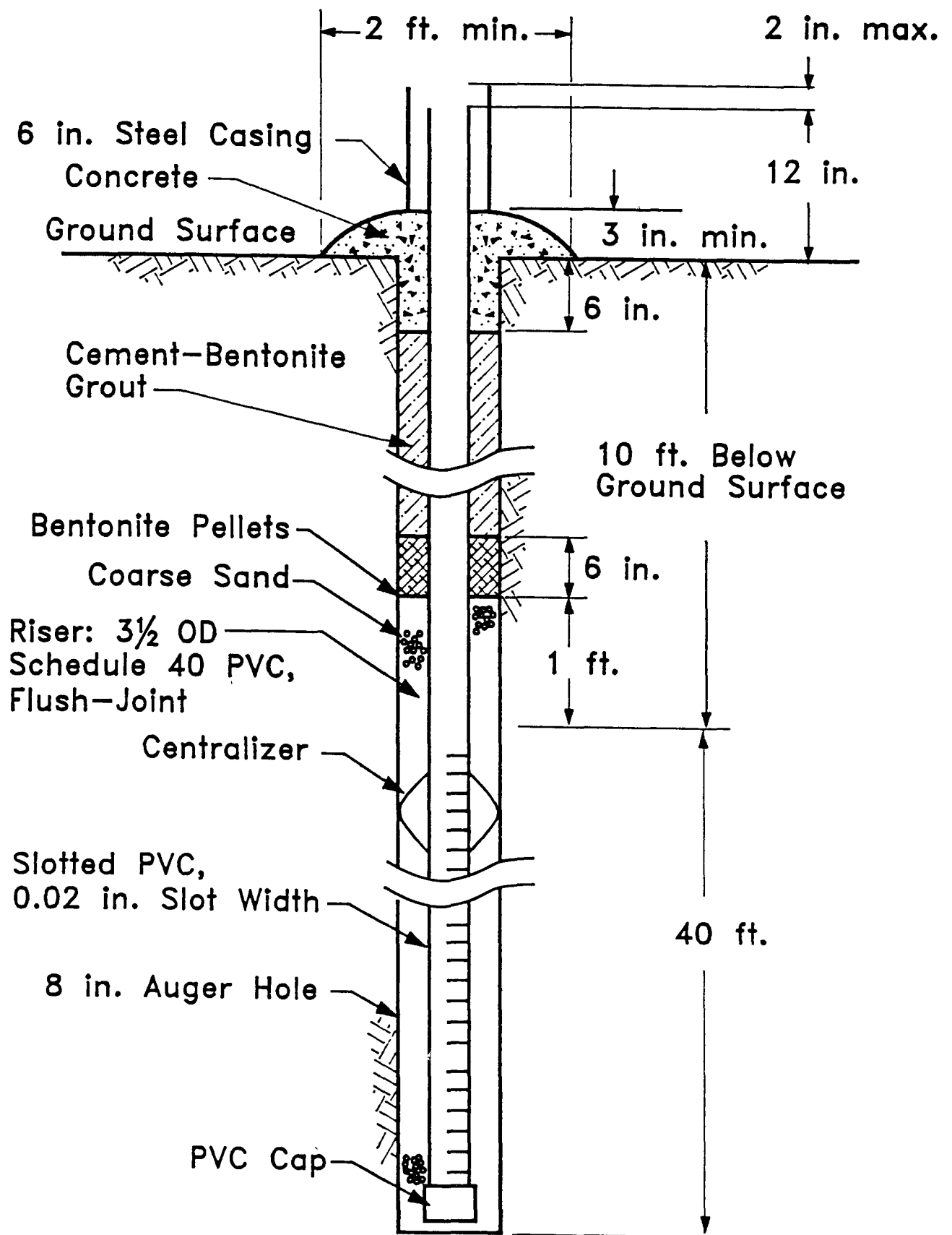


Figure 3. Vent construction.

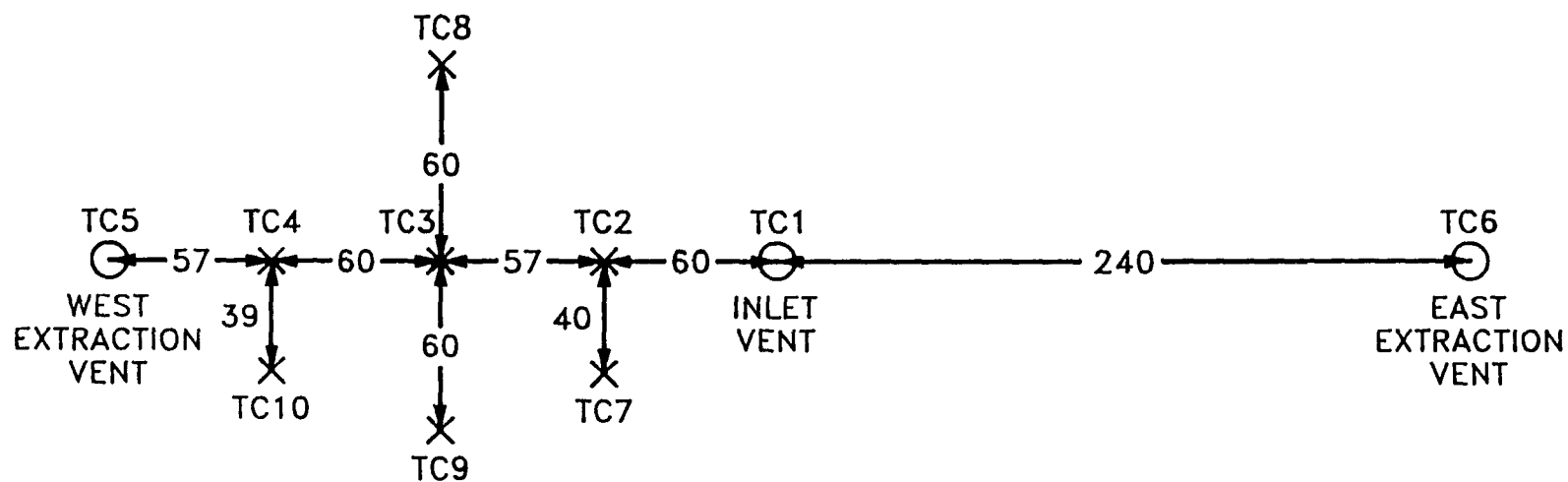


Figure 4. Positions of thermocouples.

NOTE:

Thermocouples TC1, TC5, and TC6 measured temperature of gas at vent head. All other thermocouples measured soil temperature at depths ranging from 11 to 13.5 ft below land surface.

Dimension are in inches.

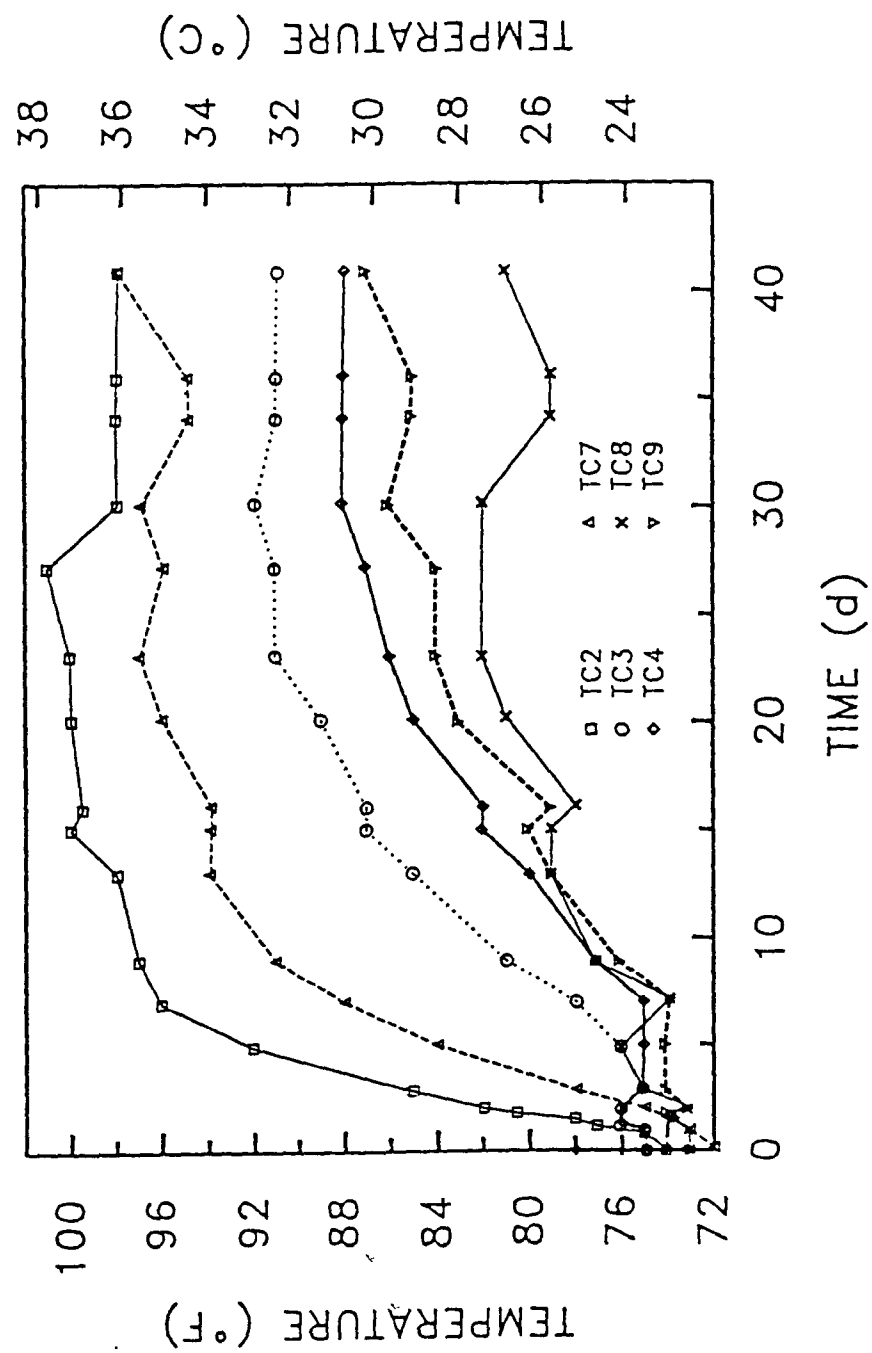
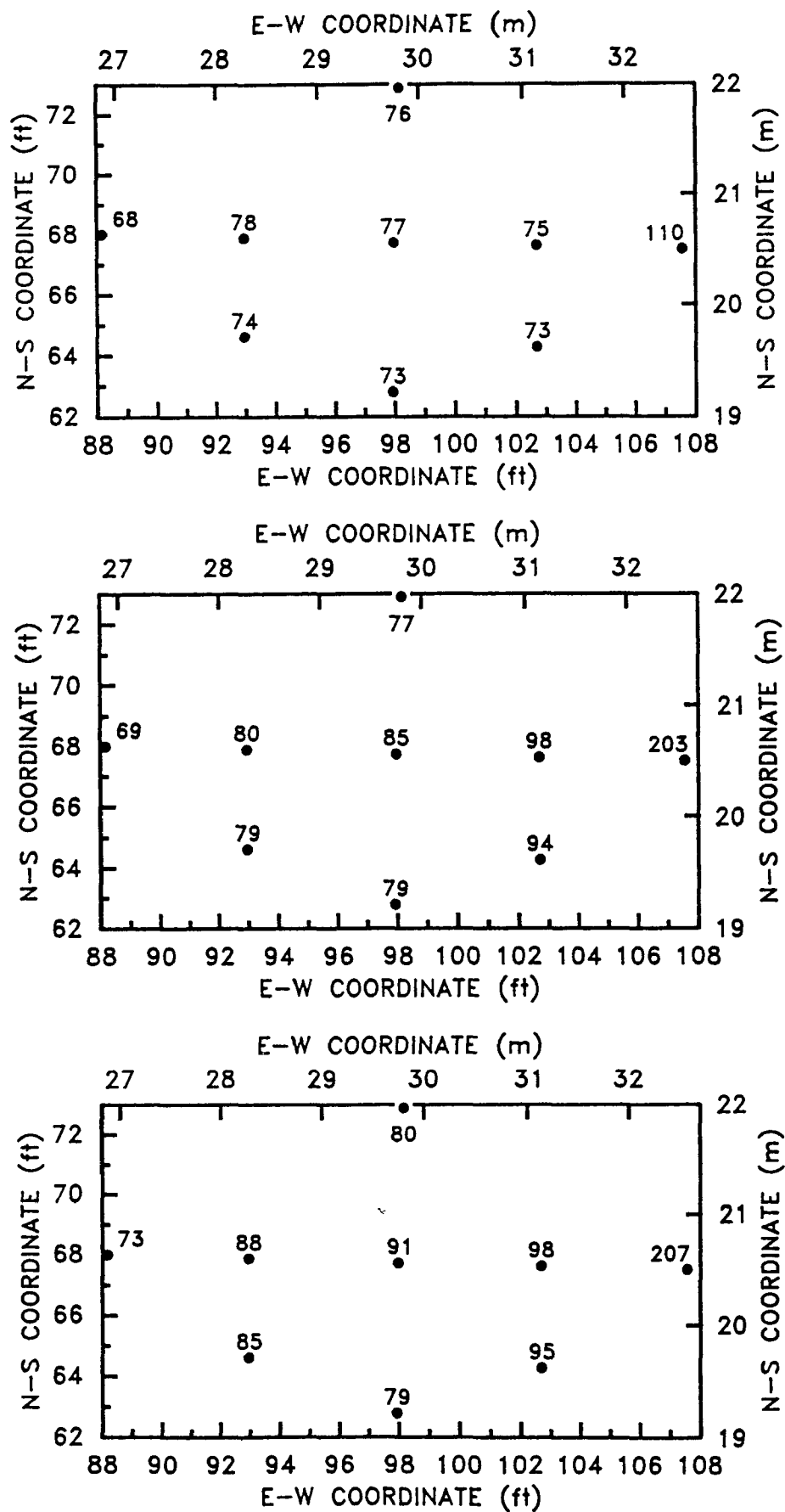


Figure 5. Variation of measured temperatures with time during Hill AFB heat injection test.

Figure 6. Temperature distribution at three points during heat injection test. Top frame - 16 August 1989 (start of test); Middle frame - 29 August 1989 (13 days into test); Bottom frame - 21 September 1989 (36 days into test). All temperature values are in degrees Fahrenheit.



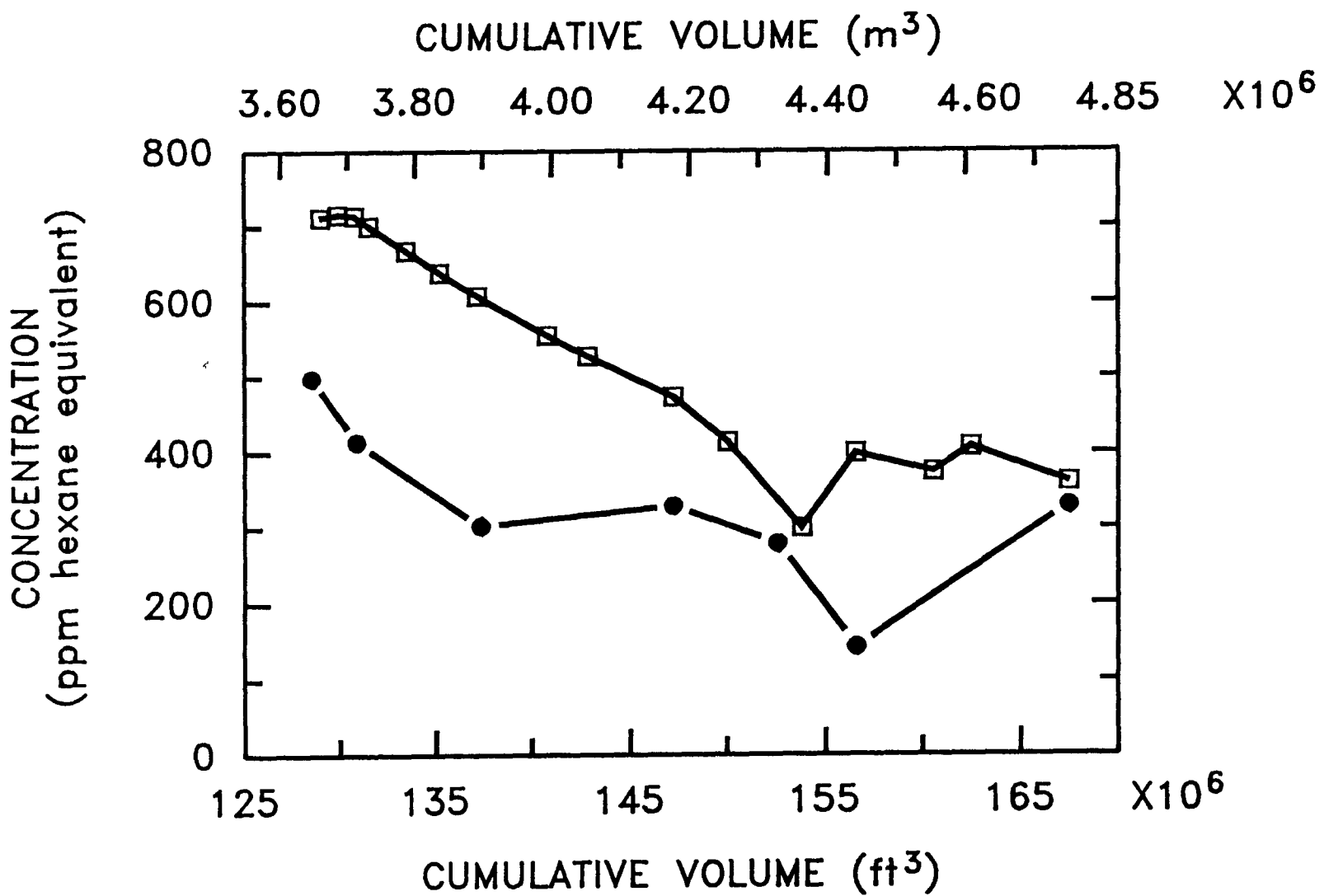


Figure 7. Variation of hydrocarbon concentration in the combined extracted gas stream. Opensquares - measurements by total hydrocarbon analyzer, solid circles - gas chromatographic analysis of samples.

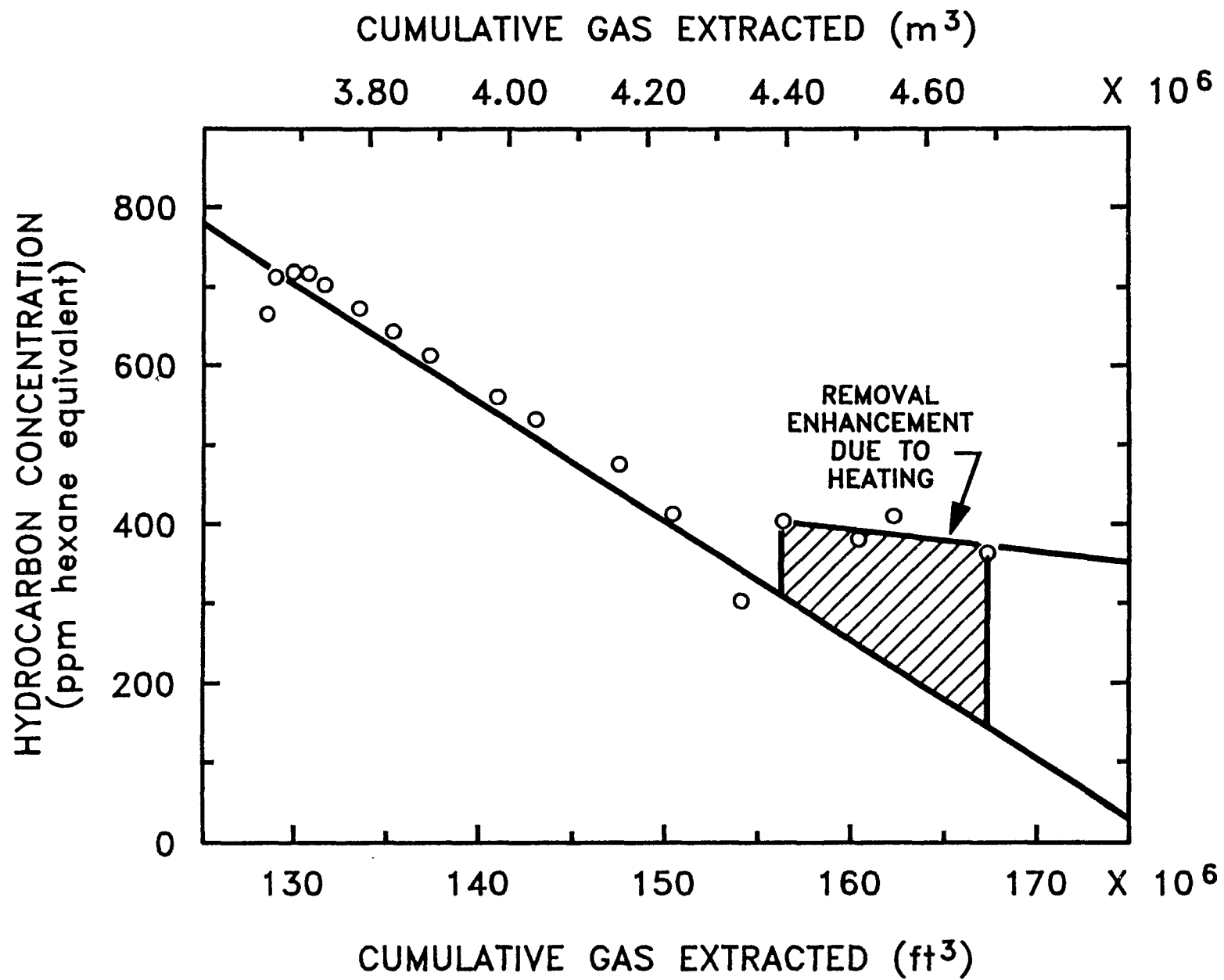


Figure 8. Treatment of hydrocarbon concentration data for calculation of removal enhancement by heating.

Hydrocarbon concentrations in the extracted gas are displayed in Figure 7 as ppm, hexane total hydrocarbons as a function of cumulative standard cubic meters (and feet) of gas extracted during the entire demonstration (the heat injection test commenced at the $3.60 \times 10^6 \text{ m}^3$ - $127 \times 10^6 \text{ ft}^3$ mark). The upper points are from THA measurements, whereas the lower points were calculated from GC samples taken from each extraction vent. The GC results remained lower than THA results. The two sets of results display a common trait in the general shape of the curves. Each showed a consistent decrease in concentration until the 4.39 to 4.53 million cubic meter (155 to 160 million cubic feet) range. At this point (approximately 12 September through 15 September, or 27 to 30 days into the test), roughly the point at which the farthest soil thermocouples reached steady state temperatures, the concentration in the extracted gas is seen to markedly increase. This concentration increase qualitatively correlates with the temperature front approaching the extraction vent. The nearly constant measurement of concentration by the THA from 4.45 to 4.73 million m^3 (157 to 167 million std ft^3) is postulated to be due to a balance of two factors, one being higher gas concentration because of increased temperature and the other being decreased gas concentration due to decreasing soil contaminant concentration and change in composition to a heavier hydrocarbon mixture.

Estimates of the removal enhancement by heat injection are made possible by analysis of the data as shown in Figure 8. In this analysis, the THA data is used because of a greater number of points and less scatter. The 12 data points from 3.60 to 4.36 million m^3 (127 to 154 million ft^3) were fitted with a straight line which appears to be valid over this limited range. Another line was regressed to the four points from 4.45 to 4.73 $\times 10^6 \text{ m}^3$ (157 to 167 $\times 10^6 \text{ ft}^3$). The integrated difference between these two lines, as shown by the highlighted area in Figure 8 is the calculated removal enhancement due to heating. From 4.45 to 4.73 $\times 10^6 \text{ m}^3$, 245 kg (540 lbs) is the quantity that would be expected to be removed in the absence of heating by extrapolation of the straight line trend. The upper line indicates that approximately 417 kg (920 lbs) were removed during the period. The difference is 172 kg (380 lbs), or an increase of 70%. The removal increase over the entire period of the test, from 3.60 to 4.73 $\times 10^6 \text{ m}^3$ (127 to 167 $\times 10^6 \text{ ft}^3$) extracted is 8.9%, 2127 kg (4690 lbs) actual and 1955 kg (4310 lbs) expected without heating. It is obvious that this ratio would increase with further operation. Only limited soil sampling was performed in the soil zone of the heat injection test after the demonstration, so little can be inferred as to the transport of contaminant with the temperature profile.

4. DISCUSSION

The results of this test of enhancement of removal with soil heating must be treated with care in predicting the effectiveness of the technique in other site applications. The most obvious measures of performance in this test are the 8.9% and the 70% values obtained above. However, these values are artifacts of the length of the test - for instance, if the test were only operated for a period during which the heat front had not reached the extraction vents, the enhancement value would have been 0%. Likewise, if the test had been conducted for a longer period, a value of much greater than 8.9% would have been obtained, perhaps on the order of the 70% enhancement measured in the period after the development of the steady-state temperature profile.

Another test condition which had a significant effect upon the measured removal enhancement was the ratio of the inlet air rate to the extraction rate. Hydrocarbons were extracted from soil zones which were not contacted with the heated air as well as from the soil zone of interest. Indeed, since the inlet air amounted to a small fraction of the extraction flow rate, the majority of the hydrocarbon extraction could be assumed

to be relatively unaffected by the heated air flow. Upper bounds on the achievable enhancement for this test could be estimated by assuming homogeneous contaminant distribution in the soil and negligible heat conduction. With these assumptions, the hydrocarbon removal may be split proportionally by air flow ratios into two portions: that affected by heating and that unaffected by heating. In this approach, of the 1955 kg (4310 lbs) that were expected to have been removed over the entire test period, 281 kg (620 lbs), as calculated by $(4310 \text{ lbs} \times 93 \text{ scfm inlet rate} / 650 \text{ scfm extraction rate})$ would have been extracted from the soil zones affected by the heated air. Therefore, 1674 kg (3690 lbs, or $4310 - 620 \text{ lbs}$) would be extracted from outside the heated zone regardless of whether heat was applied or not. Therefore, the amount extracted from the heated zone during the test was 454 kg (1000 lbs, or $4690 - 3690 \text{ lbs}$), resulting in an enhancement factor for the entire course of the test to be 61%. Likewise, consideration of only the period after the temperature front arrived at the extraction vents results in an enhancement factor of nearly 500% (207 kg removed, 35 kg expected) from the heated zone. Thus, if a temperature rise similar to that achieved during this test could have been applied over the entire site for long-term operation, it is possible that the cleanup could have been significantly accelerated. Given the measured temperatures and extraction rates, a cleanup period perhaps as short as one-sixth the time required for unheated soil treatment would be necessary for a well-designed and well-operated heated system.

Despite the apparent success of heating enhancement in this test, the results do not conclusively prove the universal value of heat injection for optimization of venting system operation. This is due to several shortcomings of the test and to the fact that the results of this test may not be applicable to systems with different characteristics. Shortcomings of this test entailed limitations of heat input to the soil and distribution of the heat in the soil. Although $0.307 \text{ m}^3/\text{s}$ (650 scfm) of gas at or above 316 to 371°C (600 to 700°F) was available at the stack, only about $0.045 \text{ m}^3/\text{s}$ (95 scfm) at about 99°C (210°F) was delivered at the inlet vent, due to limited vacuum at the vent and heat losses in the 107 m (350 ft) of piping. With the limited heat input, only a modest but measurable and effective soil temperature increase was induced. Certainly, large improvements could be made using forced injection with a high temperature fan and increased insulation and/or a shorter piping run. More important in uncertainty for extrapolation is the fact that the heat was obviously not evenly distributed in the soil because of the flow geometry.

Upon consideration of these test results, one could conceive of test designs that would allow for greater heated air flow more uniformly distributed. Two such examples are shown in Figure 9. The first shows a ring of inlet vents (either forced or passive) surrounding an extraction vent. With a large number of inlet vents and a surface barrier, a nearly uniform radial flow distribution could be achieved. This design is attractive in that a balance may be achieved between the tendencies for higher temperatures and lower flow rates in outer zones, and lower temperatures (due to conductive heat losses) but higher flow rates near the extraction vent. The other design, more suitable for larger sites, is based upon an attempt to develop one-dimensional linear flow between lines of inlet and extraction vents. The flow patterns would simplify the monitoring of progress of temperature and concentration fronts and would be much more amenable to modeling.

Future tests should also address the impact of heated air injection upon bioactivity. One may be concerned that elevated soil levels may harm bioorganisms in the soil. However, two points may be made upon consideration of the results of this test: 1) the temperatures achieved in this test were shown to have the potential for significant increases in removal rate by volatilization, while they were certainly not in the range of harm to most bioorganisms except in the direct vicinity of the inlet vent (in fact, bioactivity may have been increased in much of the heated zone due to the temperature increase), and 2) temperatures high enough to

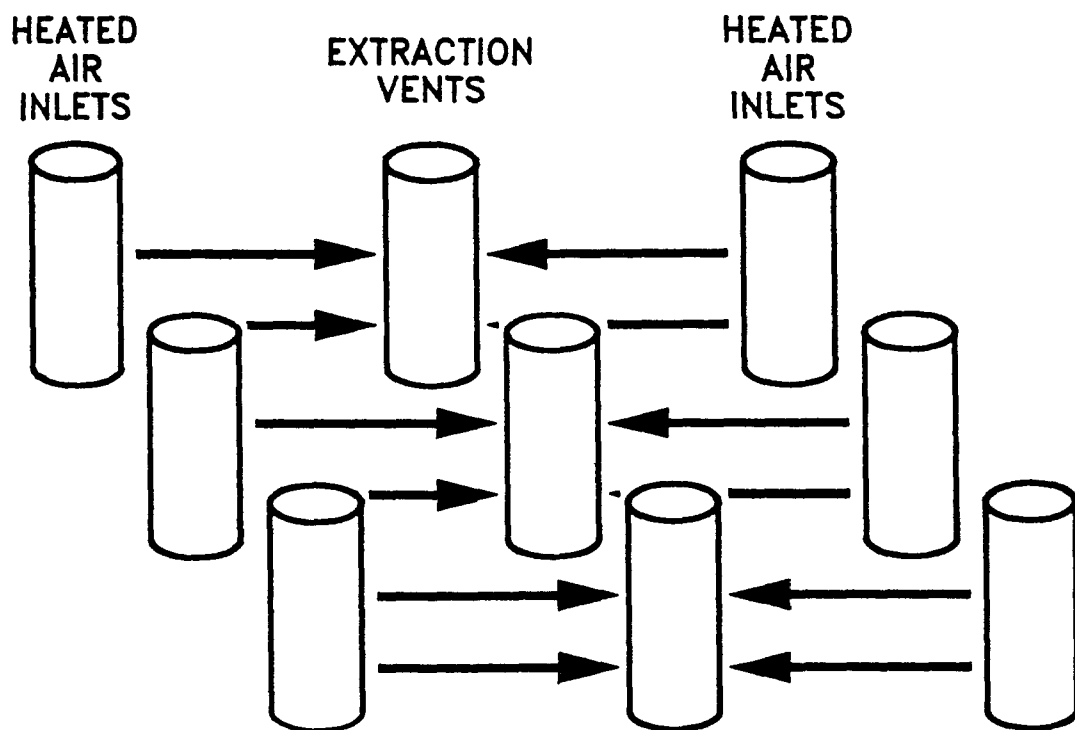
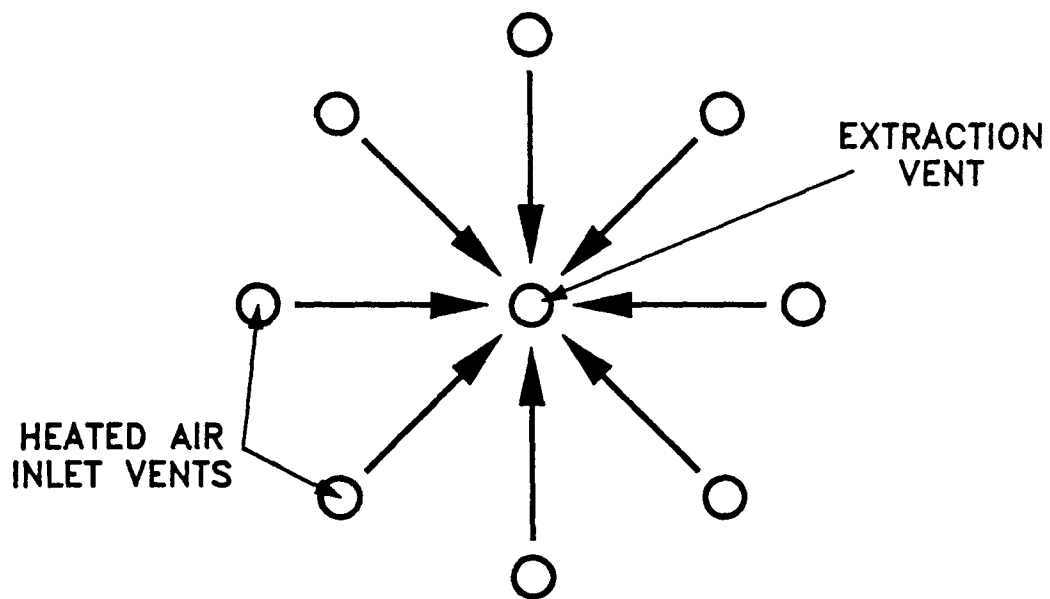


Figure 9. Suggested vent configurations for improved heat injection systems.

adversely affect bioactivity are also high enough to significantly increase the vapor pressures of contaminants for which biodegradation may be the major means of removal in an unheated case. As was noted earlier, monitoring of bioactivity by measurement of carbon dioxide generation was not possible during this test because of the low O₂ and elevated carbon dioxide levels in the stack gas. One possible means to avoid this complication would be to transfer the stack gas heat to an injection stream of atmospheric air using a heat exchanger.

Despite the shortcomings of this test, some rough estimates of the economics of heat injection at this site may be made. In these estimates, an equilibrium removal model was used to provide an estimate of approximately 1000 liters of air per gram of initial spill material necessary for removal of the weathered JP-4 at 12.8°C (55°F), or 8.07×10^7 std m³ (2.85×10^9 std ft³) of air would be required. Thus, at an extraction flow rate of 0.47 std m³/s (1000 scfm), 66 months would be required for removal by volatilization in the absence of heat injection. It is with this base case that the heat injection cases are compared. Comparison of the cases would include operating costs and any additional capital cost for the heat injection system components. The piping and stainless steel vents for this demonstration were estimated to cost about \$40,000. For application to the entire site possibly all five central vents or the vents on the fringes could be installed as heat injection vents. It would be preferable to use the latter strategy, since contaminants will be driven away from the heat inlet points. A conservative estimate of additional capital cost for the heat injection system is \$50,000. Operating cost rates would be common to each case, with or without heat injection, with a blower cost of \$1100/month. An average catalytic oxidation cost of \$1900/month was assumed.

Four cases of heat injection corresponding to ranges of removal enhancement deduced from this test are compared with the base case as shown in Table 2. The estimated cost of remediation in the absence of heat injection is \$750,000 (12). It is projected that a removal enhancement of approximately 33% would be necessary for cost-recovery of the heat injection system. The first case assumes that the approximately 9% removal enhancement obtained during over the length of this test would be applied to the entire site for the complete remediation. At this rate, a considerable cost is projected for a 10% faster clean-up time. The intermediate value of 70% percent, which may be considered a reasonable estimate of long-term removal enhancement results in significant savings of both time and cost. As would be expected, the optimistic removal enhancement value of 500% would yield remarkable savings.

The calculations of Table 2 show that heat injection would be likely to provide savings at the Hill AFB site if reasonable removal enhancement (greater than 33%) were achieved. The results of this study indicate that during long-term operation in venting configurations such as those discussed above this would certainly be achieved. Savings would be greater if the site were less permeable (increasing blower costs) or if emissions control were more costly. Certainly, heat enhancement would be much less attractive if emissions control were not required.

Table 2. Comparison of heat injection cases

	REMOVAL ENHANCEMENT				
	0 %	9 %	33%	70%	500%
Air needed	$2.85 \times 10^9 \text{ ft}^3$	$2.61 \times 10^9 \text{ ft}^3$	$2.14 \times 10^9 \text{ ft}^3$	$1.68 \times 10^9 \text{ ft}^3$	$4.75 \times 10^8 \text{ ft}^3$
Time at 1000 scfm	66 months	60.5 months	49.6 months	38.8 months	11 months
Additional capital	0	\$50,000	\$50,000	\$50,000	\$50,000
Operating Cost at 1000	\$3,000/mo.	\$3,000/mo.	\$3,000/mo.	\$3,000/mo.	\$3,000/mo.
Total operating & additional capital	\$198,000	\$232,000	\$199,000	\$166,000	\$83,000
Savings due to heating	\$0	- \$34,000	- \$1,000	\$32,000	\$115,000

5. CONCLUSIONS

This field test has proven the feasibility of the enhancement of soil venting through heating with the stack gas of a catalytic incinerator emissions control device. Despite the shortcomings of the test, a measurable enhancement of removal due to heating was detected. Results suggest that a system designed with a uniform flow field for more even heating could remediate a site several times faster than an unheated case.

In general the concept of heat injection appears attractive when waste heat is readily available. Heat enhancement will become more economical for systems with higher operating costs, such as sites with soils of low air permeability or costly emissions control. Problems of poor air flow and heat distribution may extend the time required for cleanup and decrease the economical advantage.

Further work in this area, using improved field demonstration systems as described above and complemented with heat and contaminant transport modeling, is urged. Such work would be valuable to further illustrate the advantages of the technique, to define ranges of site variables for which the technique is applicable, and to provide practitioners with a means of estimating soil venting system performance with heating.

ACKNOWLEDGEMENT

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PERFORMANCE CHARACTERISTICS OF VAPOR EXTRACTION SYSTEMS OPERATED IN EUROPE

DIETER H. HILLER, PH.D.

HPC HARRESS PICKEL CONSULT GMBH
Marktplatz 1
8856 Harburg
Germany

ABSTRACT

Vapor extraction, an in-situ process to remove volatile organic compounds (VOC) from soils of the vadose zone, has been applied in Europe since the early 1980s. With considerably more than 1,000 systems operating under virtually all subsoil conditions, vapor extraction is considered to be a standard procedure in Germany.

In a vapor extraction well a negative differential pressure is created by a blower or similar device. This generates a steady flow of soil gas towards the extraction well, providing a purging of the soil with air undersaturated with contaminants. After removal of the vapors existing under equilibrium conditions, VOC will partition into the gaseous phase both from the liquid phase (contaminated soil moisture and/or free product) and from the soil matrix.

Differential pressures applied to the extraction well typically range from 15"-350" of water, creating an effective radius of hydraulic influence of about 15 ft to 150 ft. Beneath sealed surfaces, even higher radii of influence are observed in high permeability soils.

Parameters that influence the performance of the vapor extraction system (VES) are the contaminants involved, stratigraphy, soil type, size and type of cover materials, length and position of the screened section in the well, and the pressure differential applied.

Discharge data from case histories of sites with halogenated hydrocarbons contamination reveal common results, if the systems were optimally designed. Those data show that contaminant concentrations and mass removal are high during a first phase of about two weeks, merging into a short transition phase which is followed by an asymptotic decrease in concentrations to background levels. While concentrations in the extraction system's discharge are reduced to some 10% of their initial value after a few weeks, it takes several months to as long as two years to achieve a satisfactory clean-up. Because of these reductions, a discontinuous mode of operation is applied during the closure phase.

In Germany, action levels and cleanup goals are increasingly being based on measurements of contaminant concentrations in the soil gas rather than concentrations measured in discrete soil samples, due to potential

inaccuracies related to soil sampling or uncertainties related to the representativeness of data derived from a limited number of samples.

INTRODUCTION

Contamination by volatile organic compounds (VOC) has turned out to be widespread due to the almost ubiquitous presence of those substances in industrial processes. Specifically, VOC include halogenated hydrocarbons like trichloroethylene (TCE), perchloroethylene (PCE), or 1,1,1-trichloroethane (TCA), aromatic hydrocarbons or petroleum products such as gasoline. Halogenated hydrocarbons, in particular, exhibit physical properties that enable them to penetrate even coated concrete pads and seep into the ground rapidly, both as liquids and vapors. Significant contamination not only occurs at underground storage tanks, but also originates from above ground storage, handling and application areas as well as along pipelines or transport pathways.

Rather than the excavation and disposal or aboveground treatment of contaminated soils, regulatory agencies increasingly favor remedial techniques operating insitu. In the case of VOC contamination, vapor extraction has shown to be an effective and economically feasible insitu alternative (1), (5).

VOC retained in the vadose zone represent a continuous source of groundwater contamination, as even after a complete volatilization of free product, vapors will continue to migrate. Remediation of the unsaturated zone by vapor extraction intercepts this migration path and is cost effective, since it captures the contaminants prior to their dissolution in the groundwater.

PURPOSE

Vapor extraction has become a standard technology in Europe, particularly in Germany, where several thousand systems have been operating since 1981. This has created an extensive database, facilitating the assessment of typical performance characteristics. The comparison of case histories is suitable to:

- demonstrate the common discharge characteristics of vapor extraction systems operated under different subsoil conditions and at varying contaminant concentrations
- predict the development and progress of the remediation
- allow for the design of a treatment system for the extracted vapors.

DESIGN PARAMETERS

Aside from the type of soil and the stratigraphy, the effective radius of hydraulic influence of a vapor extraction system is determined by a number of factors, in particular by the length and position of the screened interval of the extraction well, the thickness of the vadose zone, and the permeability of the surface, respectively the size of a surface seal. Differential pressures decrease exponentially with increasing distance from the extraction well. While higher differential pressures create considerably higher volume flow rates, the effects on the range of influence are small. However, higher pressure differentials may be required in low permeability soils (e.g. clayey silts). This is reflected in the application of different suction devices. While

in high permeability soils centrifugal fans or regenerative blowers are preferred, vacuum pumps are used in low permeability soils.

Given a constant differential pressure, variations of the screen length reveal a linear relationship between the length and the volume flow rate. Longer screens also produce a distinct increase of the effective radius. Accordingly, the position of the screened interval of identical length creates reciprocal effects: shifting it to deeper portions of the vadose zone reduces the volume flow but increases the range of influence (2).

Under the assumption of a screened interval of constant length positioned in the middle portion of the vadose zone, an increasing thickness of the vadose zone results in a distinct increase of the range of influence, while it seems to have only minor effects on the volume flow (2).

The same effect can be observed if variably sized areas of surface sealing are regarded. The presence of an impermeable cover, such as a concrete pad, gives rise to significantly increased ranges of influence at almost constant volume flow rates. However, a sealed surface is not a prerequisite for the successful application of vapor extraction systems, unless highly permeable soils without a silty topsoil cover are encountered.

Aside from the casing configuration, the screen type and structure of the gravel pack have to be selected carefully to inhibit turbulent flow in the immediate vicinity of the well. This has significant effects on the volume flow achievable and the moisture retrieved from the soil. A vapor extraction well should be developed similar to a groundwater well prior to continuous operation.

Independent of theoretical model calculations which, in their accuracy are limited by the data available on the three dimensional structure of the subsurface, the actual range of influence of single systems or arrays should be determined in the field. This can be done in several ways, by repeatedly measuring the soil gas concentrations in vapor monitoring points at varying distances from the well, by measuring the differential pressure created in vapor monitoring points or wells, or just by qualitatively determining the existence of a differential pressure through the observation of the behavior of smoke trails created by air current tubes at such points.

PROBLEMS ENCOUNTERED

Numerous sources for a deviation from the ideal progression of vapor extraction exist, leading to either an extended remediation or, in the worst case, to a failure in achieving the cleanup goal. The two most common problems for an inefficient cleanup of the vadose zone are the placement of the vapor extraction well(s) outside or at the periphery of the source area, and an ongoing recharge of contaminants into the subsurface. Such recharge can result from leakage and spills or from evaporation of VOCs from considerably contaminated groundwater. Misplacement of vapor extraction wells can be avoided by carefully defining the extent and the center of a source area.

A precise source definition is, in shallower soils, most efficiently done with soil gas investigations, the results of which also supply an appropriate basis for the calculation of projected contaminant concentrations in the discharge air.

Given this information, a vapor extraction system might still operate inefficiently if, in the presence of a very shallow groundwater table, vertical extraction wells with short screens are used. In such cases, a horizontal screen installation within a trench provides an effective solution.

RESULTS

Case Histories

Six case histories have been selected for demonstration. The specific cases were chosen on the basis of their documentation, variety of settings, difference in contaminant concentration, and ideal performance of vapor extraction. The justification for the latter lies in the intention of this paper to show the predictability of the cleanup process, if all relevant parameters are adequately considered. Knowledge of what to expect in an ideal case allows for a timely detection of deviations which can point to deficiencies in the design or operation of the particular system, potentially impeding a successful remediation.

For the purpose of comparison, the discharge concentration data were compiled into a composite graph (Fig. 1). Table 1 summarizes geological and technical data. To eliminate the influence of significantly different chemical or physical substance properties, only cases with either tetrachloroethene (PCE) or trichloroethene (TCE) as the primary contaminant were selected.

The data appear to reflect two phases merging into each other. A steep decline lasting for about 20 days (Phase 1) is observed initially, eventually continuing in a gradual asymptotic decrease to background concentrations for the remainder of the operation (Phase 2). In all cases, the discharge concentrations decreased by 80-90 % within the first 20 days of operation. Phase 1 is more pronounced if the discharge starts out at high concentration levels. During Phase 2, it is conspicuous that the absolute concentrations vary within a comparatively narrow range, mostly on a level of less than 20 ppm and, in the final stage, about 2 ppm. This is even more expressed if mass flow rates are regarded.

The decline of contaminant concentrations with time appears to be independent of the particular type of soil (provided the organic carbon content is low), initial concentrations or the specific characteristics of the suction device and extraction well applied in each particular case.

Figure 2 shows calculated means of discharge concentration versus elapsed time for the case histories discussed. The measured data can be approximated by two regression curves. One of the curves fits the steep branch of the empirical contaminant concentrations curve, the second regression curve approximates the asymptotic decline in contaminant concentrations. The empirically derived relations are

$$\text{Phase 1: } C = 530 t^{-0.5}$$

$$\text{Phase 2: } C = 230 - 44 \ln t$$

$$C = \text{discharge concentration} \quad t = \text{elapsed time}$$

While the regression curves do not allow a precise prediction of the ultimate time required for a complete cleanup, they can serve as a guideline to monitor the progress of the remediation.

Although concentrations decrease rapidly during Phase 1, mass balance calculations illustrate the considerable contribution of Phase 2 even at low concentrations. Typically, 50% of the total amount of removable contaminants are discharged after a time period ranging from about two to eight weeks, which is consistent with other published data (e.g., Lisiecki et al., 1988). The removal of the remaining 50% is only achieved within an additional four to twenty months of operation. Historically, the total cleanup time has ranged from some 100 days to approximately 2.5 years, depending on the mass of contaminants retained in the soil and the type of substances involved.

Physical Processes in the Soil

Unless a continuous recharge of separate phase material at significant rates is encountered, the presence of free product in soils is typically limited to small fluid particles trapped in soil pores (7). At the expense of these fluid droplets as well as of compounds dissolved in the soil moisture or adsorbed to the soil matrix, a contaminant vapor phase will develop and spread over time controlled by diffusion and advection.

After an initial exchange of the soil gas volume in the pores, ambient air will be drawn continuously from outside the contaminated area. While passing through the subsurface the air will be charged with VOC partitioning into the vapor phase and subsequently be discharged through the vapor extraction system (1). The process resembles a continuous purging of the soil with clean air and will continue until volatilization and desorption of contaminants is complete within the limits of equilibrium partitioning.

The two phases describing the system performance are attributable to different processes becoming prevalent in the respective stages of the operation. During the first phase, the contaminant saturated soil gas which is present in the pore space under equilibrium conditions is discharged. A rapid evaporation of free product droplets due to disturbance of the equilibrium is presumably also in part occurring during the first phase. According to field tests, the time required to develop the steady state flow pattern and effective radius ranges from about 15 to 30 minutes. It may take days for soil gas to flow from the edge of the affected soil volume to the extraction well. A short transitional period, when the contaminant concentration in the discharged soil gas has already decreased by more than 80%, is most likely characterized by a shift in source of the contaminants. Rather than from an evaporation of liquid particles, the contaminants in the discharge vapors result from a desorption of contaminants from soil particles. A second process, which is believed to become important in this phase, is the partitioning of contaminants previously dissolved in the soil moisture into the gaseous phase (3).

The second phase represents the comparatively slow, diffusion controlled desorption process and a gradual reduction of the contaminated soil volume. The total cleanup time depends on the physical properties of the compounds involved, the mass of VOC retained in the soil, the soil porosity, and the soil moisture. As long as sufficient supplies of contaminants are existing, a nearly constant extraction rate is accomplished over a period of several months up to about two years.

To save energy during this low yield phase, the VES may be shut down periodically for several days or weeks, allowing a state of equilibrium to reestablish. Upon turning on the system, a concentration "spike" is observed lasting as long as it takes to build up the flow field and to draw soil gas from its perimeter to the extraction well. This discontinuous mode of operation is typically applied during the final months. The maximum concentration and duration of each spike may serve as parameters to determine the completion of the cleanup effort.

Data from air flow models indicate a rapid decrease of pressure differentials to very low levels with increasing distance from the vapor extraction well (2). The differential pressures throughout the majority of the range of influence are too low to be directly responsible for enhanced volatilization of the contaminants. However, even very small differential pressure create a pressure gradient and thus induce the flow of air towards the vapor extraction well. The equilibrium disturbance caused by this process, rather than enhanced volatilization through large differential pressures, is considered to be responsible for the extraction of contaminants.

SUMMARY

In order to achieve a successful remediation of the vadose zone by vapor extraction, a thorough assessment of the contamination pattern is a prerequisite. Factors which inhibit or impede the successful operation of a vapor extraction system are: an ongoing release of contaminants into the subsurface, evaporation of contaminants from a plume of considerably contaminated groundwater, and the positioning of the vapor extraction well outside the contamination center must be ruled out.

To properly design a VES, various system parameters must be considered. These include the length and position of the screened well interval(s), the type of screen and gravel pack, as well as the selection of the appropriate suction device.

The application of the results of previous experiences with vapor extraction as exemplified in the case histories facilitate:

- a prediction of the development of contaminant concentrations in the discharge air
- the design of a vapor treatment system
- a timely recognition of factors impeding a successful cleanup by comparing actual data with the model curve
- an optimized design of vapor extraction wells.

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Case History Data

	A	B	C	D	E/F	G
Soil:	3' fill 16' silty, gravelly sands	10' fill 2' gravelly sands	20' interb. sands, gravels, fills	6' fill 7' sands, gravels	13' fill 6' silty, gravelly sands	31' weathered claystone, sands, silts
Contaminant:	TCE	TCE	PCE	PCE	PCE	PCE
Depth to Water Table:	19'	12'	20'	13'	19'	31'
Volume Flow:	85 CFM	390 CFM	110 CFM	103 CFM	70 CFM	75 CFM
Range of Influence:	65'	180'	83'	75'	40'	50'

Figure 1

Vapor Extraction Discharge Performance

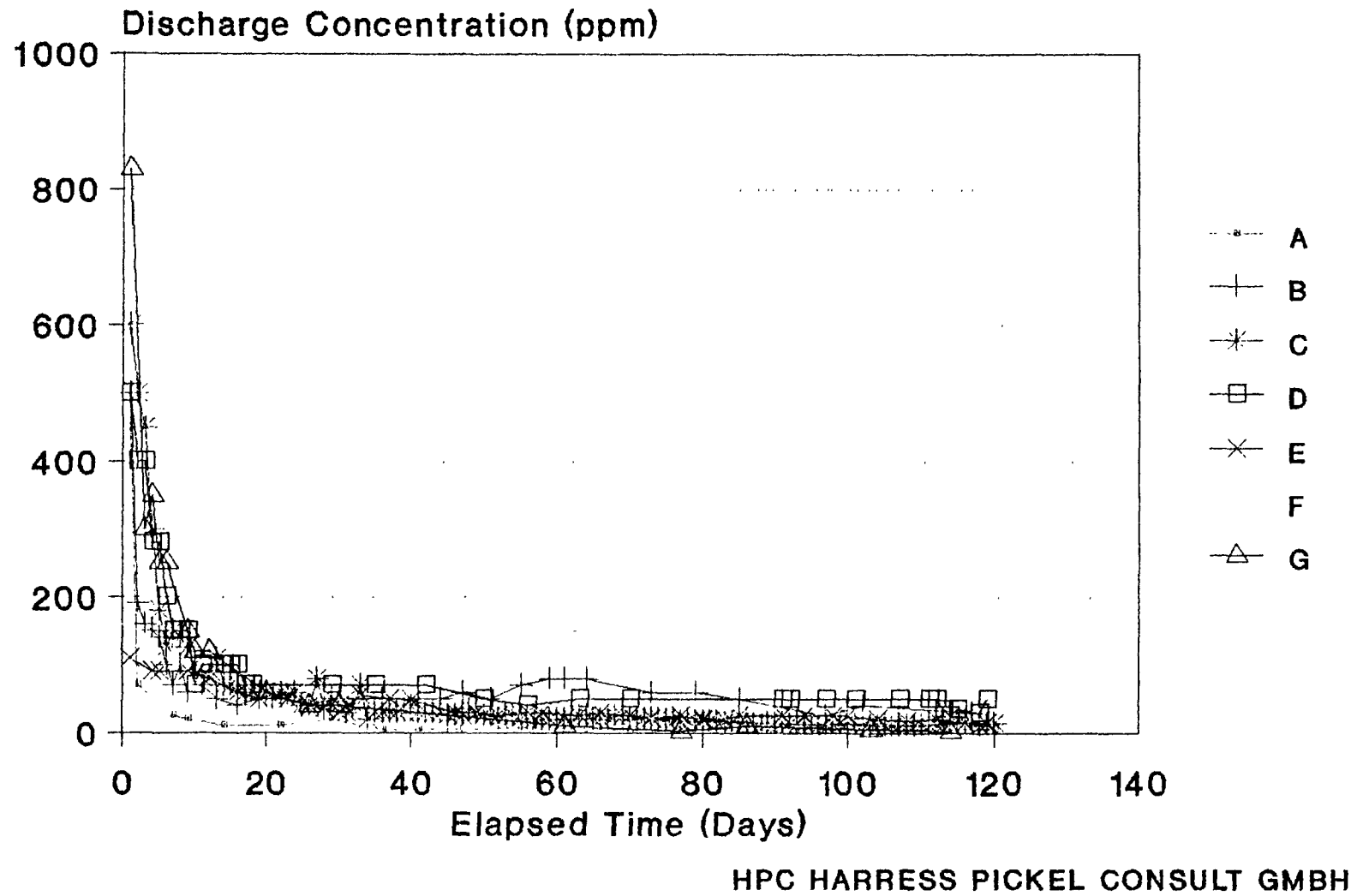


Figure 2

VAPOR EXTRACTION

Discharge Performance

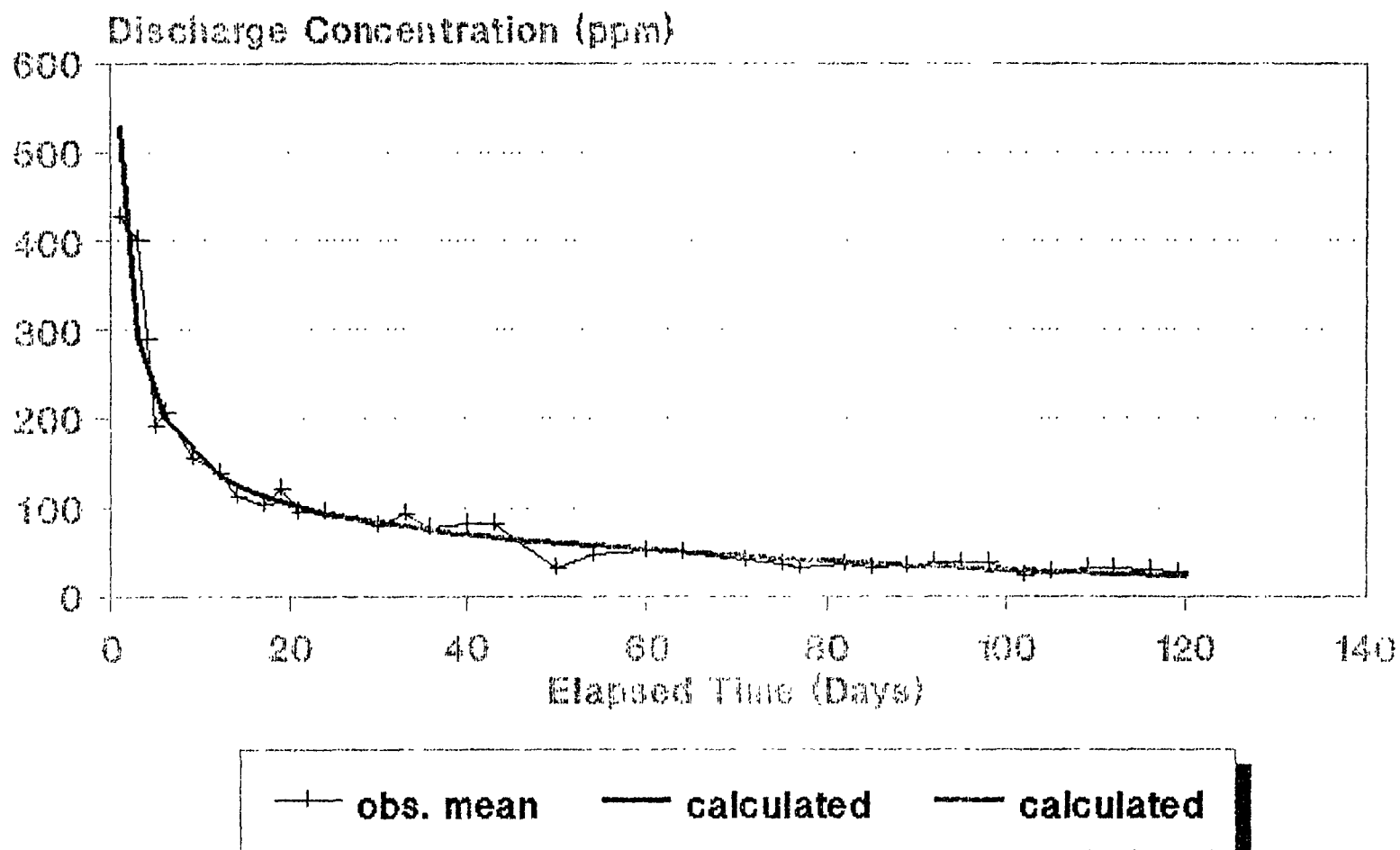


Figure 3

VACUUM VAPORIZER WELLS (UVB) FOR IN SITU REMEDIATION OF VOLATILE AND STRIPPABLE CONTAMINANTS IN THE UNSATURATED AND SATURATED ZONE

B. Herrling*, J. Stamm*, E.J. Alesi**, P. Brinzel***

* Institute of Hydromechanics, University of Karlsruhe, Kaiserstrasse 12,
D-7500 Karlsruhe, Germany

** IEG Technologies Corp., 1833D Crossbeam Dr., Charlotte, NC 28217 USA

*** PROTEC GmbH, An den drei Hasen 21, D-6370 Oberursel, Germany

INTRODUCTION

The contamination of groundwater by strippable substances is a significant problem in all industrial countries. For remediating aquifers in situ technologies are favored to reduce the investment and operating costs. The paper presents an in situ method that can remove strippable substances, e.g. volatile chlorinated hydrocarbons, and BTEX, from the subsurface (groundwater zone, capillary fringe, and unsaturated zone); it is currently being used at numerous locations in Germany. This technology is an alternative to conventional hydraulic remediation measures (pumping, off-site cleaning, and reinfiltration of groundwater) for the saturated groundwater zone and for soil air extraction methods to clean the vapor zone. The contaminated groundwater is stripped in situ by air in a below atmospheric pressure field within a so-called "vacuum vaporizer well" (German: Unterdruck-Verdampfer-Brunnen, UVB). The used air, charged with volatile contaminants, is cleaned using activated carbon. The UVB technique produces a vertical circulation flow in the area surrounding the well, which catches the total aquifer. The vertical velocity component yields a desired flow through the horizontal structure of a native aquifer. Numerical results demonstrate the size of the sphere of influence and the capture zone of a well or well field in the saturated groundwater zone; extended field measurements have been and continue to be taken (Herrling et al. 1991a). The UVB technology has most successfully been used for vapor extraction at most sites together with remediating the groundwater zone. Using a ventilator and a double-cased screen give a lot of advantages which will be demonstrated. For cleaning the vapor zone and the capillary fringe alone some special circulation systems have been developed and are represented in this paper.

IN SITU REMEDIATION OF VOLATILE CONTAMINANTS BY THE UVB METHOD

The UVB helps to remove volatile substances from the groundwater, the unsaturated zone, and the capillary fringe. When using the UVB method, a special well with two screen sections is employed, one at the aquifer bottom and one at the groundwater surface (Fig. 1) or below an aquitard in a confined aquifer. The borehole reach between the two screen sections should be made impermeable. One well should be used to remediate only one aquifer (phreatic or confined) and should not connect different aquifers.

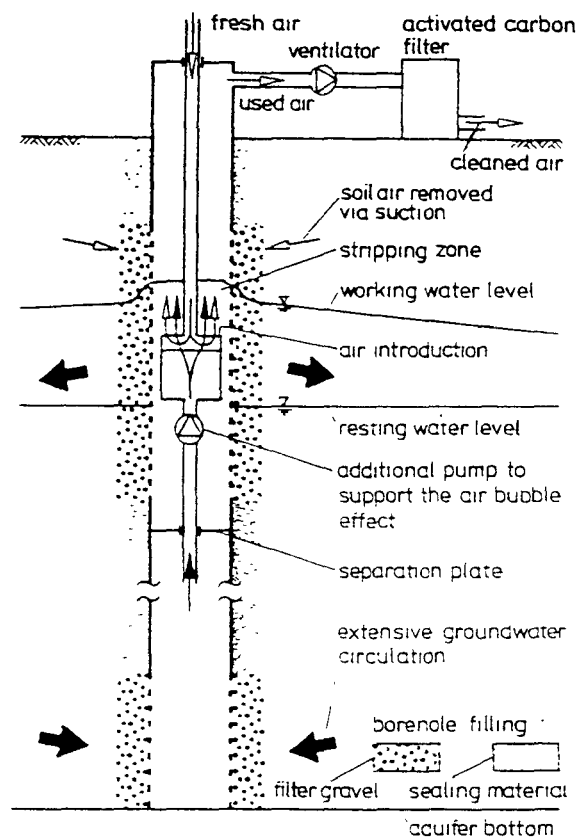


Figure 1. Vacuum vaporizer well (UVB) with additional pump and separating plate.

The upper, closed part of the well is maintained at below atmospheric pressure by a ventilator. This lifts the water level within the well casing. The fresh air for the upper part of the well casing is introduced through a fresh air pipe: the upper end is open to the atmosphere, and the lower end terminates in a pinhole plate. The height of the pinhole plate is adjusted such that the water pressure is lower there than the atmospheric pressure. Therefore, the fresh air is drawn into the system. The reach between the pinhole plate and the water surface in the well casing is the stripping zone, in which an air bubble flow develops. The rising air bubbles produce a pump effect, which moves the water up and causes a suction effect at the well bottom. In recent wells, a separating plate and an additional pump (Fig. 1) are used to reinforce the pumping effect of the air bubbles. Additionally, soil air is drawn from the surrounding contaminated unsaturated zone at many sites. Stripped air and possibly soil air are transported through the ventilator and across activated carbon, onto which the contamination is adsorbed. Thus, only clean air escapes into the atmosphere. The cleaning effect

of the well is based on reduced pressure, which reinforces the escape of volatile contamination out of the water, and as a result of the air intermixing, onto the considerable surface area of the air bubbles and onto the concentration gradient between the contaminated groundwater and the clean air. In this sense, the permanent vibration caused by the air bubbles is beneficial to the escape process of the contamination. This vibration is transmitted as compression and shear waves into sediment and fluid, and presumably influences the mobility of the contaminants, even outside the well.

The upward-streaming, stripped groundwater leaves the well casing through the upper screen section in the reach of the groundwater surface, which is lifted in a phreatic aquifer by the previously explained pump processes and the below-atmospheric pressure. It then returns in an extensive circulation to the well bottom. In this way, the groundwater surrounding the well is also remediated. The expansion of groundwater circulation is positively influenced by the anisotropy existing in each natural aquifer possessing greater horizontal than vertical hydraulic conductivities. The artificial groundwater circulation determines the sphere of influence of a well and is overlapped with the natural groundwater flow (as described below).

The pinhole plate and all the installations within the well casing are designed as a float so they can adjust automatically to changing groundwater levels.

For special contaminants of lower density than water, a special installation within the well is available: the contaminated water enters the well through the upper screen, is stripped there, and with help of the additional pump, leaves the well through the lower screen. Both installations can be used within the same well casing.

At many remediation sites, the UVB is used without an additional pump and separating plate (see Fig. 2). In this case, a circulation flow occurs within the well casing, which is produced by the strong pumping effect of the rising air bubbles. For the most part, the stripped water follows the path of least resistance and flows down to the end of the suction pipe. Thus, a water of uniform temperature and oxygen content appears in the entire well casing. The water temperature is influenced by the withdrawn evaporation heat in the stripping zone, by the sinking of the air temperature in consequence of the vacuum in the air bubble zone, and by the temperature of the fresh air. Depending on the groundwater temperature around the well, the water leaves the well casing through the upper screen section and contaminated water enters the UVB at the lower screen section. This occurs when the groundwater is colder than the circulation water in the well casing. On the other hand, when the water in the well is colder than the surrounding groundwater, an outer circulation occurs which is opposite to that shown in Figure 2. The water leaves the well at the lower screen section and enters it at the upper. Both cases, influenced by density differences of the involved water bodies, have been observed at different sites.

SPHERE OF INFLUENCE AND CAPTURE ZONE OF A UVB OR UVB FIELD

The extended circulation field outside the well is of special interest. In this paper numerical results of only UVB installations with additional pump and separation plate will be discussed (Fig. 1). The effect of the above-mentioned permanent vibrations, caused by the air bubbles, will not be considered. In principle, two different cases have been considered:

- When there is no (or negligible) natural groundwater flow, the sphere of influence (or the range, R) of a UVB is of interest.

- When natural groundwater flow is significant, the extent of the capture zone has to be determined for locating the well installations at a remediation site.

The resulting flow field of one or several UVB installations differs from the natural groundwater flow field only in a limited area around the UVB. This is because sinks and sources are located at the bottom and top of the same aquifer, each at places with the same horizontal coordinates. The effected area can, therefore, be limited to the sum of the areas of influence of all the UVBs. When only confined aquifer conditions are considered to reduce the computational effort, the flow field of each UVB can be superimposed onto those of other UVBs and of the natural groundwater flow field.

To estimate the sphere of influence and the capture zone of a UVB, numerical investigations have been performed. To calculate the complex three-dimensional flow field of a single UVB or a UVB field with minimal effort, the following simplifications and assumptions have been used:

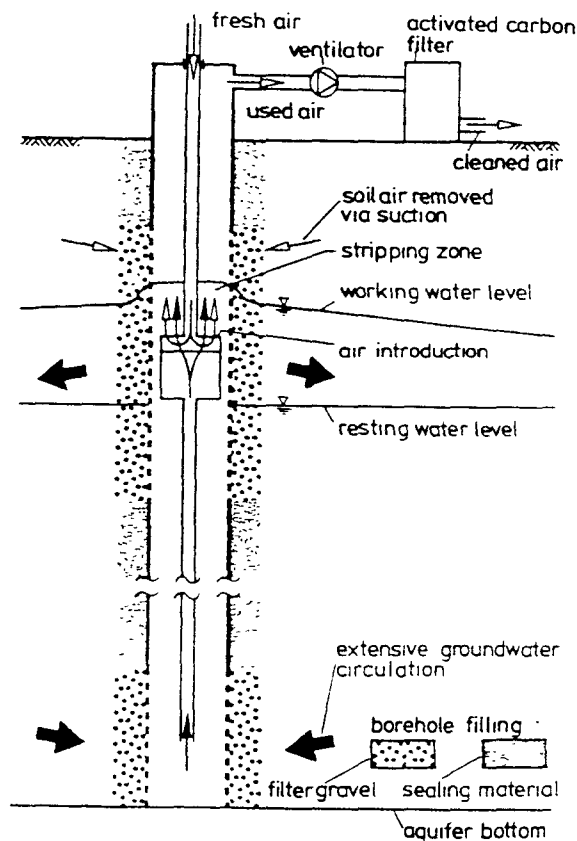


Figure 2. UVB method, driven by the air bubble effect.

- The aquifer thickness is constant.
- Only confined aquifer conditions are considered in the calculation.
- The aquifer structure is assumed radially homogeneous to hydraulic conductivities. Horizontal layers, each with different conductivities, can be used. The hydraulic conductivities may be anisotropic, but each horizontal layer may have only one vertical and one horizontal conductivity.
- The local below-atmospheric pressure field near the wells is neglected.
- Density effects are neglected.
- The computations assume steady-state conditions.
- For estimating the capture zone, only convective transport is considered.

The three-dimensional flow field in the above-defined, limited aquifer region is obtained by superimposition of a horizontal uniform flow field, computed in a vertical cross section and representing the natural groundwater flow, and of radially symmetric, vertical flow fields for each UVB. The superimposition of the different flow fields with their own discretization is achieved by interpolating and adding the different flow vectors at the various nodes of a simple rectangular grid with variable grid distances that are independently chosen for each Cartesian coordinate. The rectangular grid can be quickly and simply set up and allows for some refinements near the wells and their screen sections. More details of the numerical computations are given in Herrling and Buermann (1990).

Resulting Flow System

Before going into more detail, the complex flow field near an individual UVB is clarified for a vertical longitudinal section in the direction of the natural groundwater flow (symmetry plane of the flow problem). In Figure 3, the streamlines of three case studies are illustrated with Darcy velocities (v) of natural groundwater flow of 0.0 m/day, 0.3 m/day, and 1.0 m/day. All other parameters remain constant: the discharge (Q) through the well casing is 20.16 m³/hr, the thickness (H) of the aquifer is 10 m, the anisotropic hydraulic conductivities are $K_H = 0.001$ m/sec (horizontal) and $K_V = 0.0001$ m/sec (vertical), and the lengths of the screen sections are $a_b = 1.2$ m at the bottom and $a_t = 2.1$ m at the top.

Figures 3b and 3c show that the groundwater, flowing from the left, dives downward to the lower screen section and is transported upward within the well casing, and that the cleaned water flows out to all sides at the upper screen section. The flow situation can only be calculated and plotted in such a simple way in this longitudinal section, otherwise the complex three-dimensional flow field has to be considered.

For a deep aquifer contaminated only in the upper groundwater zone, a UVB installation can be used at a hydraulically imperfect well. The resulting flow system is demonstrated in Figure 4, clarified for a vertical longitudinal section in the symmetry plane (Fig. 4b). The used parameters are the same as for Figure 3b. The only difference is that the aquifer thickness (H) is 30 m (well length = 10 m, as before).

At most of the UVB installation sites, a natural, nonnegligible groundwater flow will exist. For a normal withdrawal well, a separating streamline can be determined: all the water within this line is captured by the well, and all water outside of it passes the well. In principle, the situation is the same when using a UVB. In contrast to a normal withdrawal well, where the flow can be considered horizontal, the flow around a UVB must be regarded as three-dimensional. Thus, the water body, flowing toward the UVB from upstream and being captured by the lower screen section, cannot be delimited by a simple separating streamline, but by

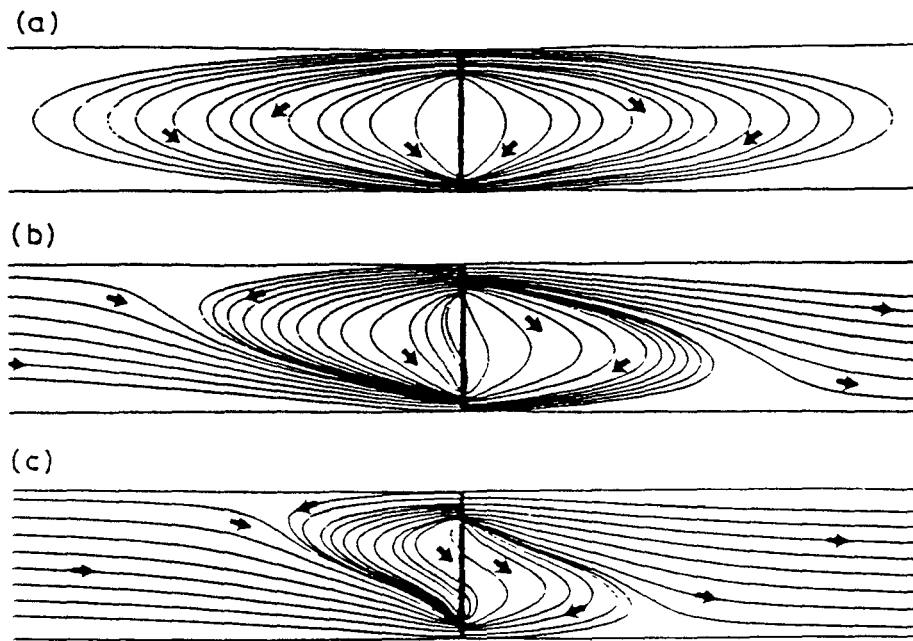


Figure 3. Streamlines clarified for a vertical longitudinal section with natural velocities: (a) 0.0 m/day; (b) 0.3 m/day; (c) 1.0 m/day.

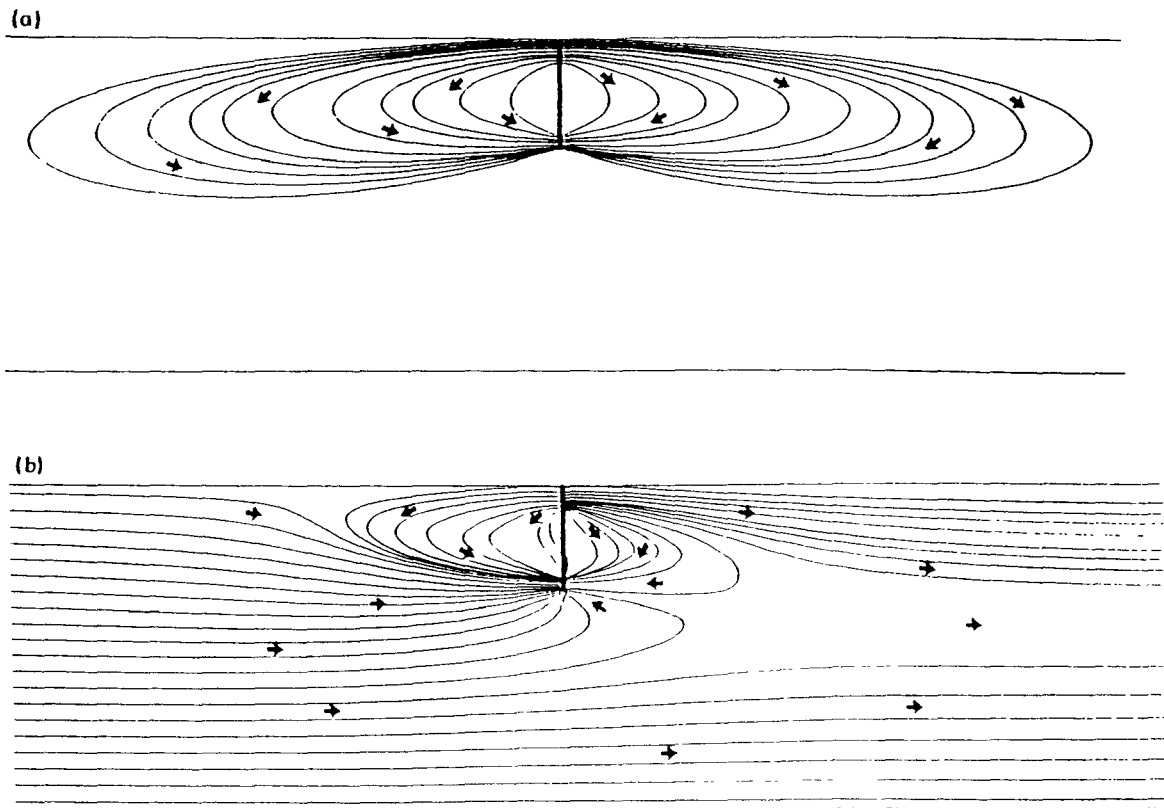


Figure 4. Streamlines at a hydraulically imperfect well clarified for a vertical longitudinal section with natural velocities: (a) 0.0m/day; (b) 0.3 m/day.

a curved separating stream surface. This can be calculated as described in Herrling and Buermann (1990): on the basis of the three-dimensional flow field, a three-dimensional, particle-tracking method is used. The water body within the separating stream surface is captured by the UVB, and that outside of it, which flows from upstream, passes the well.

In Figure 5 the outer surface of the capture zone, calculated numerically, and the surrounding horizontal aquifer bottom and aquifer top are plotted for two situations (the natural groundwater flows from the background at the right side to the UVB, as shown by the vectors). Figures 5a and 5b were calculated for the situation described for Figure 3b; the only difference is that for Figure 5a the vertical hydraulic conductivity is $K_v = 0.001$ m/sec, which means the calculation is performed for isotropic conditions. The figures have a visible basis area of $50 \text{ m} \cdot 50 \text{ m}$ (Fig. 5a) and $100 \text{ m} \cdot 50 \text{ m}$ (Fig. 5b).

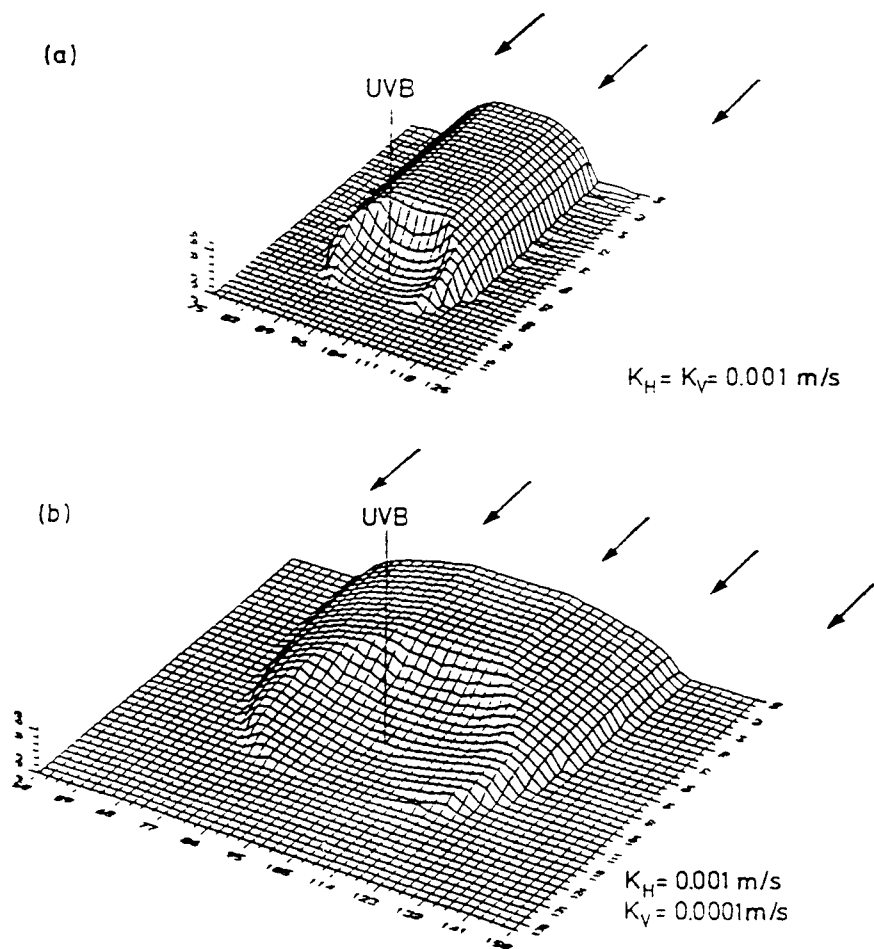


Figure 5. Separating stream surface of the capture zone for the situation of Figure 3b: (a) $K_H = 0.001$ m/sec (isotropic); (b) anisotropic $K_H/K_v = 10$.

The captured water is cleaned within the well and leaves it through the upper screen section in all directions (not shown in Fig. 5). Parts of it are again captured by the lower screen section, and the rest flows directly downstream.

If a wide plume of contaminated groundwater is to be cleaned, one UVB might not be enough to capture the whole plume. Different UVB installations can be arranged, for example, in one line normal to the natural flow. An important question concerns the maximum distance that allows no contaminated water to flow between two neighbouring wells without being cleaned. Figure 6 demonstrates such an example for the situation of Figure 5b where the maximum well distance is 46 m. The visible basis area of Figure 6 is to 150 m • 150 m.

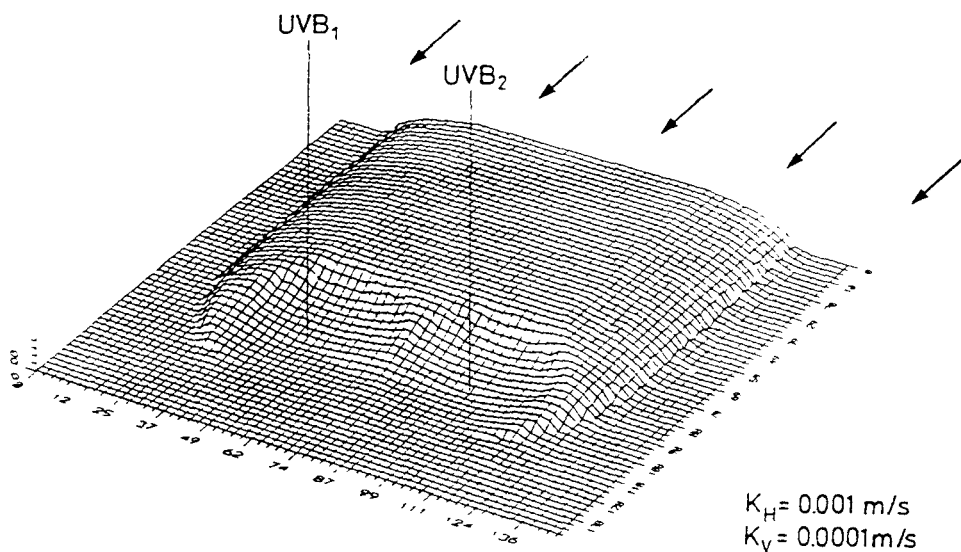


Figure 6. Separating stream surface of the capture zone for the situation of Figure 5b, but for two UVB installations at a maximum distance.

Figure 7 presents a view of the separating stream surfaces of all three water bodies in connection with the flow around a UVB. The natural groundwater flow comes from the left side. (In Figure 7b the three water bodies were artificially separated for clarification.)

At the left side of Figure 7, the separating stream surface of the contaminated groundwater captured by the UVB can be seen. In the center a water body is shown which consists of cleaned groundwater and shows the circulation flow around the UVB. At the right side of Figure 7, the separating stream surface of the cleaned groundwater flowing downstream is displayed. The calculation has accounted for the following dimensionless parameters: $Q/(H^2v) = 30$, $a/H = 0.25$, and $K_H/K_V = 5$. The screen lengths at the bottom and top are the same: $a_T = a_B = a$.

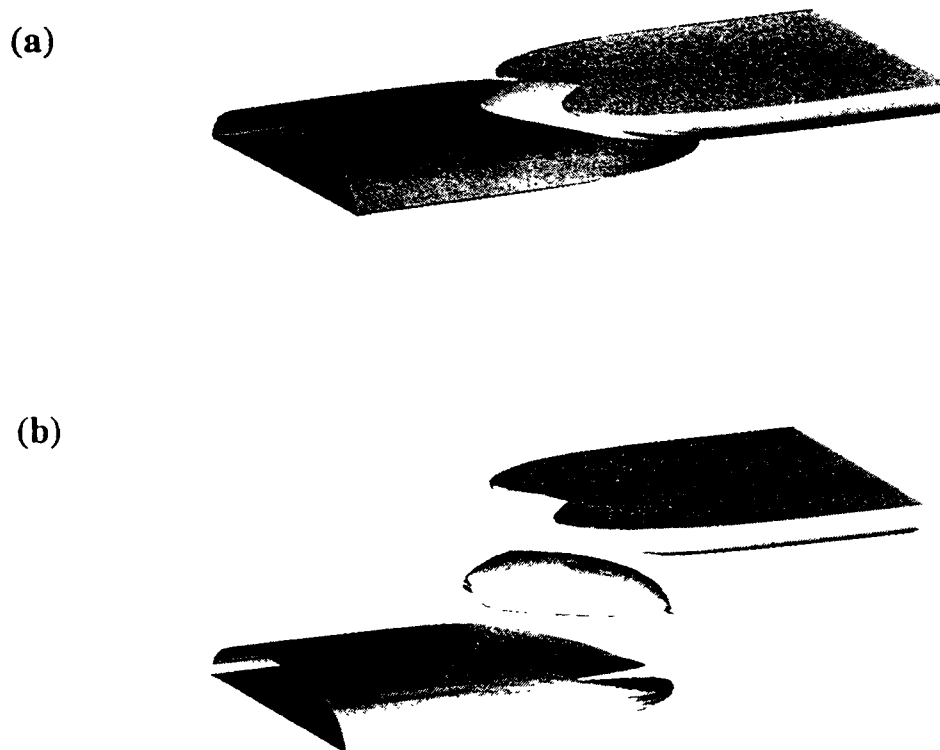


Figure 7. Separating stream surface of the different water bodies in the outside flow of a UVB: captured, circulating and flowing downstream water in (a) a real situation, and (b) water bodies separated for clarification.

Diagrams for the Dimensioning of UVB Installations

Absence of Natural Groundwater Flow. At sites without natural groundwater flow, the sphere of influence (R) of a UVB is of special interest. R is dependent on the anisotropy (horizontal over vertical hydraulic conductivity: K_H/K_V), on the thickness (H) of the aquifer, and on the length of the screen sections a_T and a_B at the top and bottom of the aquifer (see Fig. 8) or the ratio a/H (when the same length of the screen section is used for both, then only a is referred to). Although R is mathematically infinite, it is, in practice, defined as the horizontal distance from the well axis to the farthest point at which circulation flow is still significant. In a dimensionless description, R has been made dependent on the ratio Q_R/Q , where Q_R is that water quantity, which circulates within the distance R from the well. The ratio Q_R/Q , which is prescribed for practical reasons, describes the strength of a circulation flow at the distance R from the well.

In Figure 9a, results are presented for ratios $Q_R/Q = 0.98$ and 0.8 and for $a = a_T = a_B$ in a dimensionless diagram. The sphere of influence (R) is independent of the discharge through the well, but strongly dependent on the anisotropy K_H/K_V . Within usual proportions, the length of the screen sections has only a small influence. For a UVB with separating plate and additional pump, a totally screened well casing should be avoided because of hydraulic short-circuiting.

Figure 9b presents a dimensionless diagram that describes the differences (Δh) of the hydraulic heads between the top and bottom of a double-screened well through which a discharge (Q) is pumped. Δh is dependent on the parameter $Q/(H^2 K_H)$ and the ratios K_H/K_V and a/H . Abiding by the above-described assumptions, the rise of the hydraulic head at the top of the well amounts to $\Delta h/2$, and the decrease is $-\Delta h/2$ at the bottom (both referring to the position of rest). When using the UVB for stripping, the falling, stripped water in the reactor causes a dynamic effect that will influence the upper hydraulic head within the well.

For the dimensioning or examination of a site, Figure 9b is a valuable expedient. When K_H is known (e.g., by pump test) - along with H , Q , and a - Figure 9b and the measured Δh allow an estimate of the anisotropy at a site.

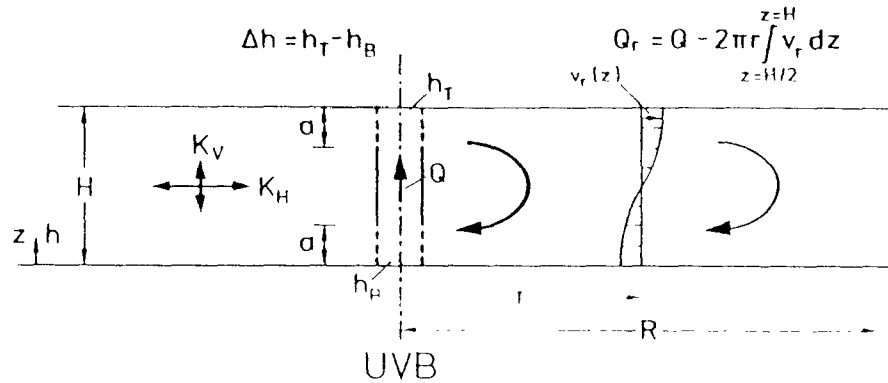


Figure 8. Notation in a vertical cross section.

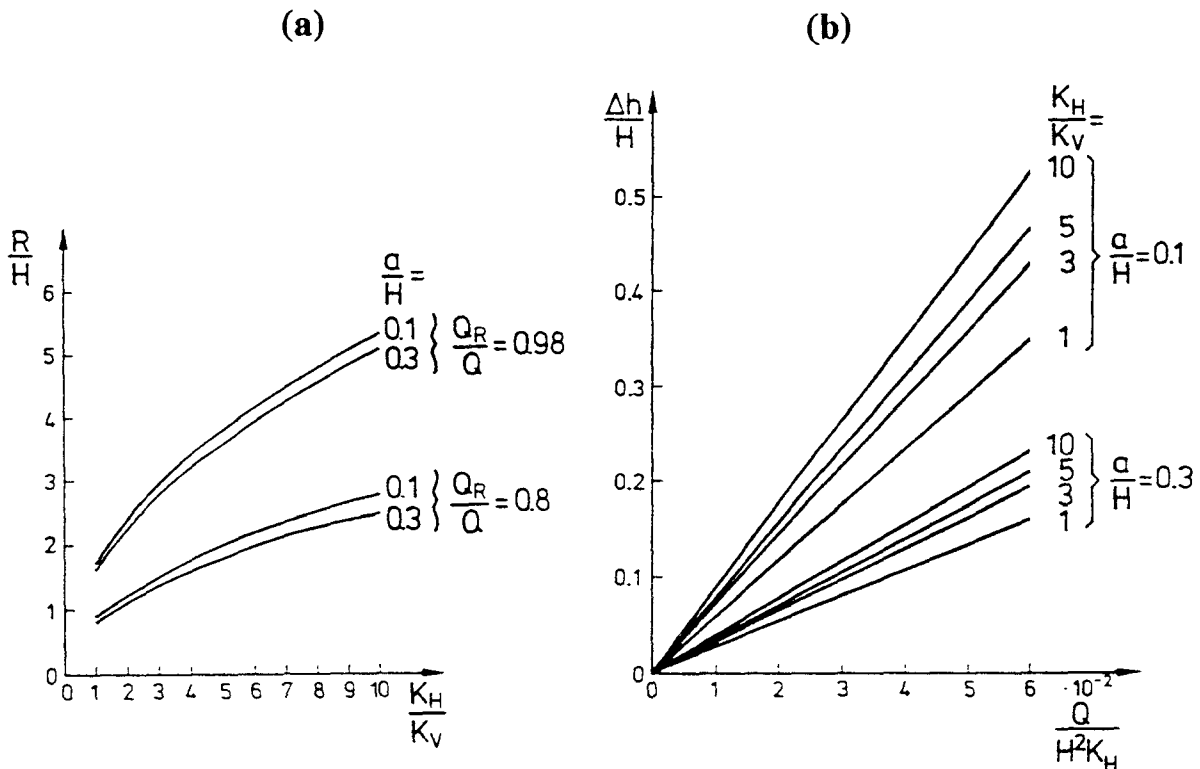


Figure 9. (a) Sphere of influence (R) for a site without natural groundwater flow, (b) differences (Δh) of the hydraulic heads between the top and bottom of a well.

Presence of Natural Groundwater Flow. At most remediation sites a natural groundwater flow exists. Figure 11 shows numerical results represented in dimensionless form for the dimensioning of UVB installations under these conditions. Figure 10 introduces the notations for an upstream cross section through the capture zone normal to the natural groundwater flow direction (comparable with the open influx region to the left of the capture zone in Figure 7) for one and two UVB installations. It is often the case when remediating a wide contamination plume, that several wells are used in a line normal to the direction of the natural groundwater flow. The length (D) denotes the maximum well distance at which the contaminated groundwater cannot pass between the wells without being cleaned. The results of Figure 11 have been calculated for an upstream distance of $5H$ from the well and for a constant ratio of $a/H = 0.25$ (screen length over aquifer thickness). The results are discussed for wells which pump upward.

The widths B_T and B_B of the upstream capture zone, measured at the aquifer top and bottom, are shown in Figure 11a. The ratios B_T/H and B_B/H are dependent on the ratios $Q/(H^2v)$, K_H/K_V , and a/H . v denotes the Darcy velocity of the natural groundwater flow; all other variables are explained above. For small values of $Q/(H^2v)$, the upper part of the capture zone does not reach the top of the aquifer. This implies that for remediating a plume, a minimum well discharge (Q) is required. Again, the results are quite sensitive to the degree of the anisotropy (see Fig. 5, as well).

Figure 11b shows the results for the influx area (A) of the upstream capture zone, and Figure 11c the maximum well distance (D) of two wells between which contaminated groundwater cannot pass without being treated. The ratios A/H^2 as well as D/H are dependent on the same parameters as the widths B_T and B_B . When a plume of width W is to be cleaned, the number (n) of necessary UVB installations can be estimated by $n = (W - B_T)/D + 1$.

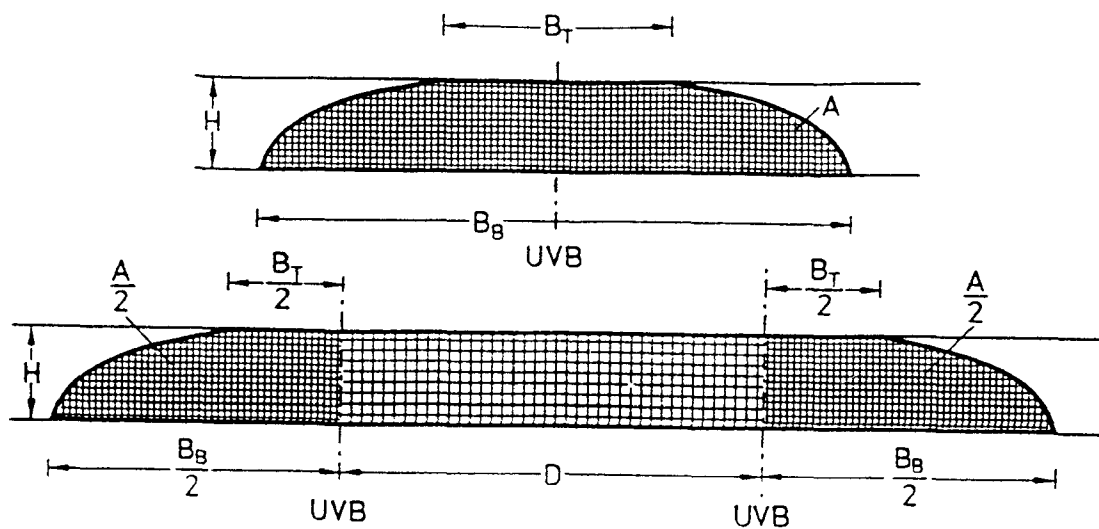


Figure 10. Notations in an upstream cross section through the capture zone for one and two UVB installations (for wells pumping upward).

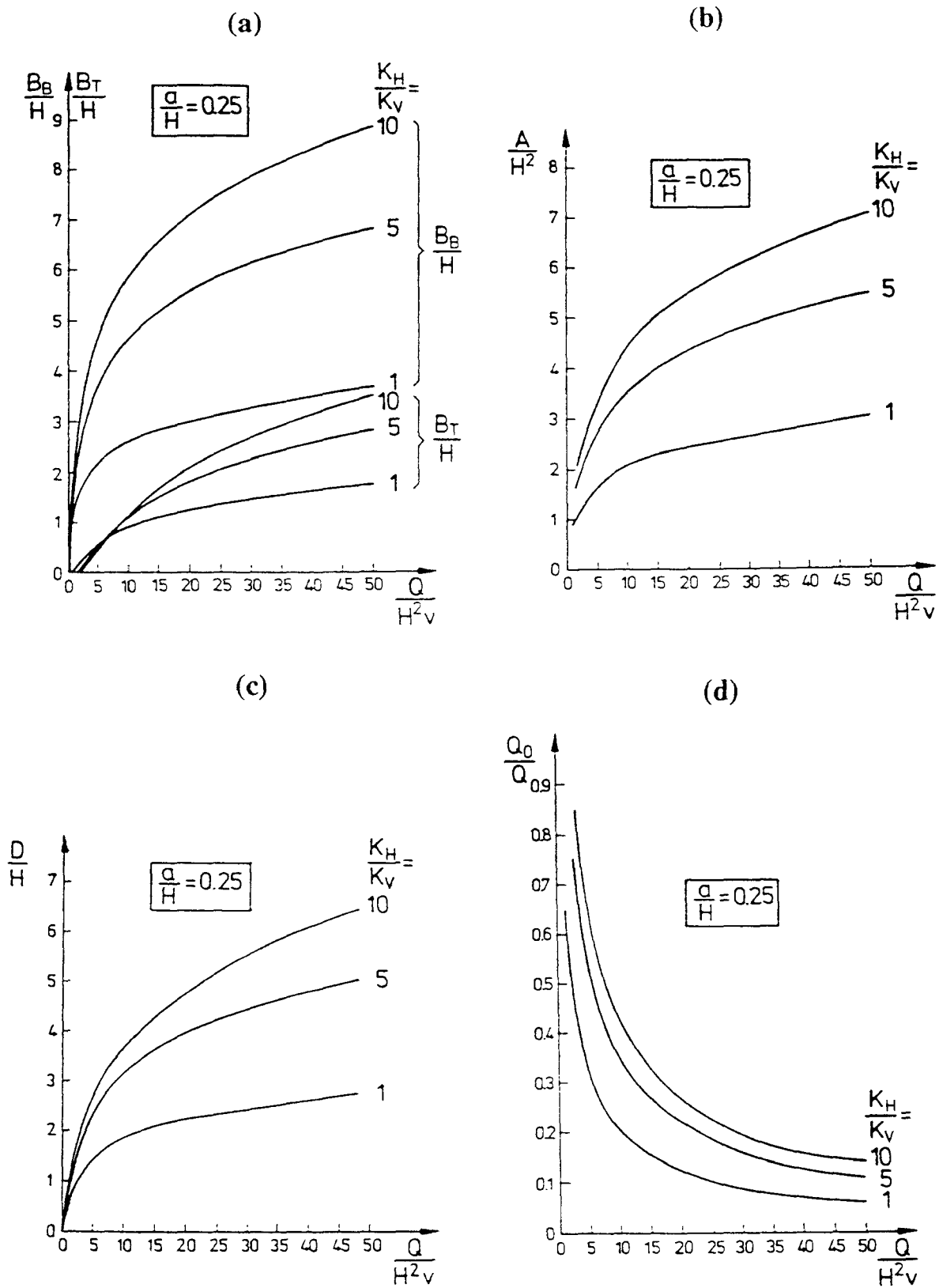


Figure 11. (a) Widths B_T and B_B of the upstream capture zone at the aquifer top and bottom; (b) Influx area A of the upstream capture zone; (c) Maximum well distance (D) at which the contaminated groundwater cannot pass between the wells without being treated; (d) Upstream discharge (Q_0) in the capture zone, which is diluted with the circulating water to the total well discharge (Q).

When a plume is remediated, the contaminated water of quantity Q_0 , flowing into the capture zone of a UVB (single well) from upstream, is diluted with treated water that has already flowed through the well and circulates around the UVB. Thus, the contaminant concentration of the water within the well casing will be lower than in the upstream plume; at wells near a contamination source the situation is contrary. Figure 11d illustrates the expected portion Q_0 which belongs to the total well discharge Q . The ratio Q_0/Q is again dependent on the same parameters as the widths of the upstream capture zone. Figure 11d can be used to estimate the expected concentration value of the water within the well casing for the dimensioning of a UVB installation. To evaluate the progress of remediation at a site it may help to determine the concentration data of the upstream plume and of the water within the well.

In Figure 12 the upstream distance (S) of the stagnation point at the aquifer top from the well axis is described (see Fig. 3b and 3c, as well). The ratio S/H is also dependent on the parameters $Q/(H^2v)$, K_H/K_V , and a/H . The location of the stagnation point is highly sensitive to the anisotropy of the aquifer. The length of the screen section is of small importance within usual proportions (as described above). The knowledge of the distance (S) from the stagnation point can be used to determine the positions of measuring equipment. The operation of a UVB can also be supervised using depth dependent measurements between the stagnation point and the well.

The sphere of influence of the circulation around a UVB at sites with natural groundwater flow is of special interest. This sphere of circulation is limited in a quite different way than at a site with absence of natural flow (Fig. 9a) as can be seen in Figures 3b, 3c, 4b, and 7. In the direction of natural groundwater flow, this sphere has a maximum expansion of (S) (see Fig. 12) to the upstream and downstream sides. Normal to this direction, the maximum radius of the sphere of circulation is approximated by $(B_B + B_T)/4$ (Fig. 11a), and, in the case of several wells in one line, by $D/2$ (Fig. 11c).

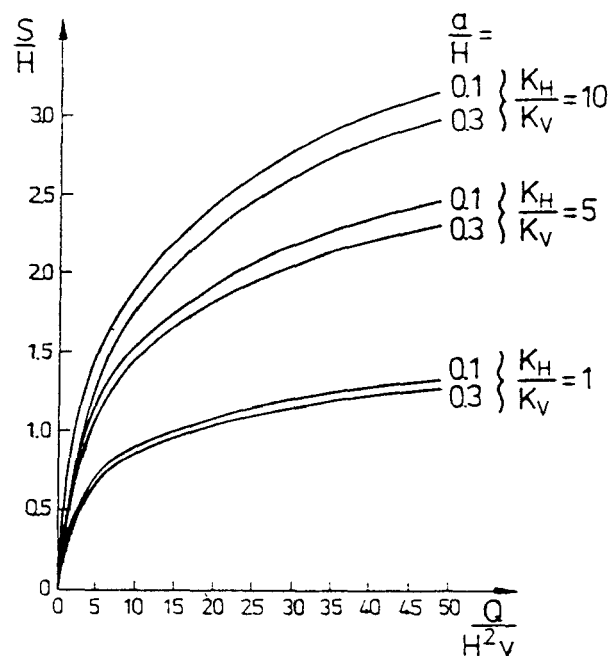


Figure 12. Upstream distance (S) of the stagnation point from the well axis.

Figures 9, 11, and 12 can be used for the dimensioning of a UVB or UVB field when the parameters K_H/K_V and $Q/(H^2v)$ can be estimated, where Q depends on the well size and on the additional pump. For an irregular well field, a layered aquifer, or special critical cases, numerical calculations can be performed.

SOIL VAPOR EXTRACTION WITH DIFFERENT TECHNIQUES: A COMPARISON STUDY

(Contribution by P. Brinzel)

Description of the Initial Situation

At a site polluted with chlorinated hydrocarbons (CHC) on the property of a metal treatment plant located in the Rhine - Main area of Germany, the soil air in the unsaturated zone was found to be contaminated with 500-800 mg/m³ of volatile CHC. Tetrachloroethene was identified as the primary contaminant. This contamination was found to exist over an area of approximately 230 m² and down to a depth of 2 m under the ground surface. On the same property evidence of additional, secondary contaminations was present. Within this study, however, these secondary contaminations will be ignored. The soil air remediation measures undertaken in this study were focused on the center of the primary contamination, which lies under a production building. For the comparison of different venting techniques under similar conditions, remediation wells were drilled in pairs with the well casings of each pair lying one meter apart from each other. The distance between the position of each pair is 10 m.

Geological Situation

Under a 0.20-0.30 m thick cement floor lies a 0.30-0.40 m layer consisting of fine gravel middle to coarse sands. The following layer is 0.60-0.80 m thick and contains silty fine sands. Under these moist, fine sands is deposited a partially fine sand silt layer with varying contents of clay which extends to 2.30 m below the surface. Beyond the boundaries of the contaminated area, this silt layer is found to extend to depths of approximately 7 m.

Design of the Remediation Wells

Two pairs of remediation wells were constructed on the site. At each position of a pair one well was outfitted with PVC slotted screens (LB1S and LB2S) and the other well with double-cased screens (LB1D and LB2D). The construction diagrams for the well are given in Figure 13. The slotted screen, a trade standard 2" PVC pipe with a slot width of 0.5 mm, possesses an open screen area of 5-7% of the screen's total surface area. The slot perforation value is given with 0.057. Using these values, the open screen area is calculated to be 89.5 cm². The double-cased screen (diameter 61 mm) possesses an open screen area of almost 42% of its total surface area. A slotted screen of a diameter of 61 mm with such an open screen area would have a perforation value of 0.421. Using this value for the double-cased screen, its open screen area is calculated to be 806.4 cm².

The double-cased screen is a double walled screen unit whose annulus is filled with a hydrophobic material. It has been patented in Europe and the United States by the company IEG mbH, Germany.

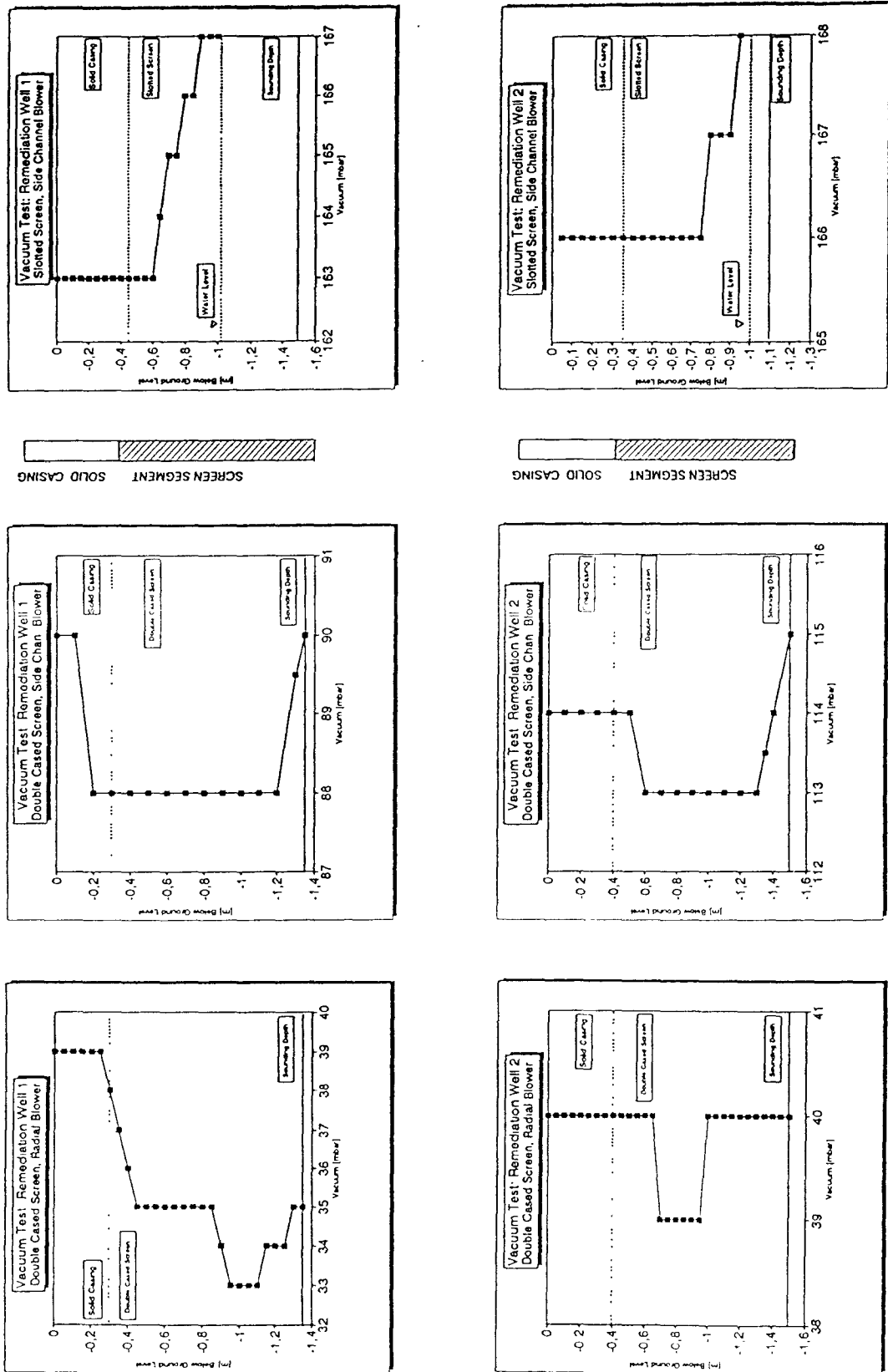


Figure 13. Construction diagram of the soil air wells and pressure distribution along the well casing.

Operation of the Remediation Wells

Due to the unknown influences from the adjacent secondary contaminations in this case, a stable, slowly descending contaminant removal curve was not to be expected. Such a contaminant removal would be necessary for examination and comparison at the effects of different techniques on contaminant removal. Therefore, the contaminant removal data and the changes of contaminant distribution within the soil were not incorporated into this study. During the ventilation of soil air, water is always additionally removed as air humidity. This phenomenon and the effects arising from it are used as parameters in this study for comparison and evaluation purposes. Specifically, the content of water within the remediation well itself and in the extracted soil air were monitored.

Each pair of remediation wells was equipped with two different types of air suction pumps; a radial blower (ventilator), which generates a large air flow volume while creating only a low vacuum, and a side channel blower, which creates a high vacuum but generates only a small air flow volume being conditioned by design. Each of the four combinations of pump/well construction was tested and results were subsequently recorded for a remediation period of more than 4000 hours. The following conditions are valid for each pump/well combination:

- (1) The remediation wells of each pair are situated in the same distance from the center of the primary contamination within the soil.
- (2) The screened segments of all remediation wells are equally long (1 m), and the wells of each pair are positioned at the same depth level.
- (3) Neither groundwater, stratum water, nor infiltration water was encountered during the drilling of the wells. The soil which was drilled through had a normal moisture content.

Data and Calculated Values

At the beginning and the end of each test run for a particular pump/well combination, the soil air temperature, humidity, and flow rate were measured as was the vacuum within the well. Soil air samples were also taken at these times. If any single test run lasted longer than 14 days, all measurements were repeated and average values were determined. In addition, the accumulation of water in each remediation well was monitored and if present, measured. During operation of the venting systems, a profile of the pressure distribution along the screen sections was determined.

From existing data and the measured parameters, the following values were calculated and utilized for evaluation purposes.

The air volume amounts are given in cubic meters, normalized to 0° C (273.15 K), 1013.25 mbar, and 0% humidity (dry air). The absolute air humidity was calculated from the relative air humidity and the air temperature. The velocity of the soil air entering the well was determined with respect to the open screen area and using the calculated air volume flow rate and the respective perforation values. The water transport rates were calculated using the normalized air volume flow rates.

Results from the Soil Air Venting Test Runs

The results of the individual test runs are graphically presented in Figures 14-16. Of particular note is that over the entire course of the remediation operation, the absolute humidity of the extracted soil air continually decreased. Large differences in water transport rate, water accumulation within the well, and vacuum existed among the different pump/well combinations. These combinations also yielded very different distributions of pressure along the screen segments of each well (see Figure 13). Comparing the air volume flow rate values obtained using the same type of suction pump, it is seen that wells at location LB1 were slightly more permeable than those at location LB2. The average values for the individual test runs are collectively presented in Table 1.

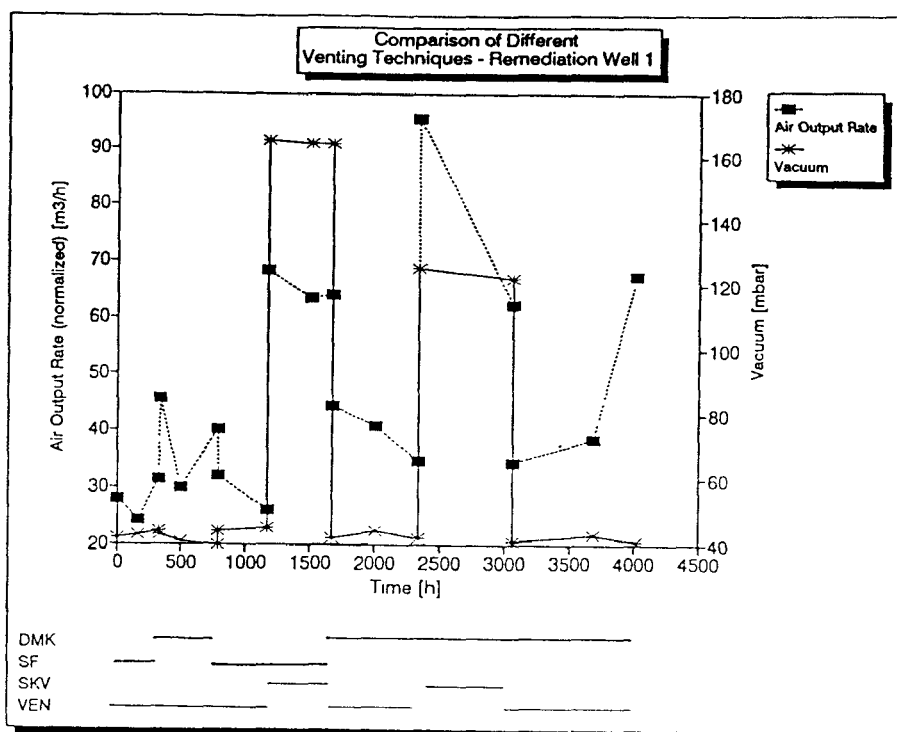
Table 1. Average values for the individual test runs (VEN = ventilator; SKV = side channel blower; SF = slotted screen; DMK = double-cased screen).

Technical combination:	VEN/SF	SKV/SF	VEN/DMK	SKV/DMK
water transport rate (g/hr)	420	850	460	850
air entrance velocity (cm/sec)	81.5	270	13.1	25.4
vacuum (mbar)	43.5	164.3	41.7	121.5
soil vapor volume (m ³ /hr)	26	61	38	74
operating period (days)/maximum	16/0	14/46	87/0	28/0
water level above well bottom (cm)		21/46		

Analysis of Results

The results obtained from the test runs show that the soil - soil air system reacts to the different venting techniques in quite different ways. The most significant result was that water accumulated only in the remediation well which featured the highest vacuum and the screened segment having the smallest open screen area, which in turn generated the highest air entry velocities. Soil air is by nature saturated with water and shows during a venting process relative humidity of approximately 100%. During a soil air venting remediation featuring a high air entry velocity through a slotted screen having sharp inner edges, the moisture present as air humidity will most likely precipitate as water droplets, which will then collect in the well casing. Over a longer period of time, this effect can cause a water accumulation within the remediation well, and from this, a saturated zone with downward flowing water can develop. This zone can eventually come into contact with groundwater lying below the well site. The analysis of soil samples taken from such a zone

(a)



(b)

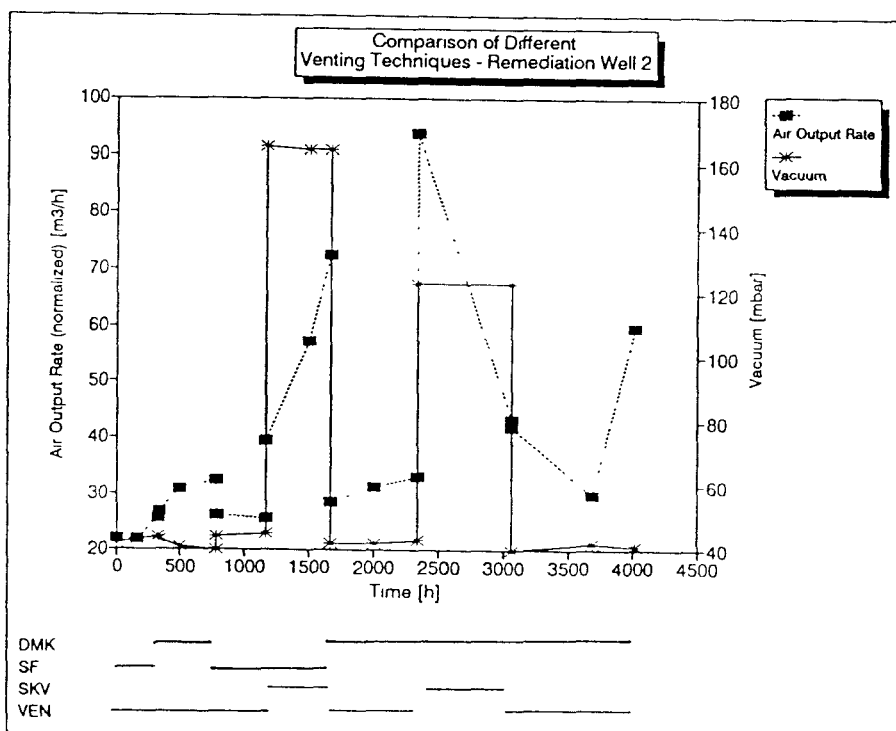
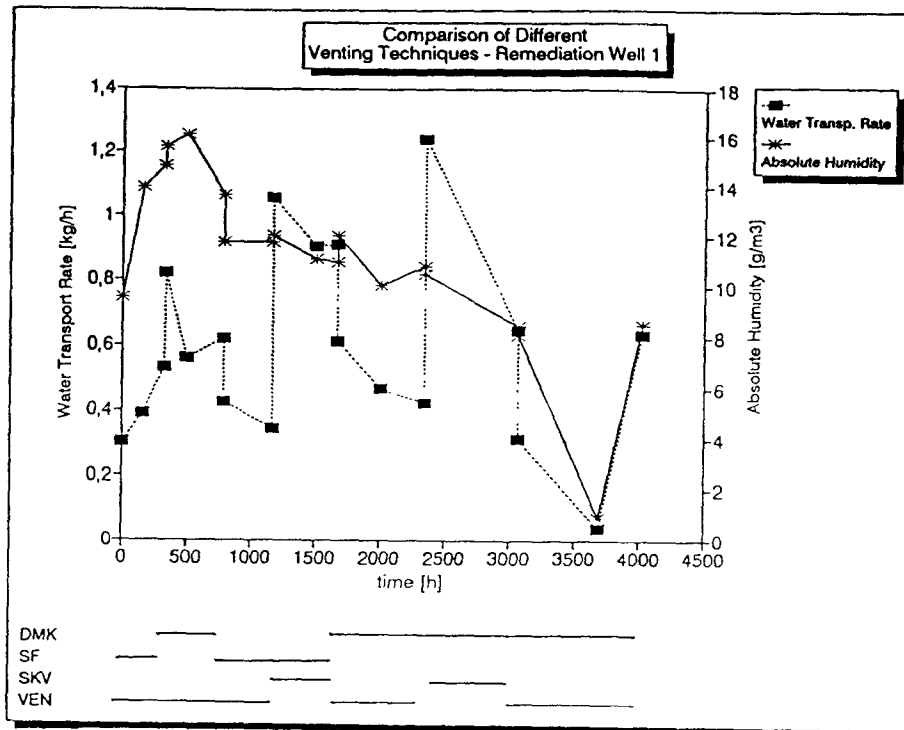


Figure 14. Comparison of different venting techniques (DMK = double-cased screen; SF = slotted screen; SKV = side channel blower; VEN = ventilator): normalized air output rate (m^3/hr) and vacuum (mbar); (a) at position 1 (LB1); and (b) at position 2 (LB2).

(a)



(b)

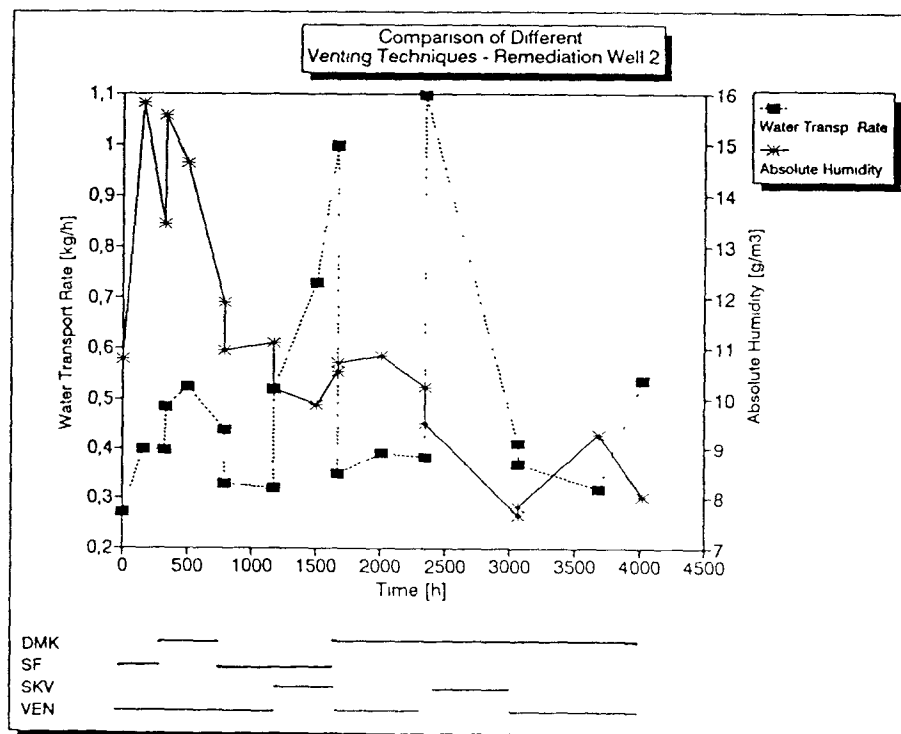
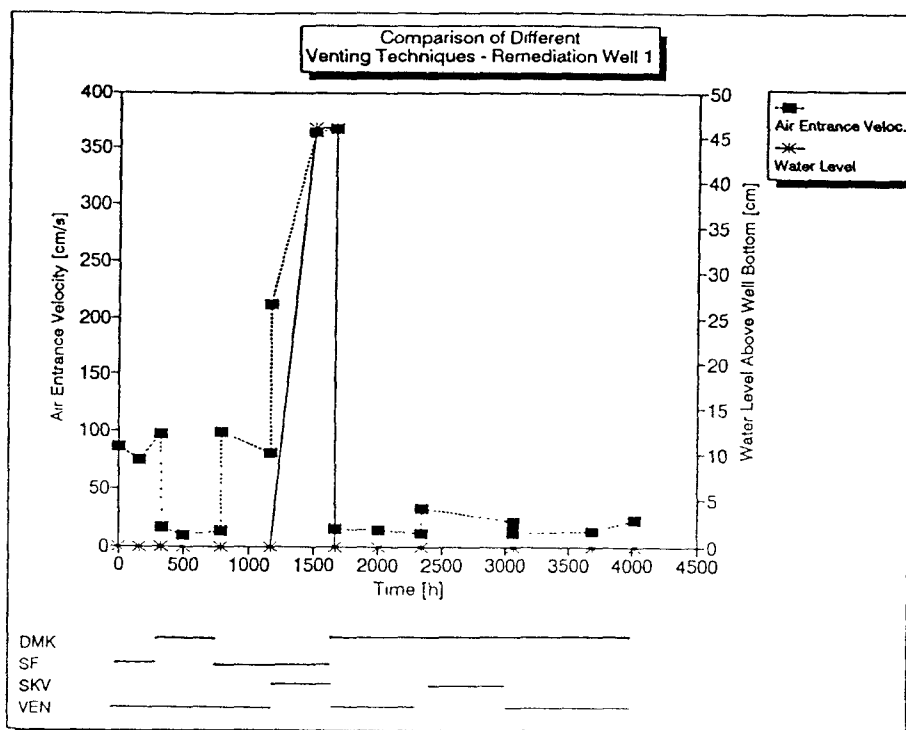


Figure 15. Comparison of different venting techniques (DMK = double-cased screen; SF = slotted screen; SKV = side channel blower; VEN = ventilator): water transport rate (kg/hr) and absolute humidity (g/m^3); (a) at position 1 (LB1); and (b) at position 2 (LB2).

(a)



(b)

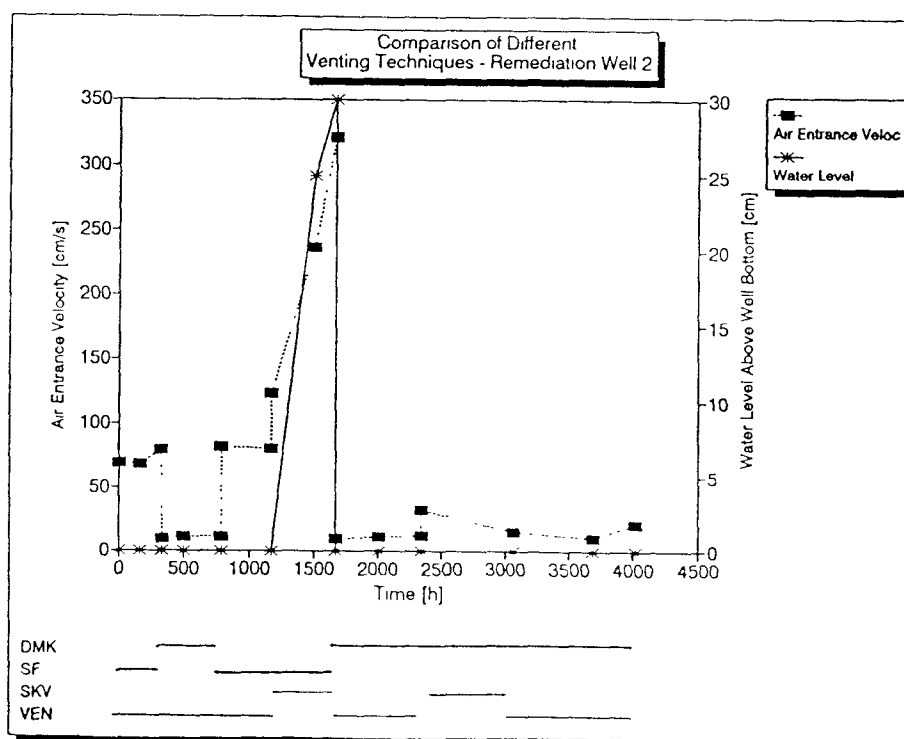


Figure 16. Comparison of different venting techniques (DMK = double-cased screen; SF = slotted screen; SKV = side channel blower; VEN = ventilator): air entrance velocity into the well (cm/sec) and water level above the well bottom (cm); (a) at position 1 (LB1); and (b) at position 2 (LB2).

underneath the bottom of a soil air venting well being developed during a remediation case, where slotted screen segments were utilized, showed the soil to contain high concentrations of volatile CHC. The continuous decline in the humidity of the extracted soil air over the entire remediation period could be an indication that the soil in the immediate vicinity of the remediation wells slowly lost moisture and became drier. Due to the situation present in this case, this phenomenon could not be linked to any specific venting technique or combination. High air entry velocities at the screen segments of a remediation well, however, create high nonuniform air flow velocities within the soil. When this occurs, a slow drying out of the surfaces of the fine-grained soil particles can take place. This can result in the vaporized contaminants being removed from the soil air and will be absorbed onto these dry surfaces (see Pederson and Curtis, 1991, p. 29ff), and thus only being displaced within the soil without being removed from the underground. Further studies should demonstrate if these processes can be confirmed by taking soil samples near the screen section of a remediation well throughout a remediation period.

The results obtained from these test runs suggest the venting techniques which produce high soil air velocities yield significant negative side effects within the soil - soil air system. In order to better understand these effects, more research is necessary. For the formulation and optimization of soil air remediation strategies, venting techniques which do not cause the accumulation of water in the remediation well and do not promote the drying out of the soil in the vicinity of the soil air venting well are preferable. For keeping these negative effects to a minimum, a greater open screen area, low air flow velocities within the soil and at the screen segment openings, screen openings free of sharp edges, and the establishment of an even vacuum distribution along the length of the screen segments are required.

The pressure values obtained from the test runs, which used screen segments of 1 meter in length, show that the achievement of an equal vacuum distribution occurred most likely and was mostly even with the combination of the double-cased screen and the radial blower. All the data indicate that the flow conditions at the entry surface of the screen and within the soil surrounding the casing promoted the development of a laminar flow of the soil air to the greatest possible extent. When considering the major factors involved in the development of a thorough, fast, and cost-effective remediation process for a contamination of the unsaturated zone, namely screen segment's entry speed (slow), vapor volume flow rate (high), and water transport rate (low), the combination of double-cased screen and radial blower offer the best solution of the four combinations tested.

In order to create comparable operating conditions for the test runs carried out in this study, remediation wells with small diameters and relatively short (1 m) screened segments were utilized. Further studies should show if the results obtained here can also be achieved using wells of greater diameter and longer screened segments.

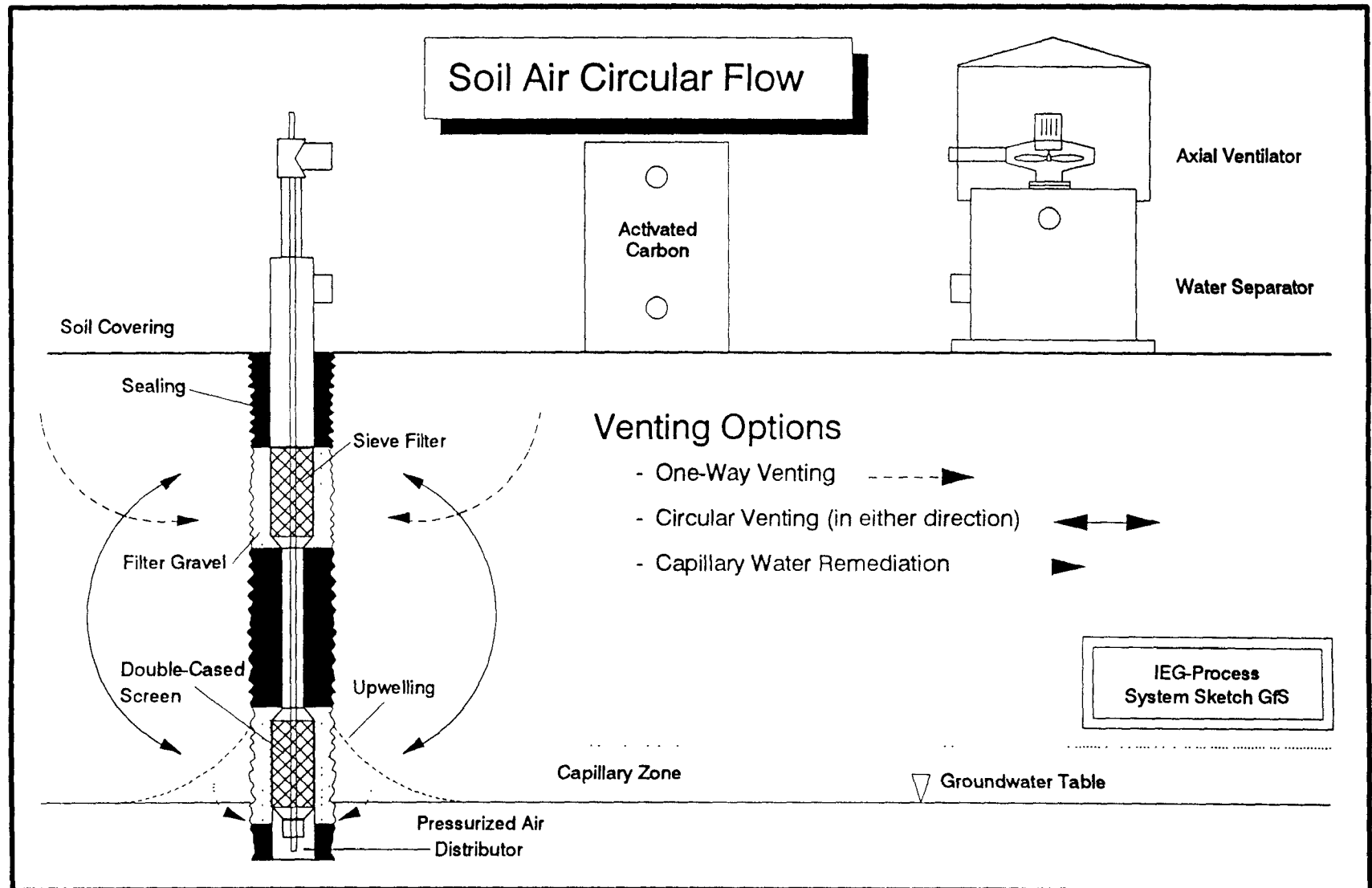
SOIL AIR CIRCULATION FLOW AND COAXIAL GROUNDWATER VENTILATION

(Contribution by E.J. Alesi)

Soil Air Circulation Flow

Directed soil air circular flow systems (SACF) are employed for the remediation of soils polluted with volatile contaminants (see Figure 17). In addition, it can be used to inject gas into the soil for the stimulation of biological or chemical degradation. SACF is a process patented by IEG mbH, Reutlingen, Germany. The

Figure 17. Principle sketch of the soil air circulation flow.



filter casing built into the bore-hole is separated into an upper and a lower section, each of which is connected to the above-ground ventilator. This allows for the withdrawal of air from either segment individually or from both simultaneously. The air extracted, after passing through a suitable remediation unit (i.e. activated carbon filter), is reinfiltrated into the soil. Horizontal and vertical flow circulation are generated in the soil surrounding the extraction well. The circulation direction is reversible and can be adjusted according to the distribution in the soil.

The SACF, in contrast to conventional venting methods, is capable of generating a directed circulation through the center of the contamination. No fresh air is added to the circulation system. Air passing through the ventilator is heated, thereby enhancing desorption of contaminants adsorbed onto soil particles. This leads to a more effective remediation of the site.

For stimulating the biological degradation of contaminants, nutrients, in liquid or gas form, can be introduced into the circulation. Chemical conversion of toxic substances into harmless and/or immobile material can be achieved in situ by introducing, for example, strongly reactive gases into the soil.

If only biodegradable substances are to be removed from the subsoil a SACF system (without an above ground extraction unit) consisting of an axial ventilator in the screened well can be implemented.

Should the capillary fringe be remediated along with the unsaturated (vadose) zone, it is possible to rinse the capillary fringe by creating a circulation directly around the well casing. This is achieved by a combination of SACF and coaxial groundwater ventilation (see next section).

Coaxial Groundwater Ventilation

Coaxial groundwater ventilation (CGV) is used in the remediation of groundwater and of stratum water contaminated with volatile pollutants, but can also be employed to inject gas into the groundwater for the enhancement of microbiological degradation (see Figure 18). CGV is a method patented by IEG mbH, Reutlingen, Germany.

CGV consists of a combination of soil air venting with in situ groundwater stripping ("push and pull technique"). Clean compressed air is pumped into a pressurized air distributor located between the capillary fringe and the aquifer base according to the vertical distribution of the pollutants. The air bubbles rise within the well, causing the water inside the well casing to flow upward (air-lift effect).

The design of the pressurized air distributor regulates the air flow so that the air can only flow upward. Consequently a continuous circulation of groundwater is generated in the area surrounding the remediation well, delivering new contaminants to the stripping site.

In contrast to other in situ stripping methods, the clean water leaving the upper screen section of the well has no air bubbles, therefore no air-water phases can impede the flow.

Volatile contaminants dissolved in the groundwater are transferred from the liquid to the gas phase in an amount relative to their gas-liquid distribution coefficient and are extracted from the groundwater surface via the double-cased screen. Soil air from the unsaturated zone is also extracted and remediated. By

Soil Air Venting with a Double-Cased Screen Coaxial Groundwater Aeration

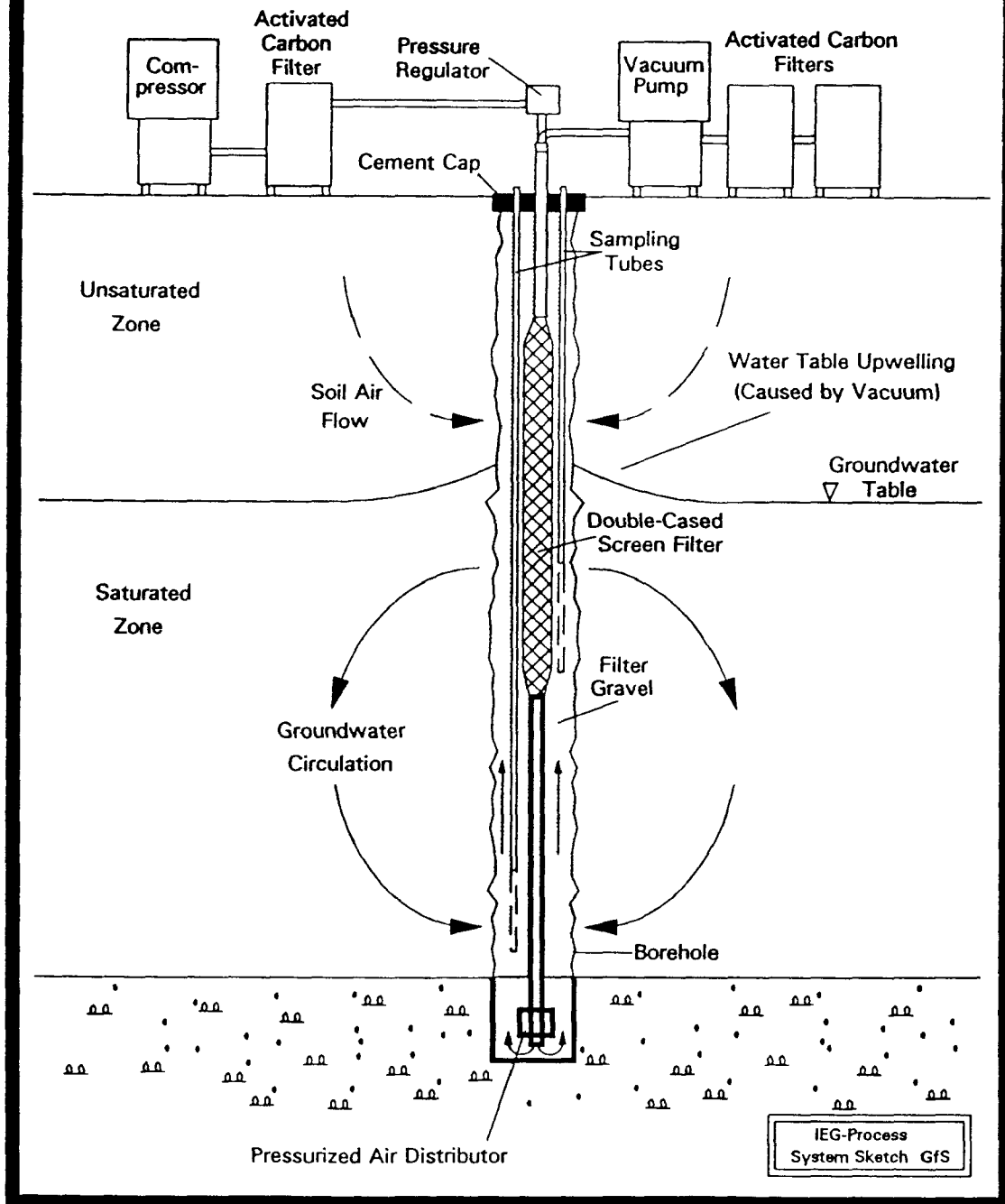


Figure 18. Principle sketch of the coaxial groundwater ventilation.

monitoring the volume of exhaust air the amount of air extracted from the unsaturated zone can be calculated (exhaust air - air injected into well). Small monitoring tubes located in the annular space of the remediation well allow the concentration of the contaminants in the groundwater to be measured before and after passing through the well.

Vertical water and air flows differentiates the CGV from other in situ stripping methods. Of special note is that groundwater need not be removed to prevent contaminant propagation when using the method. Best results can be achieved if fresh air is continuously sucked into the pressurized air distributor. Heating the groundwater and consequently increasing the off-air moisture is thus avoided.

A special advantage of the CGV is its ability to effectively remediate the often highly contaminated capillary fringe.

The difficulties that arise during conventional remediation procedures due to contaminated stratum water, which collects in the remediation well do not occur with the CGV. Stratum water can be stripped directly in the ground without having to pump it up to an above-ground treatment system.

CONCLUSION

The UVB technique can be used for in situ stripping of volatile contaminants from the groundwater zone and to clean the unsaturated zone at the same time by soil vapor extraction. For the saturated groundwater zone, the hydraulic circulation system of the UVB offers many advantages, particularly when compared with a typical hydraulic remediation system of pumping, off-site treatment, and reinfiltration of the groundwater. Such advantages include:

- No lowering of the groundwater level
- No groundwater extraction
- No waste water
- Less permeable, horizontal layers are penetrated vertically
- Remediation of the groundwater takes place down to the bottom of the aquifer
- Even at low well capacity, remediation operation is continuous
- Soil air extraction is possible at the same time
- Low space requirement
- Investment and operating costs will be considerably lower.

When the water discharge through the well casing is directed downward, the hydraulic head is lowered at the well top ($-\Delta h/2$, Fig. 9b; neglecting the increasing groundwater level in consequences of the vacuum), but this amount is much smaller than that caused by a normal withdrawal well.

The total aquifer is caught by the circulation flow of a UVB. When using different wells for extraction and infiltration, only those areas of an aquifer which are more permeable are penetrated. The other areas are reached mainly by diffusion. The groundwater flow system will only locally be influenced, there is no need for large extended groundwater flow investigations. Further, a plume can directly be treated without pumping lots of clean water as in case of using pump and treat methods.

A layered aquifer enlarges the sphere of influence or the distance between the well and the stagnation point. This has been found by numerical simulations and by comparison with field measurements of a tracer test. On the other hand, the positive effect of a layered aquifer is limited when an aquitard is present. Here, several remediation systems must be installed, one for each aquifer.

Different techniques of soil vapor extraction are compared by measured field data at a remediation site. It has been clarified by this investigation that a combination of slotted screen and side channel blower can cause water accumulation in the well casing which may contaminate the groundwater lying underneath the air well. The latter is avoided using a double-cased screen and a radial blower (ventilator).

For the vapor zone, circulation systems can be used as well, e.g. to realize special treatment technologies. A special remediation system allows for cleaning the capillary fringe.

ACKNOWLEDGMENTS

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RESULTS OF A YEAR LONG SIMULATION OF THE END OF A SITE REMEDICATION USING IN SITU VAPOR STRIPPING

ANN N. CLARKE, PH.D.

ECKENFELDER INC., Nashville, Tennessee

ROBERT D. MUTCH, JR., P.E., P.H.G.

ECKENFELDER INC., Mahwah, New Jersey

DAVID J. WILSON, PH.D.

Vanderbilt University, Nashville, Tennessee

1.0 INTRODUCTION

Vapor extraction, alternatively called in situ vapor stripping (ISVS), soil vapor extraction (SVE), or soil vacuuming, in the literature, has been used in treatment trains as well as being the single remedial technology selected. While other technologies are available which target the same compounds, they are often more expensive, pose increased exposure to workers and/or the public, or have other types of site specific disadvantages. Given the positive characteristics of vapor stripping, it is not surprising that the technology has been successfully applied to many sites but with varying knowledge of the scientific and engineering bases behind it. Since the initial phase of vapor stripping usually performs “like gang busters”, we thought it would be a valuable contribution to the field to evaluate what happens at the end of a site cleanup, when the residual levels are low in the soil and low in the extracted vapor. While much of the behavior could be predicted once the site specific kinetics were known, it was thought important to monitor behavior at an actual site. The specific objectives of this test are given in Table 1-1.

In addition, a mathematical model which had already been developed would be tested using the data. Table 1-2 contains the objectives of the mathematical modeling. It was anticipated that from the site and modeling data general conclusions and recommendations could be made regarding the end of a site cleanup by vapor stripping.

An industrial site in New Jersey was selected as the location for these efforts. The specific location was the site of recently demolished manufacturing buildings which had been constructed in the 1950's. This site offered the opportunity to study removal characteristics of the technology at the lower soil concentrations, levels more commonly seen at the end of a remediation program. Preliminary soil testing around the area had indicated that residual volatile organics constituents were present but at relatively low concentrations.

The vapor extraction involved a pilot scale unit which is essentially capable of full-scale operation at a single well. It was extensively instrumented and the site was extensively monitored, both levels being above those usually employed during remediation. There was a total of 42 gas monitoring probes installed around the

extraction well within the zone of evaluation. Each probe was capable of monitoring soil gas vacuum levels and allowing the collection of soil gas samples. Thermistors were employed to monitor soil temperature during the program. Some probes were constructed to monitor a location at three depths.

Table 1-1. Technical Objectives of Pilot Scale Study

-
- Define the three-dimensional flow field established by a soil gas extraction well in an anisotropic, alluvial sand aquifer;
 - Assess the extent of organic compounds removal from the test zone especially at low residual soil concentrations;
 - Understand the spatial progression of the removal over time within the treatment zone;
 - Evaluate the residual, non-strippable levels of various organic constituents in the soil;
 - Evaluate the impact of variations in soil temperature within the test zone;
 - Evaluate the quantity and quality of the liquid collected by the on-line demister;
 - Assess the effectiveness of granulated activated carbon in adsorbing volatile species from the extracted soil gas, especially low concentrations of volatile organic constituents in the vapor stream;
 - Evaluate the impact of surface soil conditions such as moisture blocking and snow cover on the flow field; and
 - Evaluate the extent to which the treatment zone can be expanded by restricting air entry into the soil around the extraction well by means of geomembranes or other techniques (mathematic model only).
-

Table 1-2. Objectives of Mathematical Modeling

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- Determine the importance of radius-of-curvature effects (the Kelvin Equation) on the vapor pressure of a volatile compound present either near or in aqueous solution in a finely divided or porous medium;
 - Estimate the temperature changes which will occur in soils during aeration as the result of evaporative cooling, as the result of heat transport by the air itself, and as the result of the gas;
 - Model volatile compound removal by in situ aeration with a vent pipe;
 - Calculate gas velocity fields in porous soil when the soil surface is covered by an impermeable barrier in the vicinity of the vent pipe; and
 - Calculate gas velocity fields in the vicinity of a vent pipe in porous soil when the Darcy's constant is not isotropic.
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These clusters took samples/data from 5, 10, and 15 feet below surface level. See Figure 1-1 for the layout of the extraction well and monitoring probes. Figure 1-2 is a schematic of the pilot scale unit employed.

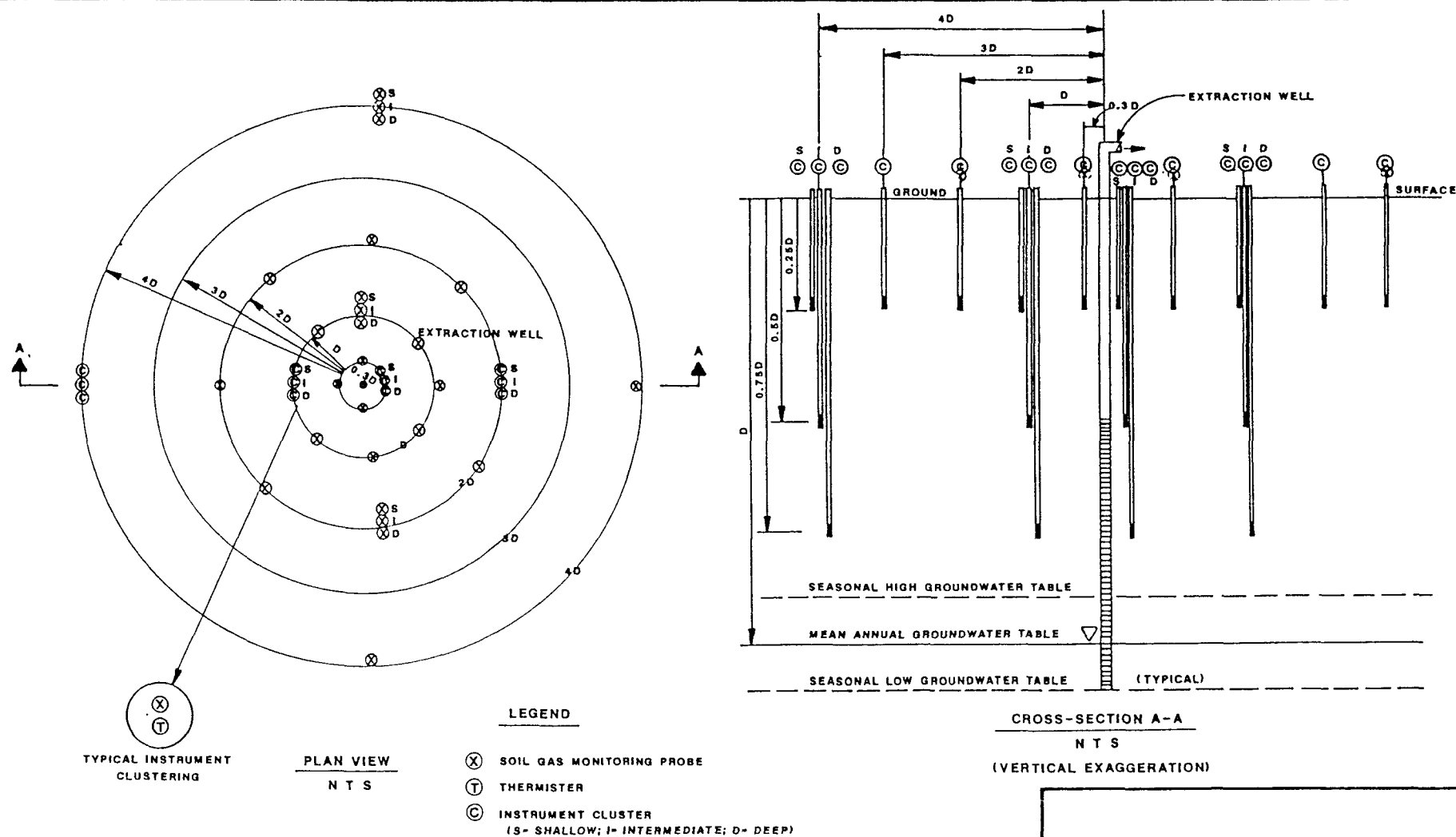


FIGURE 1-1
MONITORING ARRAY

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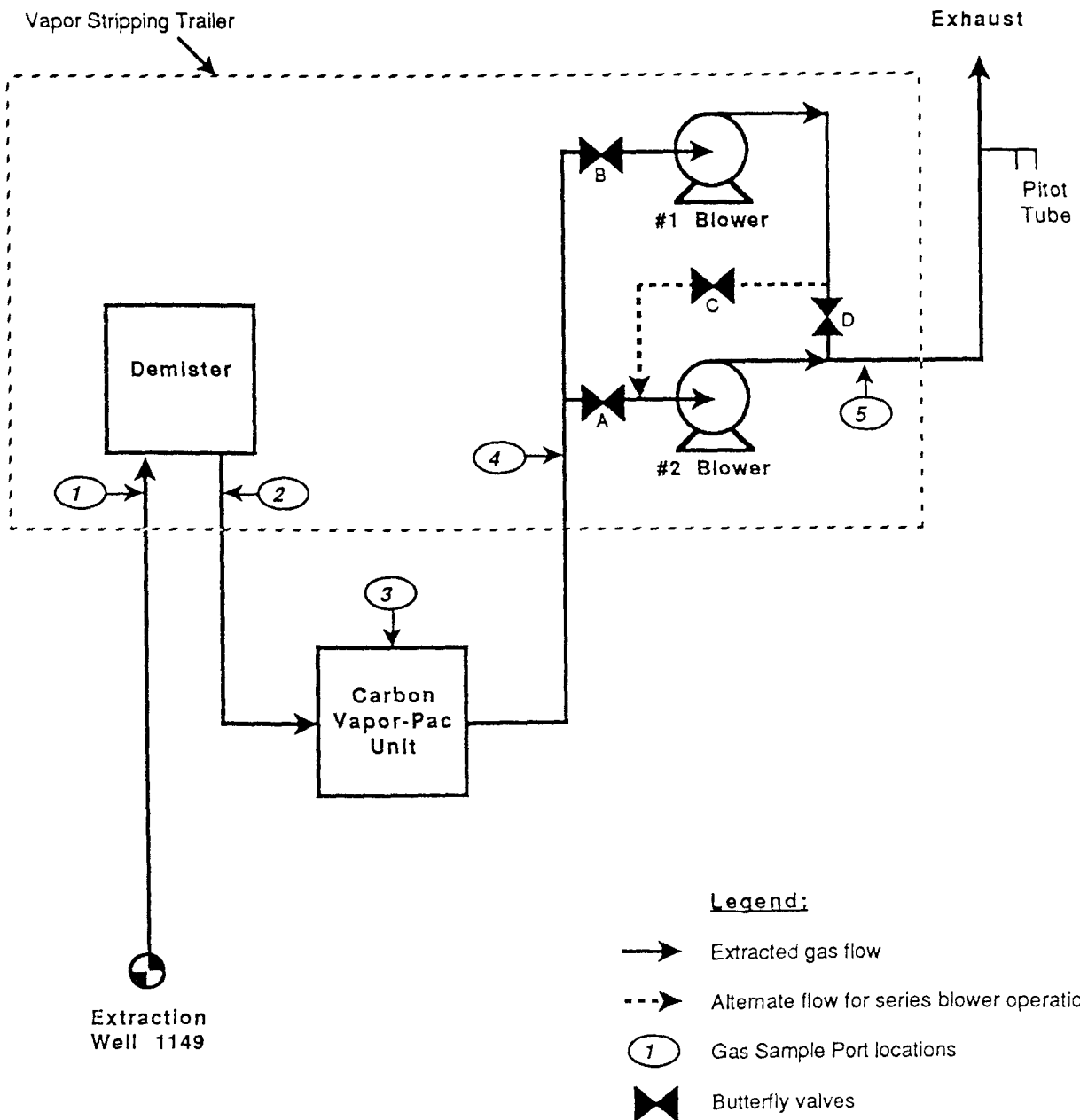


FIGURE 1-2
PILOT-SCALE IN SITU
VAPOR STRIPPING SYSTEM
FLOW SCHEMATIC

ECKENFELDER
INC. Nashville, Tennessee
Mahwah, New Jersey
Rochester, New York

The constituent concentrations in the soil within the study area were determined before beginning and after completing the 12-month program. (See Figure 1-3.) The spatial progression of volatile and some semi-volatile organic constituents and their removal from the soil were studied during this period using a photo ionization detector and chemical specific analysis of the soil gas. The study also addressed the effectiveness of granular activated carbon treatment in the collection of the vapors at the low concentrations extracted and the amount of moisture collected within the demister.

2.0 SUMMARY OF THE TEST PROGRAM

The vapor stripping unit employed at the site was capable of extracting and processing up to 400 cfm of vapor during various weather conditions. Vacuums up to 108 inches of water were capable of being pulled at a 200 cfm flow rate. The unit was equipped with sampling ports at five locations to permit the monitoring of vapor composition, temperature, pressure, and flow. The system was designed to sequentially access each of the ports for a predetermined time period. The unit was operated at one location for 227 nonconsecutive, 24 hour days over a one year period. Down time was limited to routine maintenance, carbon unit breakthrough and exchange, and planned pulsing experiments to assess nonequilibrium mechanisms, such as desorption and diffusion.

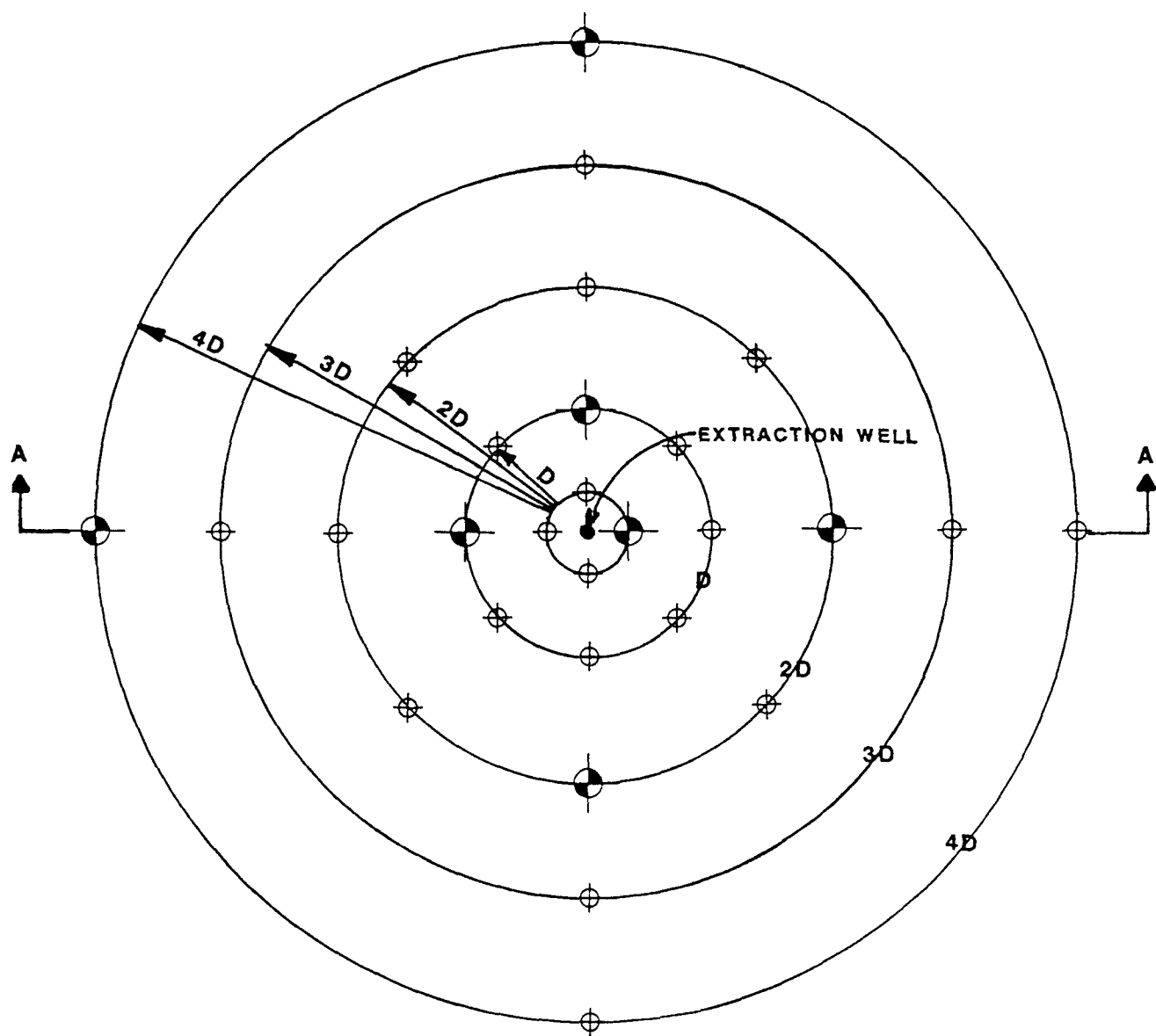
Removal of Volatile Organic Compounds

The study location was selected in order to study VOC removal at relatively low soil concentrations. It was thought that this scenario simulated the latter phases of a site remediation. During the year-long study, several series of off gas analyses were performed using one-liter Tedlar® bags in which the vapors were collected. The bags had not previously been used and had been cleaned prior to use. The bags were outfitted with Teflon(®) and stainless steel fittings. The filled bags were shipped by air in pressurized compartments by express carrier for overnight (non weekend) delivery. The samples were analyzed the next day for the volatile organic constituents at the ECKENFELDER INC. laboratory in Nashville, Tennessee.

Soil gas samples were collected at the ports in the mobile unit previously described and at the monitoring probes. Initial soil gas concentrations were monitored after the installation of probes using an HNu meter. The readings at the probes were generally consistent with the compound-specific soil concentrations identified by the laboratory analyses.

The qualitative/quantitative port data were taken to assist in evaluating the behavior and efficiency of the activated carbon as an off gas treatment option at low concentrations of volatiles in the extracted air stream as well as to assess the overall performance of the technology. It must be remembered that concentration in the extracted air does not directly relate to the residual concentration in the soil.

Figure 2-1 shows the behavior of the concentration of VOCs in the extracted soil vapor with time. Table 2-1 provides a qualitative summary of the volatile organic constituents identified in the soil before and after treatment as well as the VOCs in the condensate collected in the demister and in the soil gas itself. Quantitative results are provided later in this paper.



LEGEND

- ⊕ SHALLOW BOREHOLE DRILLED WITH HAND AUGER
- DEEP BOREHOLE DRILLED BY TRUCK-MOUNTED DRILL RIG

No. of shallow boreholes : 21
No. of deep boreholes : 7

D = Depth to groundwater table

FIGURE 1-3
INITIAL AND FINAL
SOIL SAMPLING ARRAY

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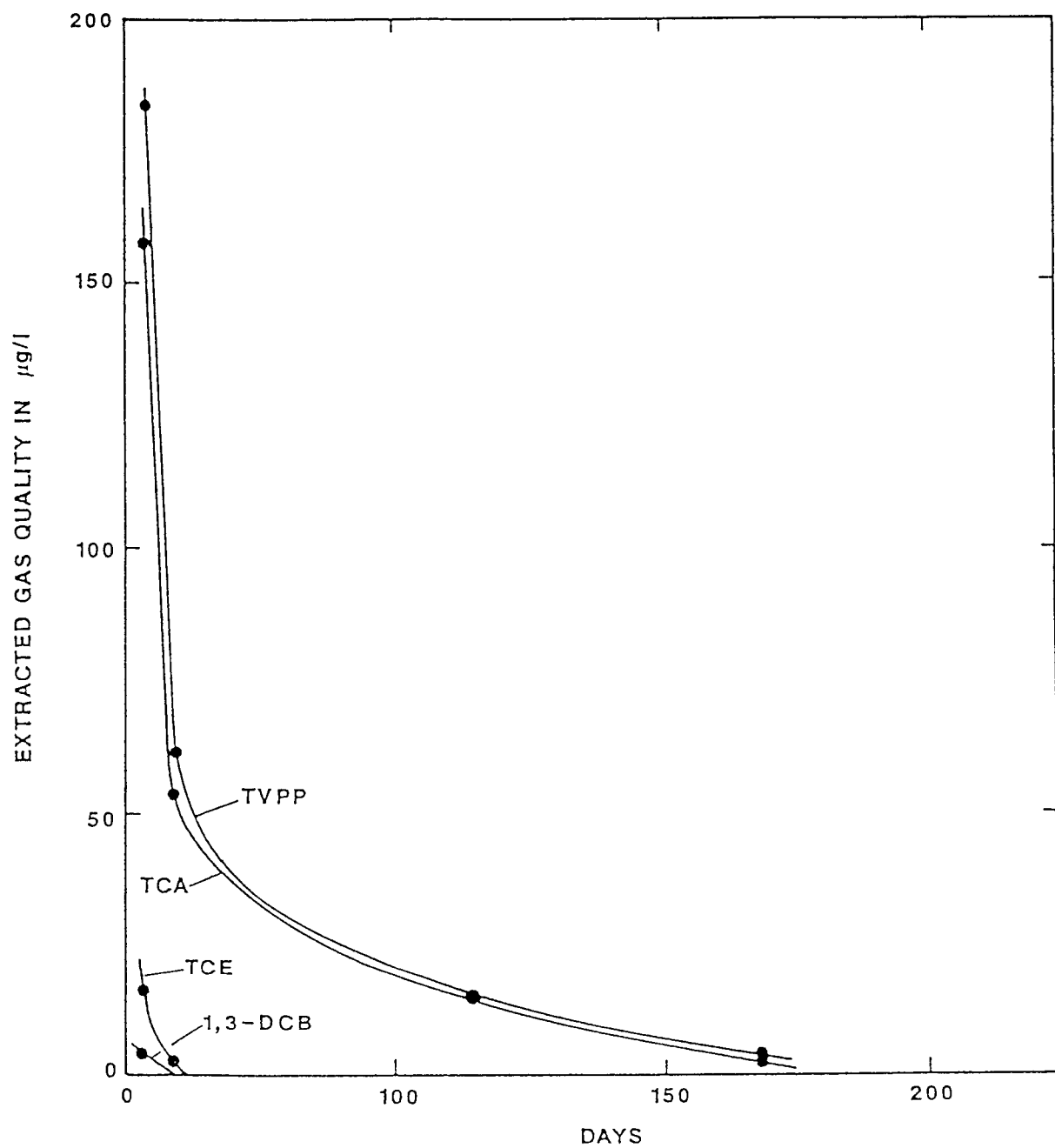


FIGURE 2-1 BEHAVIOR OF VOC CONCENTRATION IN EXTRACTED SOIL GAS WITH TIME

Soil Vacuum Behavior

Prior to the initiation of the continuous operation of the system, the site was tested to see how rapidly it responded to cessation of blower operation (reduction to zero vacuum) and then how rapidly the soil recovered to a steady state vacuum upon reintroduction of blower operation at the same setting. This test was performed analogous to recovery tests performed in water wells. Figure 2-2 is a graphic representation of the response of five monitoring probes to system shutdown. Figure 2-3 is a corresponding graphic representation of the response at the same monitoring probes during the system startup. Each of the five probes monitored recovered their initial vacuum readings within 11 minutes of restart. The zero vacuum readings had been reached for all monitoring probes in 10 minutes or less after system shutdown.

The data collected at the most distant monitoring probes help to establish the radius of influence exerted by the extraction well. This radius was determined by linear extrapolation to zero vacuum under the same operating conditions. An effective radius of influence of 8D (eight times the depth of the well) was determined. It was impossible to monitor the vacuum at this distance since much of the area was paved and had buildings situated upon it.

Vacuum response correlated in a predictable way to weather events. There were uniform increases in the vacuum levels monitored at all probes during snow cover. The vacuum level responses from the water cover developed by the continuous irrigation of the hydroseeded plots were less uniform. This could be anticipated from the nature of the irregular water cover that was generated by these operations, designed to relandscape the site after the demolition of the buildings.

Table 2-1. Summary of Volatile Constituents Identified on Site

Constituent	Identified In		Soil gas stream	Condensate in demister
	Soil before stripping	Soil after stripping		
Trichloroethylene	Y	Y	Y	Y
1,2-Dichlorobenzene	Y	Y	Y	N
1,3-Dichlorobenzene	Y	Y	N	Y
1,4-Dichlorobenzene	Y	Y	N	N
1,1,2,2-tetrachloroethane	Y	Y	Y	N
Tetrachloroethylene	Y	N	N	N
1,1,1-Trichloroethane	Y	N	N	Y
Chloroethane	Y	N	N	N
Methyl chloride	Y	N	N	N
Chlorobenzene	N	Y	N	N

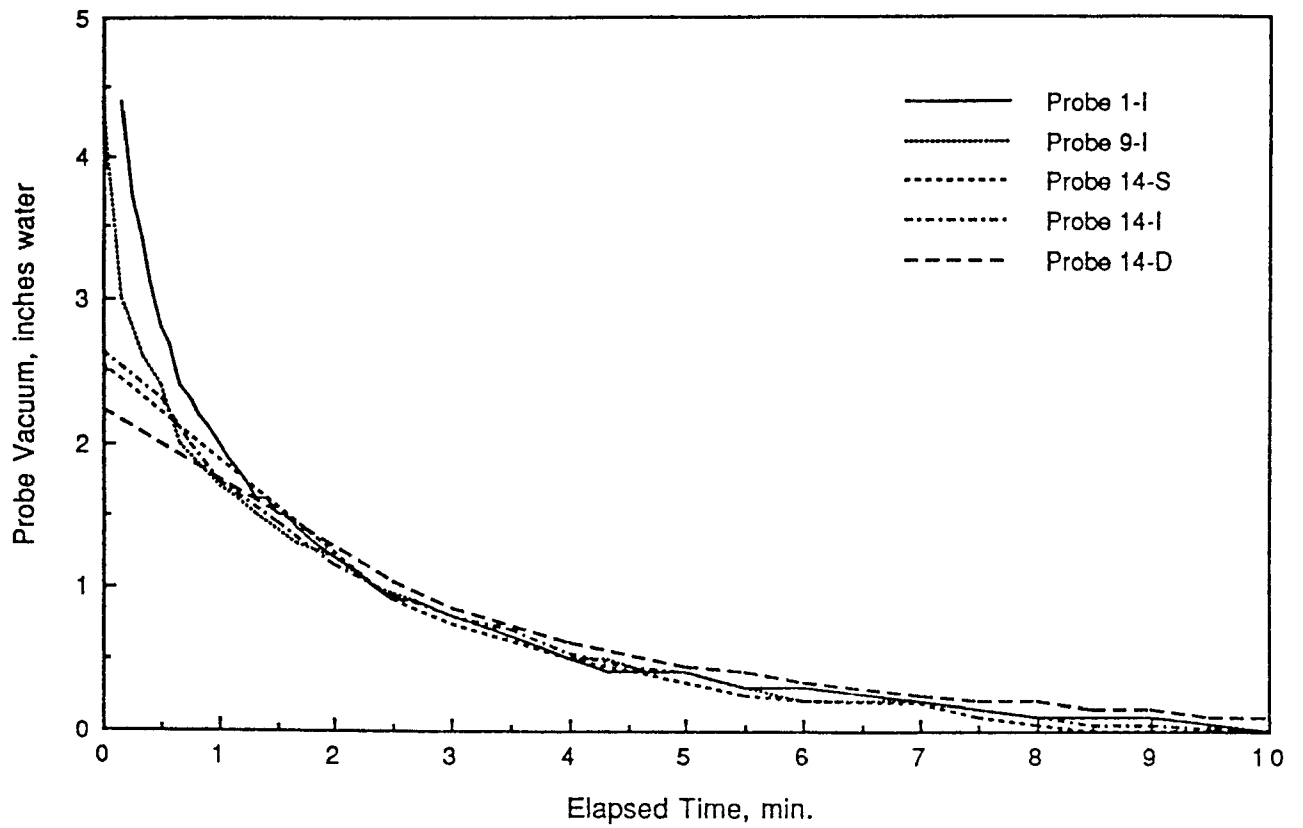


FIGURE 2-2 RESPONSE OF VACUUM IN SELECT MONITORING PROBES TO SYSTEM SHUT DOWN

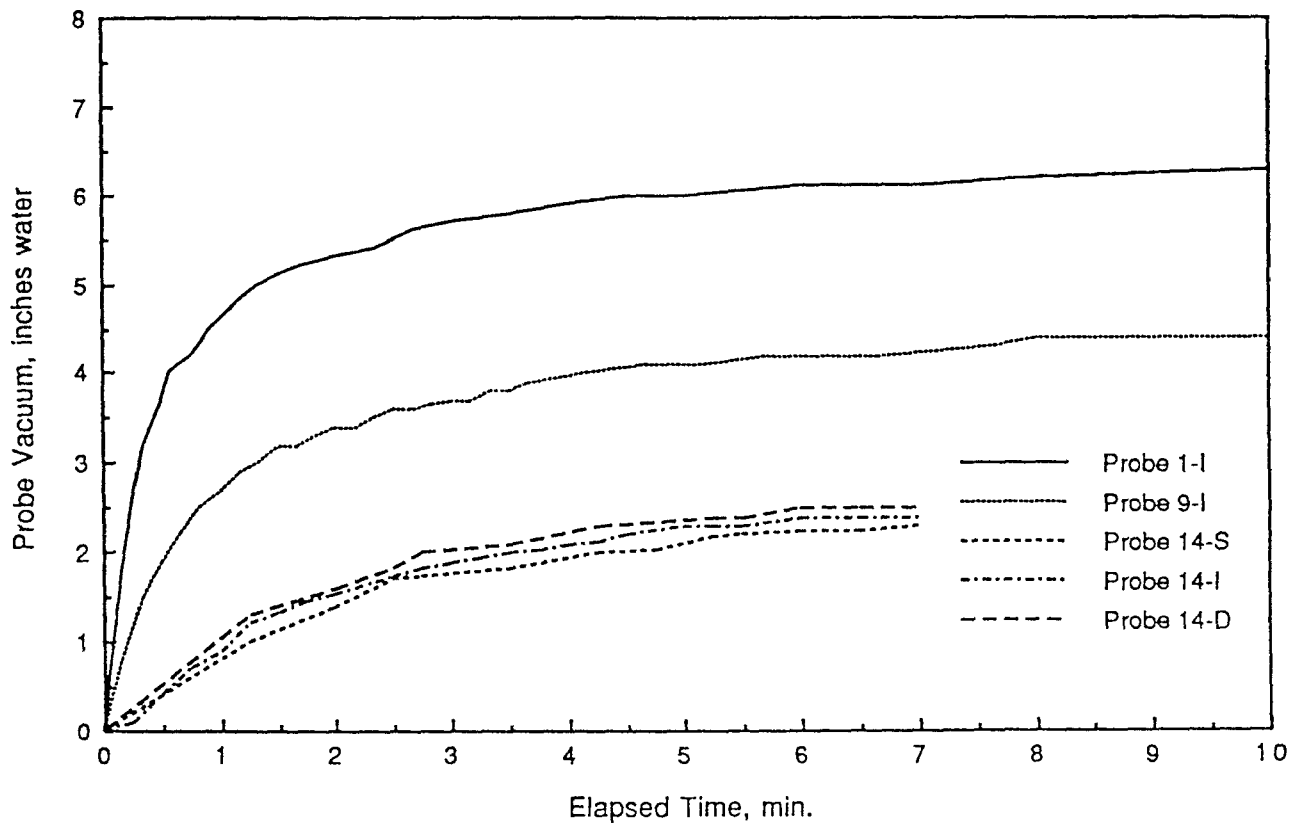


FIGURE 2-3 RESPONSE OF VACUUM IN SELECT MONITORING PROBES TO SYSTEM START UP

Temperature Behavior

Throughout the study, temperature was monitored in the ambient air, the extracted soil gas, and in the soil itself. Because of the insulative properties associated with deep soil, “overtun”, as is frequently experienced in deep lakes, rivers, etc. was seen. The surface soil was most sensitive to the ambient temperatures and in the cooler months, exhibited the lowest temperatures. The temperature of the surficial soils increased until it exceeded the deeper soil temperatures in the warm months. There was also a general correlation of the temperature peaks and valleys at the three soil depths with the sharp rises and declines in ambient temperatures.

As could be anticipated given the heat capacity of soil, the soil gas exhibited only a 10 to 15°C variation over the year while the ambient conditions ranged over 35°C. The data reflected a relatively smooth transition over the period of study. (See Figure 2-4.)

3.0 IMPACT OF NON EQUILIBRIUM KINETICS

At best, the non equilibrium considerations e.g., desorption/diffusion, which normally extend the remediation time, can be capitalized upon to increase activated carbon performance near the end of remediation. At worse, non equilibrium behavior can greatly extend the time required to reach target VOC levels. This is especially true if the system is poorly designed. It is also the non equilibrium factors that cause the VOC concentrations in the vapor not to correlate well to the residual soil VOC concentrations.

A series of three pulsed experiments were performed after the continuous operations had been terminated. System shutdowns times included: 1 hour, 48 hours, and 7 days. The response displayed in all three tests was the same. The response was a relatively rapid increase in VOC concentrations subsequent to turning the system back on followed by a leveling off of the VOC level. For most situations one would normally anticipate a rapid decrease in the VOC level after the initial use in concentration. After the initial increase, the rapid decline was not seen in this study area because of the presence of a hot spot located near the periphery of the zone of influence of the extraction well.

The VOCs desorbed from the hotspot were drawn over this distance to the well. If a hot spot were located close to the extraction well, spike behavior (the rapid increase followed by rapid decrease in VOC concentration) would be seen. The data indicate behavior consistent with a site not totally cleaned up. This was, indeed, confirmed by the existence of a hot spot remote from the extraction well but within the zone of influence. (Remember that the actual zone of influence was twice what was initially anticipated, 8D vs. 4D.) This is an example of a problem that could arise if a hotspot were not originally detected and accommodated for in the design (i.e., location of an extraction well close to the hotspot). The presence of an unanticipated hotspot extends remediation time as well as increases costs.

4.0 PERFORMANCE OF ACTIVATED CARBON ON RELATIVELY LOW CONCENTRATION AIR STREAMS

The use of granulated activated carbon for the treatment of vapor phase organics is a widely employed technology. It is known that the carbon system performs more efficiently at higher VOC concentrations. The presence of water in the extracted gas from an ISVS system further exacerbated the reduced efficiency of

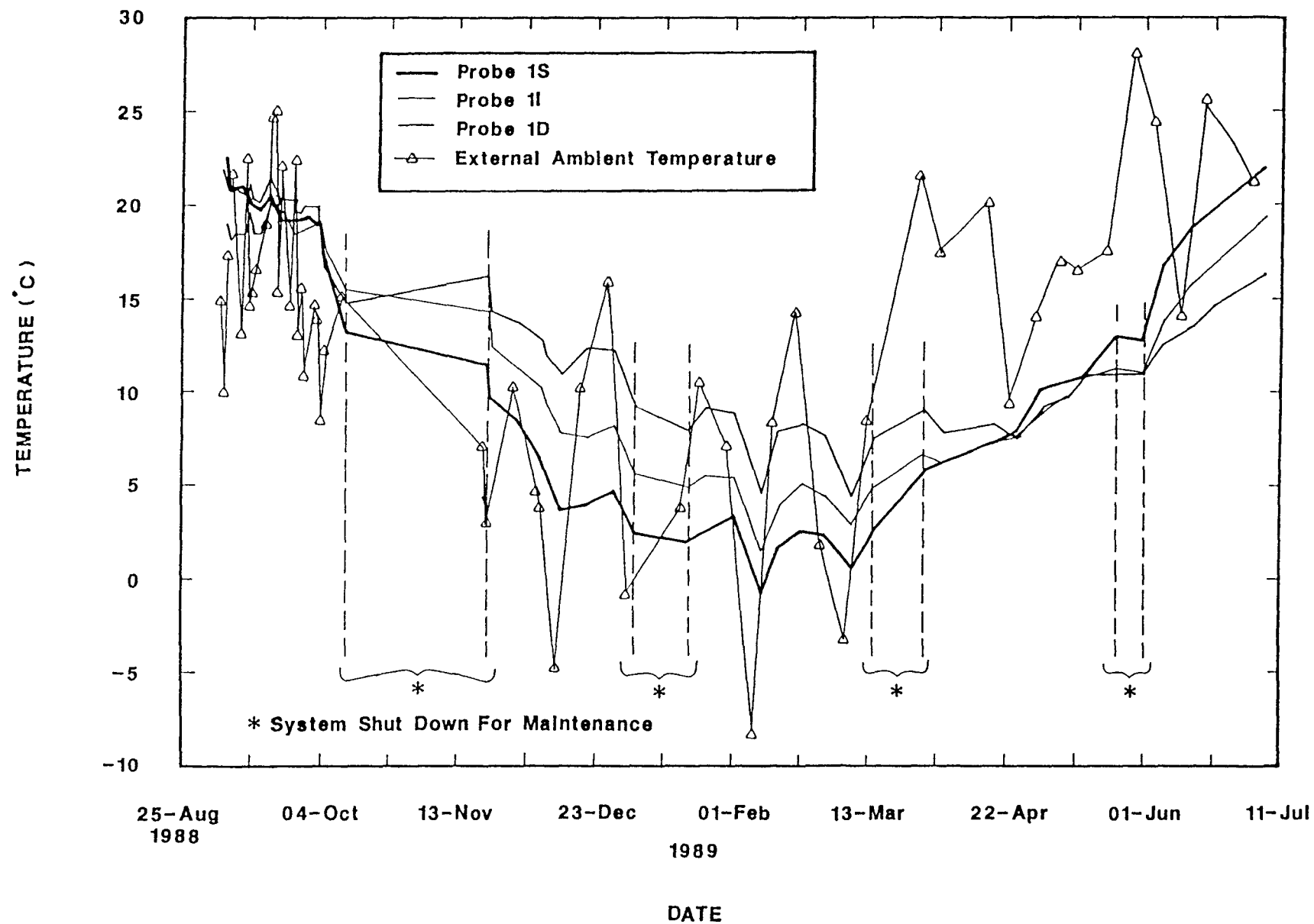


FIGURE 2-4 SOIL AND AMBIENT TEMPERATURES

the carbon at the low VOC concentration. The water vapor successfully competes for sites on the carbon, thus reducing the efficiency further. Thus, it would seem that acknowledging the already high cost of off gas treatment for ISVS systems, the cost can be further increased as the cleanup progresses toward completion. This would be true for other off gas or vapor treatment techniques such as thermal incineration as the contribution of BTUs by the extracted gas steadily declines with declining VOC concentration.

Over the 227 days of operation, approximately 2,900 cubic feet of vapors were adsorbed. This is 0.053 percent of the total 55 million cubic feet of air that passed through the carbon during the test. Based upon the results from the Kriging (described below), approximately 209 kilograms of mass were removed from the zone of influence for an average concentration of 134 mg/L. The removal of 209 kilograms by 5 carbon units containing 1,800 pounds each of the activated carbon represents an average of 5.1 percent efficiency. This is a rather lower efficiency that can normally be realized during the early stages of vapor stripping. Other operating conditions have yielded a percent efficiency in the 10 to 15 percent range, up to as high as 30 percent in some applications.

Consistent with the fact that the gas initially extracted is usually the most concentrated, a smaller volume of gas was treated by the first Vapor Pac unit before the permitted breakthrough level (50 ppm VOC) was reached. The level of efficiency of the carbon for the first flush of VOCs from the soil is approximately one and a half times the system average of the last four units. This behavior tends to support the use of a pulsed approach to vapor stripping near the end of a remedial program. By shutting the system down and permitting a desorption/diffusion controlled build up of the VOCs in the interstices of the soil to develop, a more highly concentrated flow of air can be flushed from the soil when the ISVS unit is turned back on. This approach is discussed in more detail in the next section.

There are several alternatives which can be attempted to extend the useful life of carbon by increasing the efficiency for given site conditions. Efforts which need to be addressed include insulation of piping and increasing the temperature of the gas stream; shifting location of the carbon beds relative to the blower; and checking the internal bed design for short circuiting. Of course, the most obvious answer to this question of increased carbon efficiency is removing more water mass from the vapor stream being treated by the carbon. One needs to be careful, however, as this could create a disposal problem for the demister condensate since the condensed water will contain dissolved VOCs and could be listed as a hazardous waste requiring special handling and disposal. Cooling, of course, is a most reliable means of condensing the water vapor from the gas stream. Other alternatives applicable to larger, full scale operations include on site steam regeneration of the carbon. This too, creates a wastewater stream that could require special handling and disposal.

The HNu is sensitive to water vapor. Therefore, it is recommended that, especially at low concentrations of extracted gas, a flame ionization detector (which is insensitive to water vapor) be used rather than a photoionization detector, PID. Another potential problem is that the PID does not "see" methane. The flame ionization detector, FID, is sensitive to methane. It is not uncommon for areas that have served as landfills that are now being remediated to contain levels of methane which could prove a potential health and safety hazard. The FID under these conditions may "peg-out". A combination of both types of monitoring units may then be warranted.

5.0 VOCS REMOVED BY VAPOR STRIPPING

Estimates of the total amount of volatile organic compounds initially in the soil at the site and of the amount remaining after the vapor stripping are shown in Tables 5-1 and 5-2, respectively. An estimated 200 kilograms of volatile organics or about 65 percent of the amount originally present had been removed by the time the year's testing was over. See Table 5-3. The amount of volatile organic compounds removed from the soil within the measurable zone of influence of the extraction well within the 82 feet radius was estimated by the following procedures:

First, the measured concentrations in the soil before and after vapor stripping were interpolated using Kriging to produce estimated concentrations throughout the soil volume of interest. Kriging was used for the interpolation since this procedure takes into the account the correlation between measured values and produces both an unbiased estimate of the value at each point and a quantification of the estimation error. All Kriging calculations were performed using the GEOBASE system of programs developed at the Department of Mining and Geological Engineering of the University of Arizona.

The first step in Kriging is the estimation of the variogram for the system. The variogram is a measure of the correlation between measurements at a distances of "h" apart. An isotropic system was assumed here since there were insufficient data to establish any dependence of the variogram on the direction or distance from the extraction well.

The variogram was used to Krig both data sets taken before and after treatment. Kriging was performed at three different depths, 5, 10, and 15 feet below the surface corresponding to the measurements obtained from the clustered monitoring probes. The Kriging at each depth was three dimensional. The extrapolated value at each point was the weighted average of the nearest measured value. A maximum of eight neighboring points were used in the interpolation. The maximum distance for which a point was used in the interpolation was 100 feet.

Table 5-1. Average Concentration and Total Mass of Volatile Organic Compounds in Soil before Vapor Stripping

Layer	Depth (ft)	Average concentration (ppm)	Standard deviation (ppm)	Total mass (kg)	Standard deviation (kg)
	5.0	26.9	6.0	241.7	53.8
2	10.0	8.6	2.1	51.5	12.9
3	15.0	2.7	0.5	24.4	4.8
Total soil volume		13.3	2.3	317.7	55.5

Table 5-2. Average Concentration and Total Mass of Volatile Organic Compounds in Soils after Vapor Stripping

Layer	Depth (ft)	Average concentration (ppm)	Standard deviation (ppm)	Total mass (kg)	Standard deviation (kg)
2 3	5.0	9.8	1.6	87.6	14.4
	10.0	2.5	0.5	15.1	2.7
	15.0	0.8	0.1	7.1	0.9
Total soil volume		4.6	0.6	109.9	14.6

Table 5-3. Changes in Average Concentration and Total Mass of Volatile Organic Compounds in Soils as a Result of Vapor Stripping

Layer	Depth (ft)	Change in average concentration (ppm)	Change in total mass (kg)	Percent loss
2 3	5.0	17.2	154.1	63.7
	10.0	6.1	36.4	70.7
	15.0	1.9	17.3	70.8
Total soil volume		8.7	207.8	65.4

6.0 MATHEMATICAL MODELING OF THE VAPOR STRIPPING TESTING USING FIELD DATA

The mathematical model used in interpreting the data from the site assumed the system was cylindrically symmetric about the axis of the vapor stripping well. A three-dimensional model would require computer capabilities that exceed those of the IBM PC compatible units used in this study. The data that were used from the site and the facility are provided in the list of model parameters in Table 6-1.

Examination of a contour plot of log constituent concentration indicated the presence of hotspot between 10 and 13 meters southwest of the extraction well and a second hotspot having concentrations up to nearly 100 times the maximum concentration. This hotspot was located 23 meters due west of the well. This distance was near the perimeter of the estimated zone of influence from the well as discussed previously. Preliminary calculations demonstrated that the smaller hotspot was removed and that the second hotspot controlled the rate of cleanup. Had the hotspot been located closer to the extraction well, the model indicated that removal would have been substantially faster as one could anticipate. If one scaled so that the bulk of the constituents was located in a domain 1 to 9 meters from the extraction well, the model, with the other parameters remaining the same, showed a 98 percent removal of the constituent in 89 days.

Several runs were made with minor variations in the distribution of the constituents. It was apparent that moderate uncertainty in the distribution of the constituents did not have a serious effect on the rate of constituent removal.

The presence of an overlying layer of quite low permeability greatly extended the range of the effective zone of influence of the vapor stripping well at the study site. Originally, a value of four times the depth of the well, or approximately 40 feet, was estimated to be the zone of influence. The actual radius, per measurements, was approximately 80 feet. This was illustrated in a modeling run in which a constant permeability of 1.245 m²/atm • sec was assumed for the domain. Using identical parameters except that the permeability of the overlay was equal to that of the underlying material, the resultant rate of contaminant removal was far less with 951 days being required to achieve the 65 percent removal effected in 227 days. The impact of the two layers is further discussed in the next section.

Table 6-1. Site Parameters Used in ISVS Model

Depth of water table	7 m
Radius of domain	25 m
Thickness of low-permeability upper layer	1 m
Permeability of upper layer	6.5 x 10 ⁻³ m ² /atm sec
Thickness of high-permeability lower layer	6 m
Permeability of lower layer	1.245 m ² /atm sec
Well depth	5.5 m
Gas flow rate	3.34 moles/sec
Packed radius of well	0.35 m
Wellhead pressure	0.94 atm
Soil temperature	17°C
Soil voids fraction	0.25
Soil volumetric moisture fraction	0.1
Soil density	1.7 gm/cm ³
Duration of ISVS operations	227 days

7.0 MEASURED VS. PREDICTED IN SITU SOIL VACUUM LEVELS

It was evident from the previous numerical modeling of the ISVS system at this site that the observed vacuum distribution in the soil could not be simulated assuming isotropic soil conditions. Therefore, initial modeling efforts focused on determining whether the observed vacuum distribution could be simulated by employing a vertically anisotropic soil. It was quickly discovered that no amount of vertical anisotropy, including horizontal and vertical values as high as a thousand times different, could account for the observed soil vacuum distribution. Table 7-1 lists the parameters used in the soil vacuum model. Subsequent modeling efforts focused on the possibility that the observed vacuum distribution resulted from a layered heterogeneity rather than vertical anisotropy. The numerical model was reconfigured to simulate a two-layered geologic system with the upper layer assumed to be 1 meter in thickness and of a lower permeability than the underlying layer. The underlying layer was assumed to be 6 meters in thickness and of a uniformly higher permeability than the upper layer. A series of model runs determined that the best match of the modeling results to the observed vacuum distribution in the soil was achieved with a permeability of 6.5×10^{-3} m/atm s for the top layer and 1.2 m/atm s for the underlying layer. A comparison of the results of the numerical model and the distribution is provided in Figure 7-1.

The calibrated model indicated that the upper soil layer has an air permeability of approximately 1/200 of the underlying stratum. This was not surprising since 25 percent of the surface area of the study area was covered with concrete footings upon which the recently demolished buildings had stood and the intervening surficial soil was predominantly fill material of a somewhat finer texture than the underlying native soils. It was also note-worthy that the model assumed each of the two layers as individually isotropic. Since air flow in the upper stratum was essentially vertical, it is the vertical permeability of this unit that was critical. Variation in the horizontal permeability of the upper stratum had little or no effect on the outcome of the modeling. Similarly, since air flow was nearly horizontal in the lower stratum, it was the horizontal permeability of this stratum that was of importance to the modeling effort. Variations in the vertical permeability of the lower stratum had no perceptible effect on the outcome of the model.

Table 7-1. Parameters Used in Model of Soil Vacuum Level

Depth to well screen = 5.5 meters
Equivalent radius of spherical well intake = 0.35 meters
Soil porosity = 0.25
Soil gas temperature = 17°C
Extraction well pressure atmospheres = 0.94
Flux = 3.33 gram moles/second

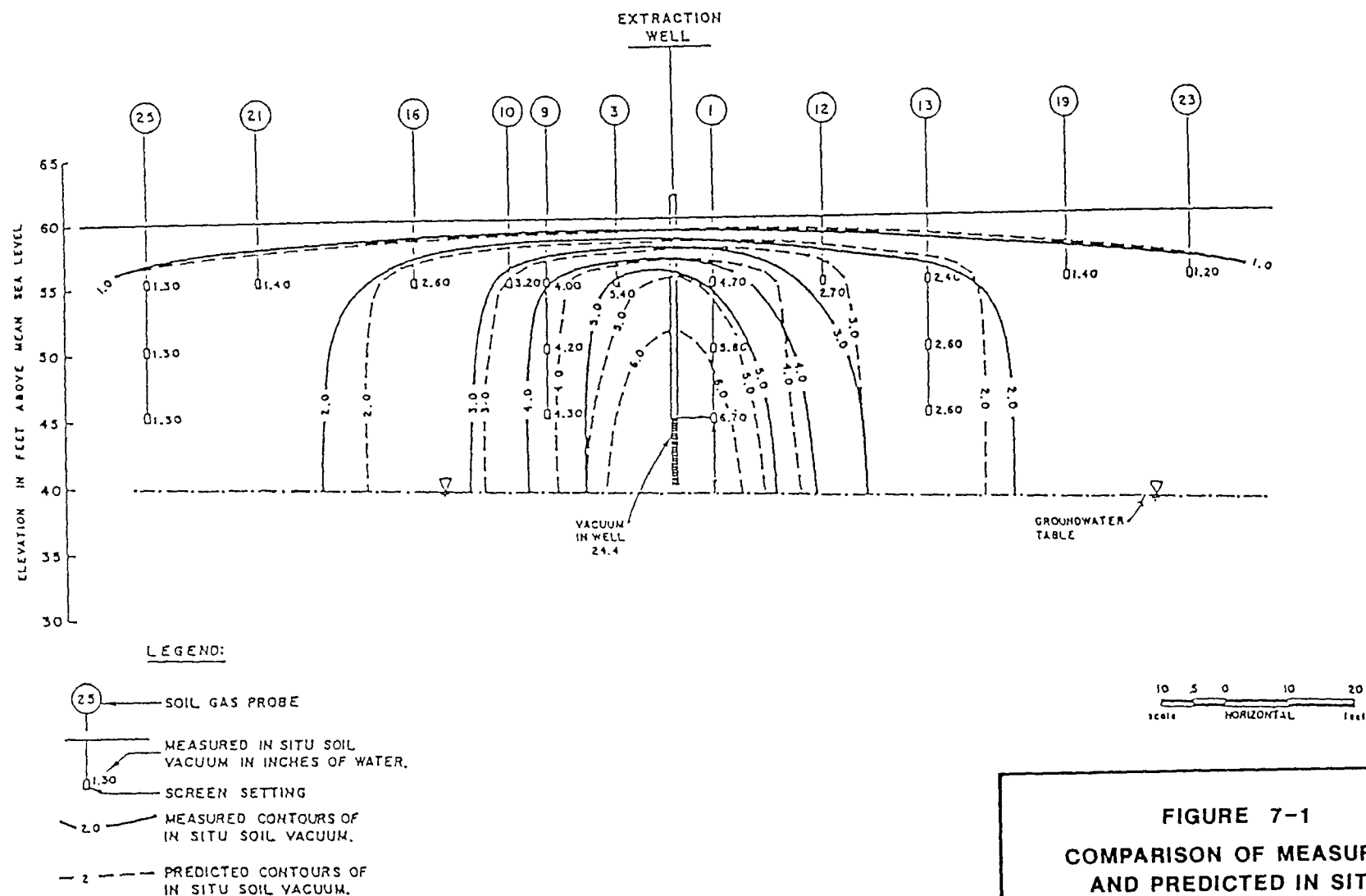


FIGURE 7-1
COMPARISON OF MEASURED
AND PREDICTED IN SITU
SOIL VACUUM LEVELS

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INC.

Nashville, Tennessee
 Mahwah, New Jersey
 Rochester, New York

8.0 SUMMARY AND CONCLUSIONS

The year-long in situ vapor stripping program showed that there are some special problems encountered near the completion of a remedial program and that these problems should be anticipated as well as possible and addressed in the beginning of the program in order to meet deadlines, budgets, and target cleanup goals. Specifically, nonequilibrium conditions and the location of contaminant hot spots with respect to the vacuum extraction well placement will drive the overall cleanup time. Because of these factors, the nonequilibrium kinetics and the contaminant distribution, one cannot simply correlate the concentration in the off gas to the residual constituents in the soil. Adequate detailed information on the spatial distribution of contaminants and the major features of the permeability of the site must be available for use when pilot scale studies are designed. If this is not done, the pilot scale testing might result in unnecessarily poor performance and excessively pessimistic assessment of soil vacuum extraction.

The results of the testing further demonstrate the importance of good site characterization to the successful remediation. If this had been an actual remediation program, an extraction well would have had to been placed closer to the major hotspot for more efficient removal of VOCs--even if this were late in the program after results were interpreted to indicate the presence of the hotspot.

Off gas treatment can be a large part of in situ vapor stripping budgets. As one nears the end of remediation, the overall efficiency of the treatment is reduced by the lower concentration of volatile compounds in the extracted air stream. This in turn results in even higher costs per unit weight VOC sorbed.

Another recommendation that can be made as the result of this year long program is the use of technology-based criteria for developing soil cleanup targets using vapor stripping technology. Efforts should be made to reduce the impact of nonequilibrium behavior through appropriate design, flow rates, control, and on and off cycling. The combination of these two factors should lead to a more realistic set of clean up objectives.

AIR SPARGING EXTENDING VOLATILIZATION TO CONTAMINATED AQUIFERS

RICHARD A. BROWN, PH.D. AND RICARDO FRAXEDAS

Groundwater Technology, Inc.
310 Horizon Center Drive
Trenton, NJ 08691

INTRODUCTION

Traditionally, soil and groundwater contamination have been treated by excavation of the contaminated soils and/or by pumping and treating the contaminated groundwater. Soil excavation is often neither a practical nor cost effective solution, and groundwater treatment often is still required following soil excavation. Groundwater pump and treat, while effective in containing contamination migration, is generally an unacceptably slow remediation process.

If, as an alternative to groundwater extraction, the dissolved/adsorbed contamination can be removed in place, accelerated remediation of the site, reduced costs, and long term protection of potential downgradient receptors could potentially be achieved. Soil vapor extraction has proven to be one of the more applicable technologies for treating contaminated soils. This approach is, however, applicable only to unsaturated soils. Volatilization can also be accomplished in saturated zones by sparging air under pressure through soils below the water table. This process removes volatiles from the sorbed and dissolved phases thereby providing treatment to both the soils and groundwater, in saturated soils.

Approximately seven to ten years ago the use of vapor extraction technology was developed and applied to the treatment of soils contaminated with VOCs. During this process, contaminants are physically removed using a form of in-situ air stripping or volatilization. This approach is normally conducted using the application of vacuum to induce air flow through soils. Because the key to its successful use is inducing air flow, soil vapor extraction technology has been limited to unsaturated soils. Treatment of soil contamination below the water table with soil vapor extraction is often unfeasible since it requires extensive dewatering of the contaminated area to create unsaturated conditions and facilitate induced air flow.

A recent innovation in remedial technology has, however, extended the utility of soil vapor extraction to water saturated soils. This technology is referred to as air sparging. In this process, air is injected under pressure below the water table. The air bubbles which have formed traverse horizontally and vertically through the soil column creating transient air filled regimes in the saturated zone. Volatile compounds that are exposed to this sparged air environment "evaporate" into the gas phase and are carried by the air movement into the vadose zone where they can be captured by a vent system.

Air sparging effectively creates a crude air stripper in the subsurface. The soil acts as the packing. Air is injected and allowed to flow through the water column over the “packing” (Figure 1). Air bubbles that contact dissolved/adsorbed phase contaminants in the aquifer cause the VOCs to volatilize. The entrained organics are thus carried by the air bubbles into the vadose zone where they can be captured by a vapor extraction system or, where permissible, allowed to escape through the ground surface. As an added bonus, the sparged air maintains high dissolved oxygen, which enhances natural biodegradation.

Air sparging also creates turbulence and increased mixing in the saturated zone, which increases the contact between groundwater and soil. This will result in higher concentrations of VOCs in the groundwater which can be recovered by pumping or stripped by sparging.

Combining air sparging and soil venting is an effective means of treating volatile organic contaminants both above and below the water table. There are two reasons why a vent system is combined with the sparge system. First, in sites where volatile contaminants have reached the water table, soil contamination is likely to occur above, at, and several feet below the water table. Addressing the soil contamination, therefore, requires application of both traditional soil vapor extraction (venting) and air injection (sparging). This combined air sparge/vent system (ASV system) is effective in treating volatile organic chemicals distributed throughout the soil column. A second reason is that the chemicals mobilized by the air sparging system could discharge, near or at ground surface if not effectively captured in the vadose zone. The vent system is the mechanism which prevents such a discharge.

AIR SPARGING CASE HISTORY

Air sparging is an effective remedial technology. The following case history illustrates its effectiveness.

The site is the former location of a dry cleaning facility. Soil and groundwater contamination resulted from leaking underground storage tanks which were located in the north-north western part of the property. The tanks, which have been removed, were used to store dry cleaning solvents. Primary groundwater contaminants have been identified as perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and some total petroleum hydrocarbons (TPH) related to heating oil. PCE is the primary contaminant of concern. TCE and DCE are present primarily due to biologically mediated reductive dehalogenation.

The subsurface environment at the property generally consists of miscellaneous occurrences of fill material (coarse sands) sporadically overlying a continuous sheet of naturally occurring Quaternary sediments. Site-specific geologic conditions are such that a natural barrier (clays of the Potomac Formation) exists which locally minimizes the potential for vertical downward migration of dissolved-phase total petroleum hydrocarbon and chlorinated volatile organic compounds (VOCs) present in the shallow water bearing zone into deeper water bearing units. This is supported by water quality data obtained from the deep wells.

PCE, TCE, DCE and total petroleum hydrocarbon constituents were detected in groundwater samples collected from shallow monitoring wells at various locations on the property. Depth to water was ~15 feet. The detection of dissolved-phase PCE and total TPH constituents is consistent with the previous use and storage of PCE product and fuel oil in underground storage tanks at the property. The occurrence of other dissolved phase chlorinated constituents such as TCE and DCE is likely a result of natural anaerobic biodegradation of the perchloroethylene product.

Based on data obtained from several pilot tests a pattern of additional vent and sparge points was developed to provide overlapping influence (negative net pressure) and favorable site coverage for the treatment system (Figure 2). A complete list of treatment points installed at the site is specified below.

7 combination vapor extraction/air sparge points (AS/VP1-AS/VP7); (see Figure 3 for typical schematic construction diagram).

1 vapor extraction only point (VP1);

7 sparge only points (AS1-AS7).

The venting system used a 15 Hp, Oil Recovery Systems soil vent system having a capacity of 500 CFM at 40 inches of water column vacuum. Influent vacuum/flow rate is controlled with an ambient air intake valve. A liquid knockout tank, particulate filter and muffler will be placed on the influent line to eliminate or reduce water generated during system operation, solids and noise respectively. An effluent muffler was specified to further reduce noise levels to meet zoning regulations. Two 1800 pound granular activated carbon (GAC) units were specified to be used in series on the vent effluent to remove contaminants from the vent air prior to discharge. These units are capable of accepting air flow rates in excess of 500 CFM.

The sparge system used a 20 Hp rotary lobe type blower capable of delivering 270 CFM at 10 psi. As with the vent system, a particulate filter is provided on the inlet to protect the moving parts of the unit. System pressure is controlled with a valve on the ambient air discharge line placed on the pressure side of the sparge blower. Noise reduction was achieved with mufflers on the inlet, outlet and ambient discharge lines of the system. The air sparge blower was also furnished with an overpressure relief valve set to open at 15 psi.

Figure 4 shows an isoconcentration map illustrating that dissolved-phase total petroleum hydrocarbon and total PCE, TCE and DCE constituents were primarily isolated to the shallow saturated Quaternary sediments with migration of the constituents occurring in a hydraulically downgradient direction from the former underground storage tank field area(s). This is consistent with the direction of inferred groundwater flow within the water table aquifer. Contamination on site ranged from 40,000 ppb near the former tank pit to less than 10,000 ppb total VOC.

In the first phase of remediation, the vent system was initiated. Total flow from the eight vent wells was approximately 450 CFM at a vacuum of 25-30 inches of water column. After about one month of operation, the vent system VOC influent concentration had dropped to <10 units. At this point, the sparge system was started beginning with the outer ring of sparge locations. The VOC levels rose in response to the sparge system from < 10 OVA units to ~60-70 units and remained at an elevated level for several months. This is an indication of removal of VOCs below the water table.

Sparging was implemented in a two stage process. First, the combined vent/sparge points (ASVP1-7) were utilized. Second, the centrally located sparge only point (AS-1) was added and finally all other sparge points were added.

Two sets of groundwater results were taken after 54 and 125 days of sparging operation. As can be seen in Table 1, there has been substantial and dramatic changes. The net reduction is greater than 98% overall. The

125 day groundwater samples were taken one week after the system shut down to allow groundwater to re-equilibrate.

TABLE 1
Change in VOC Level With Time
(VOC = PCE, TCE, DCE)

Well	Before Start-up	54 Days After Sparge	125 Days After Sparge
MW-1S	2,108	3.5	4.9
MW-1D	14	1.9	BDL
MW-2S	41,000	290	897
MW-2D	BDL	BDL	1.5
MW-3S	2,161	2.2	1.9
MW-3D	BDL	BDL	12
MW-4S	4,328	444	240
MW-5S	6,940	357	124
MW-6S	166	5	BDL
MW-7S	134	31	5

Based on the ground water results, it may be concluded that the ASV system has been effective in significantly reducing groundwater and soil contamination across the site. The only area showing even a moderate residual is the vicinity of MW-2 near the source area.

It should also be noted that MW-7 has also shown a decrease in concentration. This indicates that VOCs are not being mobilized by the sparge system. The decrease in MW-7 is also significant in that there is no active ground water pumping occurring on the site to control off site ground water movement.

Tedlar bag samples were taken of the vent effluent and analyzed in the laboratory. Only PCE and TCE were found in any of the samples; PCE was the major constituent.

The tedlar bag sample results were also graphed versus time. As was seen with the OVA results, the concentrations of PCE and TCE dropped during the vent start-up and rose again with the initiation of the sparge system (Figure 5). These results indicate that the combined system is effective in removing PCE and TCE from soils and groundwater.

Based on the tedlar bag sample results, a cumulative mass removal was calculated for the site. As shown in Figure 5, in the first six weeks of operation, approximately 900 pounds of PCE and TCE were removed from

the site. These results reflect removal of the bulk of the adsorbed phase unsaturated zone contamination. The increased VOC levels after sparge start-up indicated that the sparge system had initiated removal of contaminants contained in the saturated soils and groundwater.

VOC contamination both above and below the water table has been effectively treated by the use of a combined air sparging - soil venting system. In a relatively short period of time (125 days) groundwater levels have been reduced by over 98%.

The system has been operated without active groundwater pumping. The mounding created by the air sparge system was designed to prevent off-site groundwater migration. This system has been effective as there has been no downgradient increase in VOCs. In fact, VOC levels in the downgradient off-site well have significantly decreased during the treatment.

QUESTIONS CONCERNING AIR SPARGING

The above case history illustrates the effectiveness of air sparging technology. From appearances air sparging is a straightforward and effective means of treating volatile organics below the water table.

There are two potential concerns with the use of air sparging. The first is the spread of dissolved contamination. The second is the acceleration of vapor phase transport and the subsequent accumulation of vapors in buildings.

Air sparging has been used in Germany for several years. It has however, recently fallen into disfavor. The primary cause of this disfavor has been the increase of off-site downgradient dissolved contamination

There are three probable causes for an increase of downgradient dissolved levels. The first is geological conditions. The second is operating conditions. The third is changes in hydrogeology.

Geological conditions can impact air flow. With a sparge system air flow must be both horizontal and vertical. The vertical travel is important for the ultimate removal of the volatilized contaminant. If the geology constricts vertical air flow, then sparging can push the dissolved contamination downgradient as shown in Figure 6. Any permeability differential (i.e. clay barrier) above the zone of air injection may severely reduce the effectiveness of air sparging. The present or absence of such barriers should be determined during a pilot test study. Therefore, in low permeable/heterogeneous formations sparging may require a groundwater recovery system to prevent the spread of dissolved contamination.

A second cause of increased downgradient contaminant migration, is over pressurizing the sparge system. Ostensibly the minimum sparge pressure is that which is required to overcome the water column (i.e., 1 psi for every 2.3 feet of hydraulic head). As pressure is increased above this minimum, air is "injected" laterally into the aquifer. At low sparge pressure there is a balance vertical/horizontal flow as shown in Figure 7. The injected air "cones" up through the aquifer. At high pressure there is greater horizontal flow than vertical flow (Figure 7).

As seen in Figure 8, there is an initial linear relationship between the sparge pressure and direction of air travel. At low sparge pressure (injection pressure equal to hydraulic head) the air travels 1-2 feet horizontally

for every foot of vertical travel. As the sparge pressure increases, the degree of horizontal travel also increases.

Normally, one would desire this enhanced horizontal travel as the injected air would be able to effectively remove more contamination. Where pressure causes problems is where the air flow changes from smooth flow to turbulent flow. Figure 8 shows a point where the increase in sparge pressure does not give a corresponding increase in horizontal travel. This transition is also observed in venting systems where too high a vacuum is used causing turbulent flow. Under such sparging conditions a dissolved plume could be pushed downgradient (Figure 9).

The third potential cause of increased downgradient dissolved contamination is changes in site hydrogeology due to sparging, specifically water table mounding. Air sparging does cause mounding. Figures 10 and 11 show the impact of sparging on the water table for the case history discussed above. Figure 10 shows the normal water table with a northwest to southeast gradient Figure 11 shows contours prepared with data collected after two weeks of sparge system operation. There is an apparent mounding of the water table across the site, oriented along the northwest southeast axis. The mounding appears greatest downgradient of the source area

Normally mounding of the water table would accelerate groundwater velocity. However, with sparging the mounding is caused by the displacement of water with air. Flow may not be accelerated because the net density of the water column is decreased thus counteracting the mounding. This lowered density is dramatically seen by taking water table measurements fifteen minutes after the sparge system was shut off. The water table collapsed as shown in Figure 12 as the air exited the water. This collapse shows the displacement of water by air during sparging. Because of this density compensation, mounding may not spread any contamination.

The second “danger” of sparging is accelerated vapor travel. This is of concern where there are receptors. Since air sparging increases pressure in the vadose zone, any exhausted vapors can be drawn into building basements. Basements are generally low pressure areas, and this can lead to preferential vapor migration and accumulation in basements (Figure 13). As a result, in areas with potential vapor receptors, air sparging should be done with a concurrent vent system. A vent system provides an effective means of capturing sparged gases.

DESIGN GUIDELINES

Because of the potential dangers for enhanced contaminant transport, proper design is important to effective sparging. For a sparge system the information that is needed for effective design is:

- 1) The location of potential groundwater and vapor receptors.
- 2) The geological conditions of the site - permeability, lithology, heterogeneity.
- 3) The contaminant mass distribution within the area to be treated - soil and groundwater. This distribution should be “superimposed” on the lithology of the site.

- 4) The radius of influence of the sparge well(s) at various flow rate/pressure.

The following parameters can be measured during field testing to determine design information.

Pressure vs. distances. This is an indication of radius.

VOC concentrations in groundwater. This is an indication of what is being removed and areas being impacted, it should be done before, during (with and without the system running) and after test.

CO₂ and O₂ levels in soil vapor. This is an indication of biological activity. These measurements need to be taken before, during and after pilot test under static as well as pumping conditions.

Dissolved oxygen levels in water. This is a good indicator of effect -may be slower to see than air flow. Measurements need to have good base line to determine changes.

Water levels before and during test. Air flow will cause some mounding. This needs to be done before test to determine background.

As shown in Figure 14, there is a fairly good correlation between parameters measured during sparging. This allows for cross correlation during design. With this cross correlation it is possible to obtain effective air flow through the area of contamination.

CONCLUSION

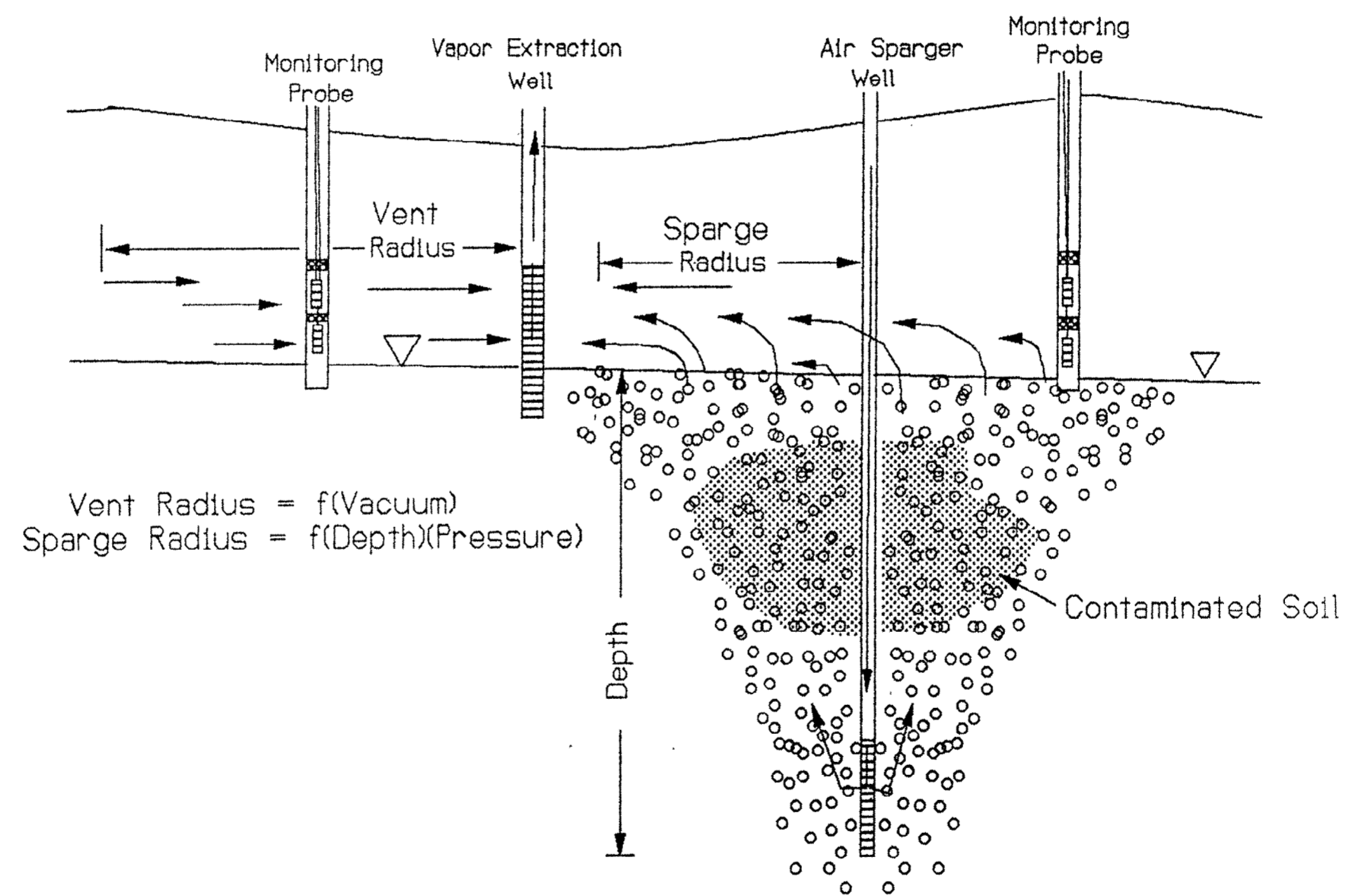
Sparging is an effective technology. It is, however, not without its dangers. Our experience on air sparging has been favorable to date. This however, has been due in part to choosing very permeable sites and paying attention to design.

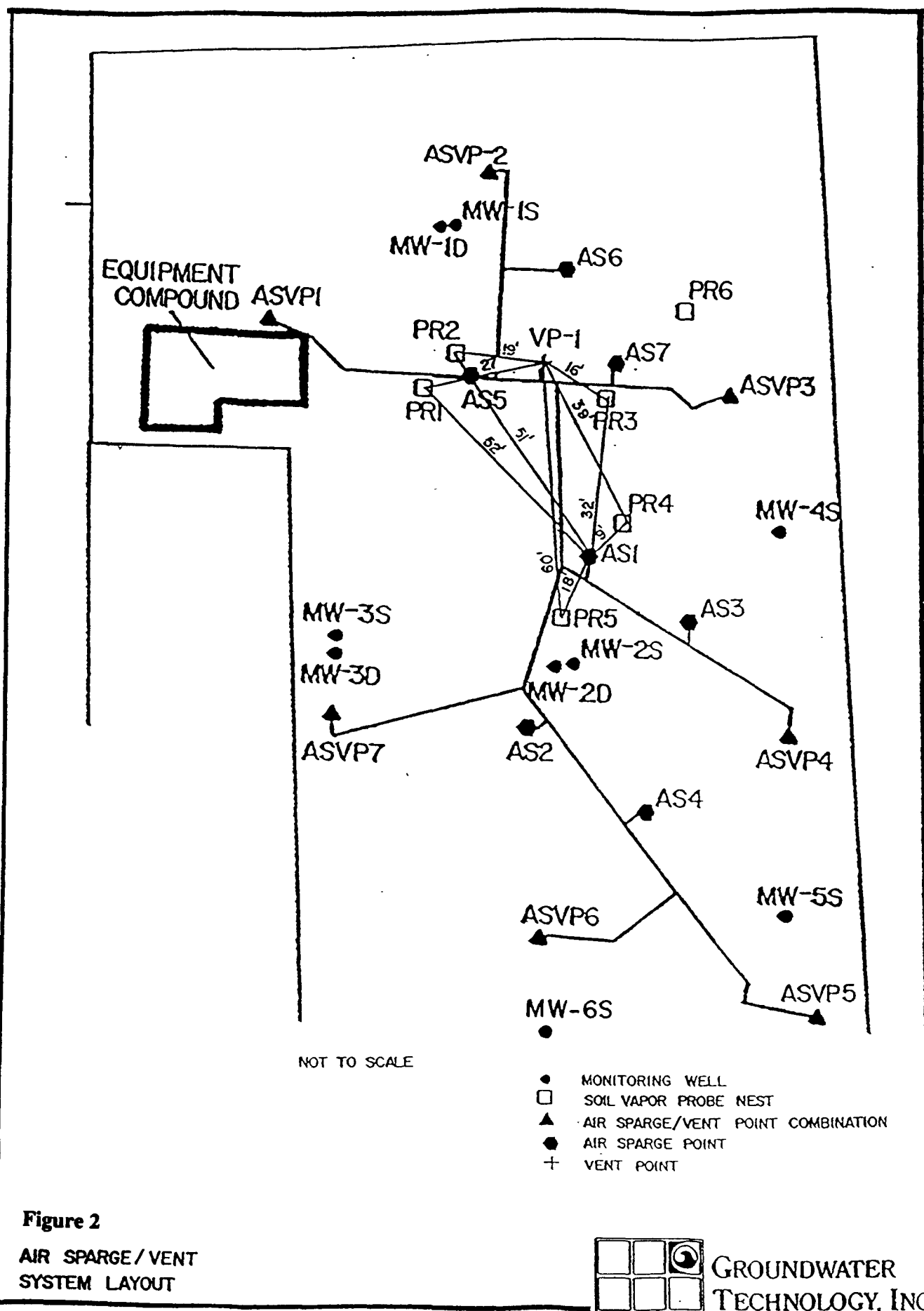
To further expand the utility of sparging, there are a number of questions that need to be addressed. These questions are:

- What are the limitations to air sparging technology.
- How does air sparging impact the site hydrogeology and contaminant transport.
- What are the most effective means of determining the radius of influence, pressure requirements, and effectiveness of a sparge system to minimize and detrimental effects.
- With effective design and careful monitoring, air sparging can be an important remedial tool. If however, it is over simplified it can be ineffectual at best or counter-productive at worse.

Figure 1: Diagram of Air Sparger System

256





TYPICAL AIR SPARGE / VENT POINT CONSTRUCTION (ASVPI - ASVP7)

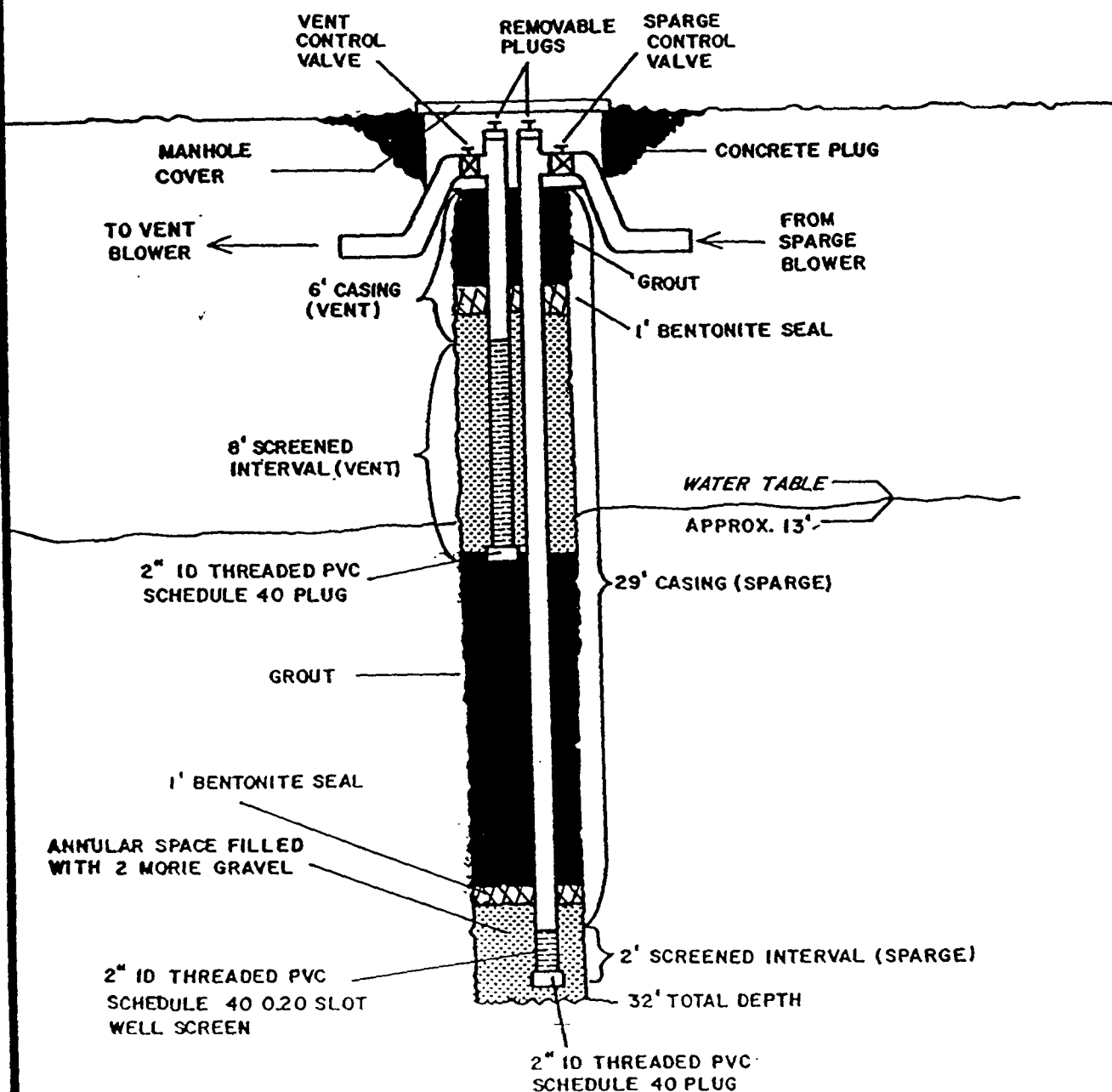
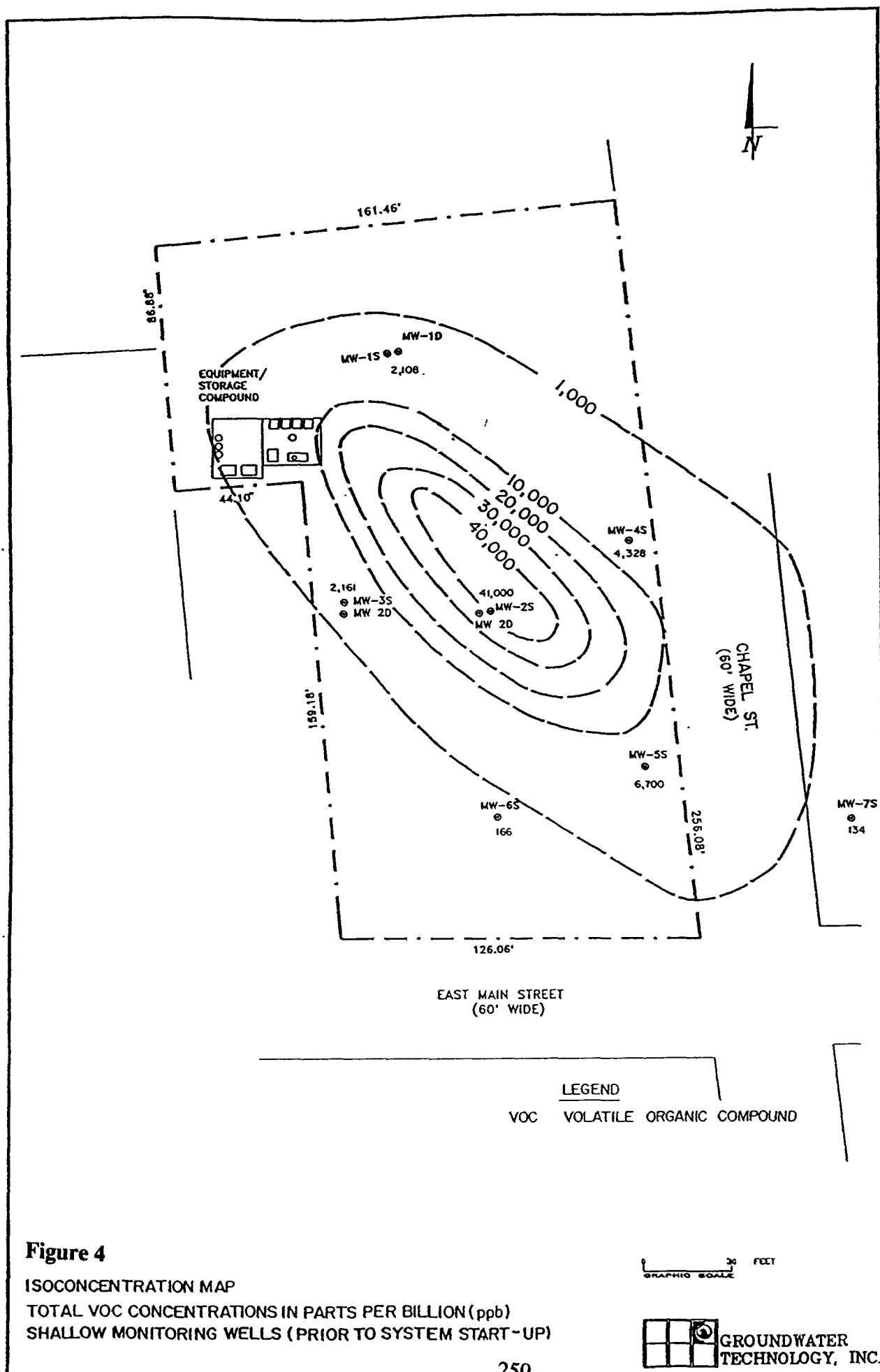


Figure 3

AIR SPARGE / VENT POINT CONSTRUCTION



GROUNDWATER
TECHNOLOGY, INC.



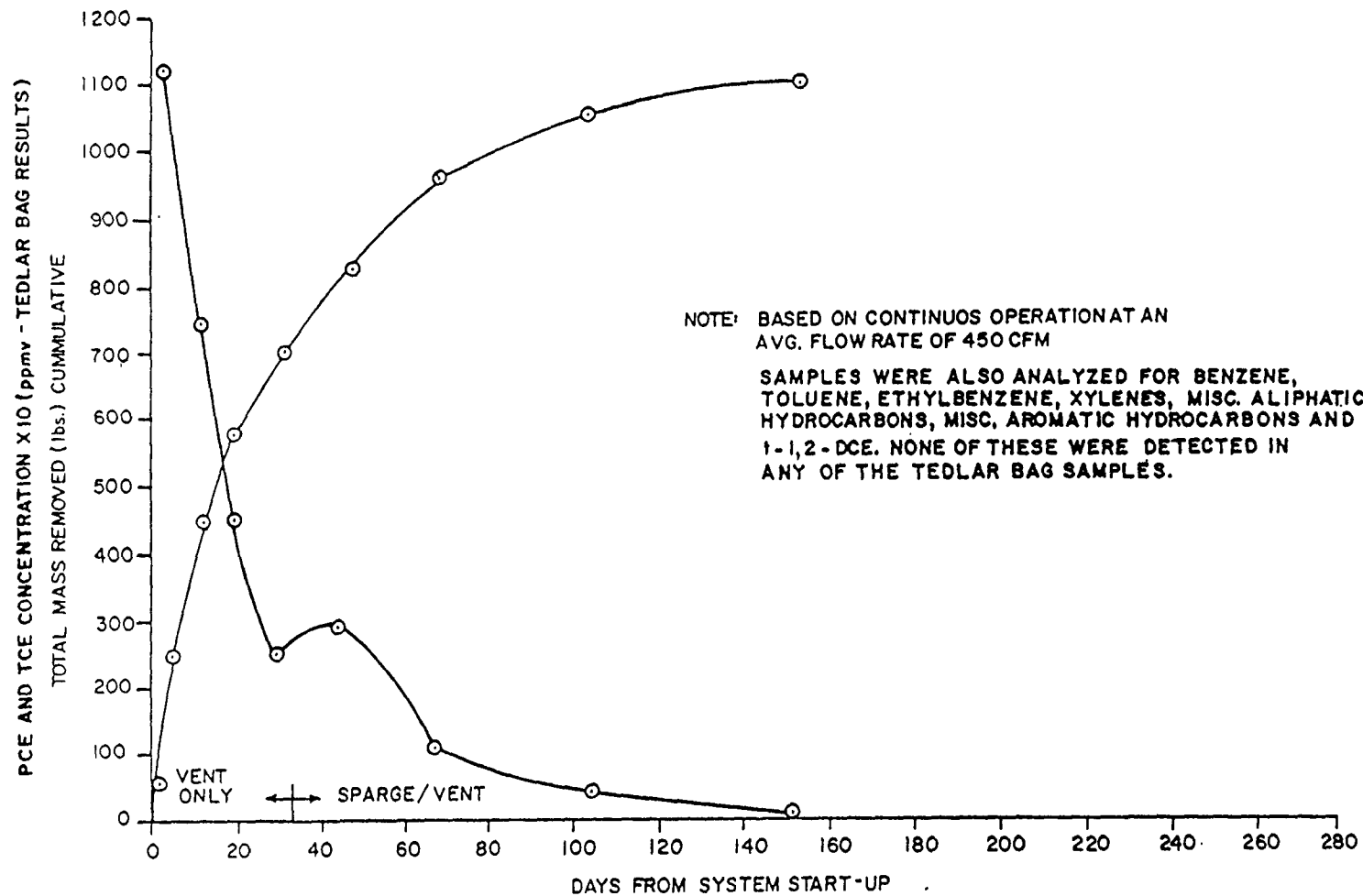


Figure 5

TOTAL REMOVAL OF VOC

GROUNDWATER
TECHNOLOGY, INC.

Figure 6:
Inhibited Vertical Migration due to Impervious Barrier

261

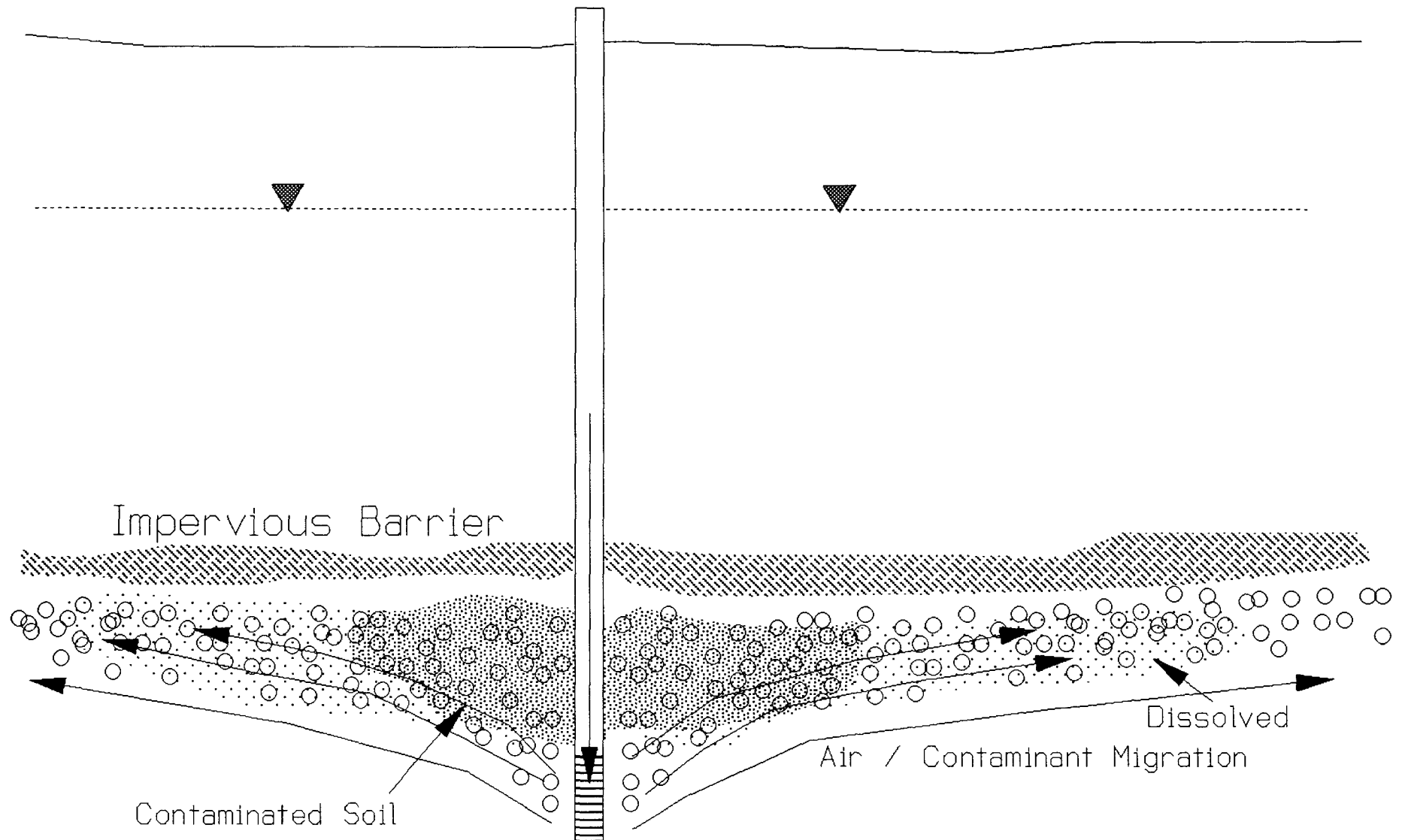
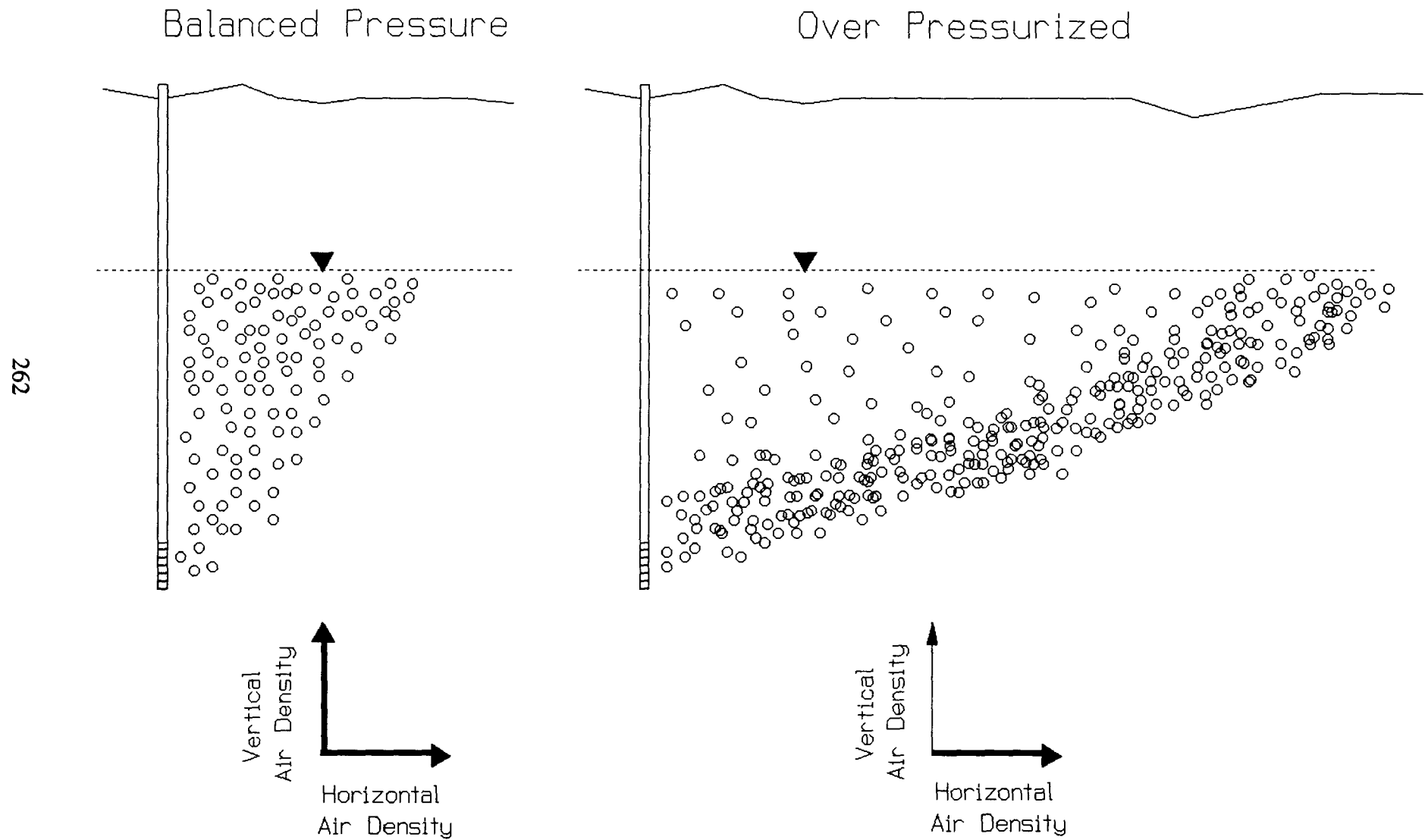


Figure 7: Effect of Sparge Pressure on Air Movement



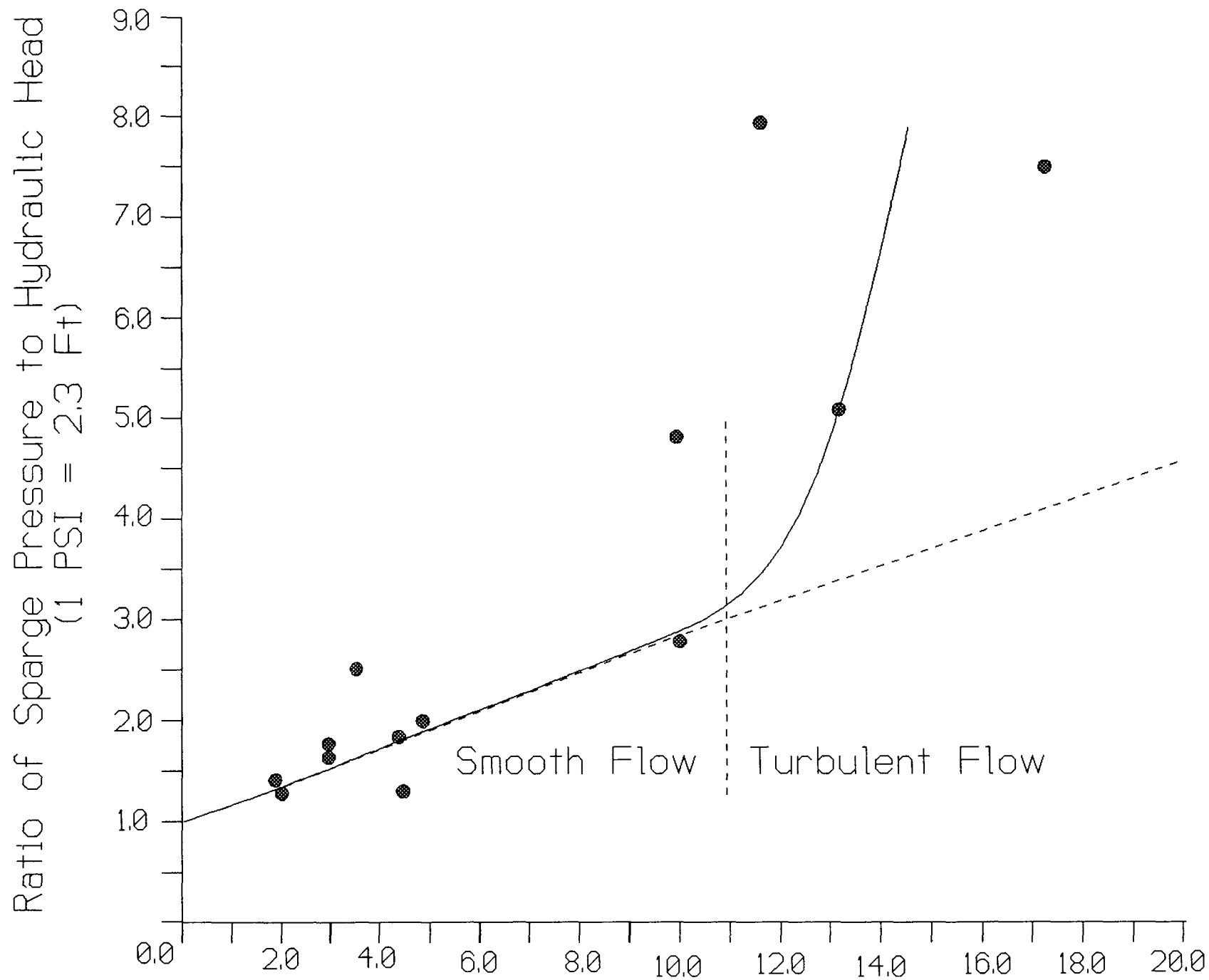
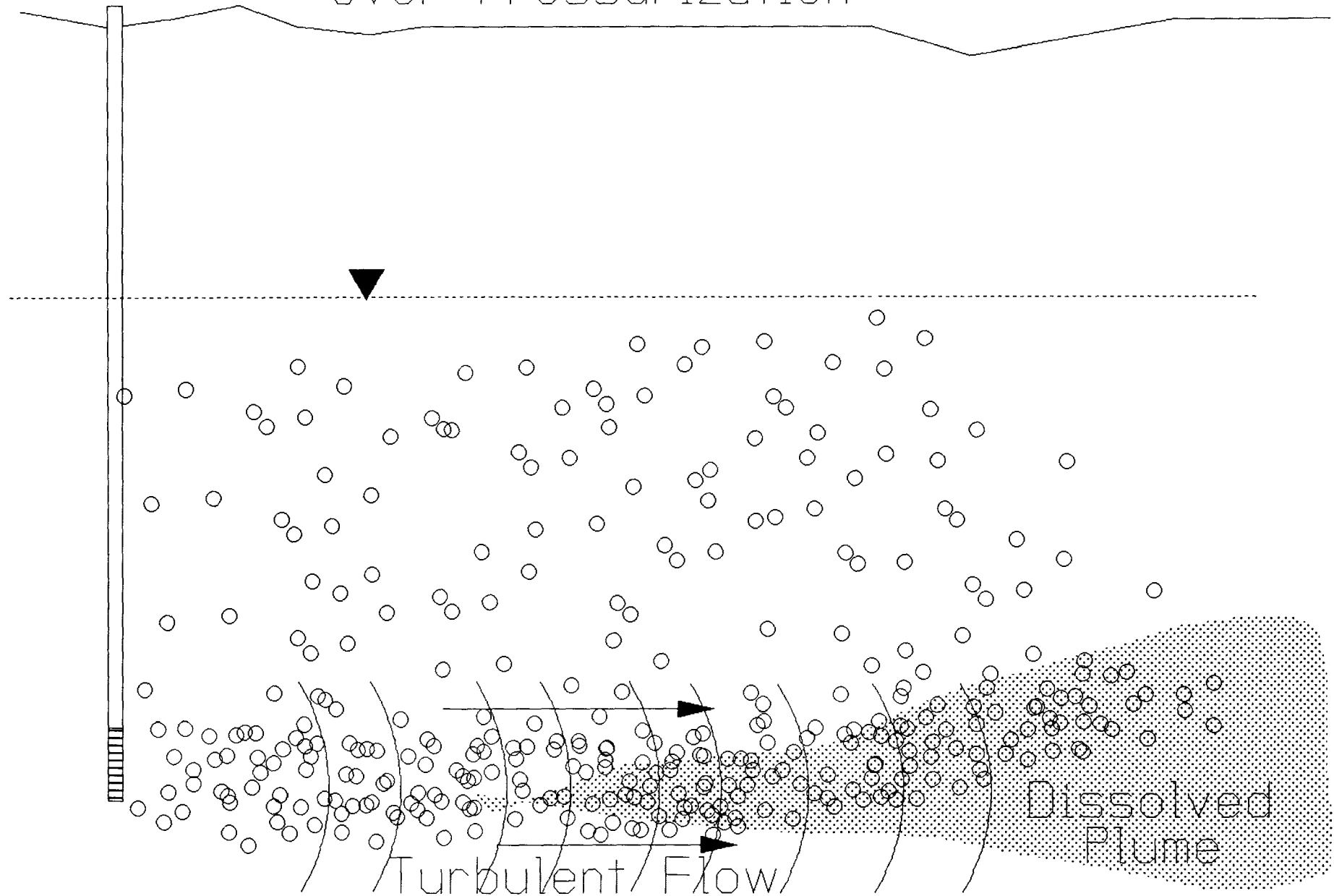


Figure 8: Ratio of Horizontal Radius vs Sparge Depth

Figure 9: Accelerated Downgradient Migration
Due to Turbulent Flow Caused by
Over Pressurization



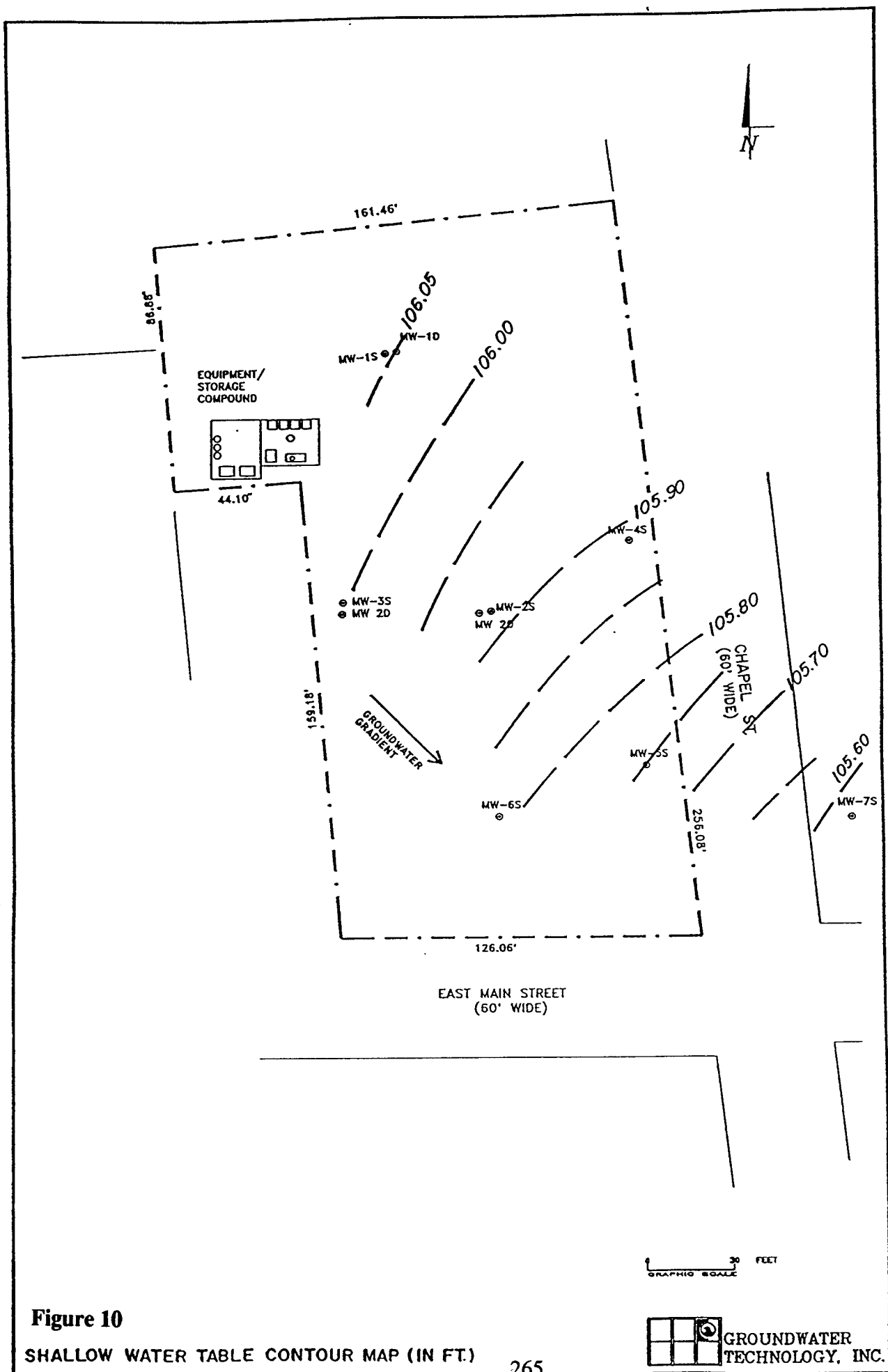


Figure 10

SHALLOW WATER TABLE CONTOUR MAP (IN FT.)



GROUNDWATER
TECHNOLOGY, INC.

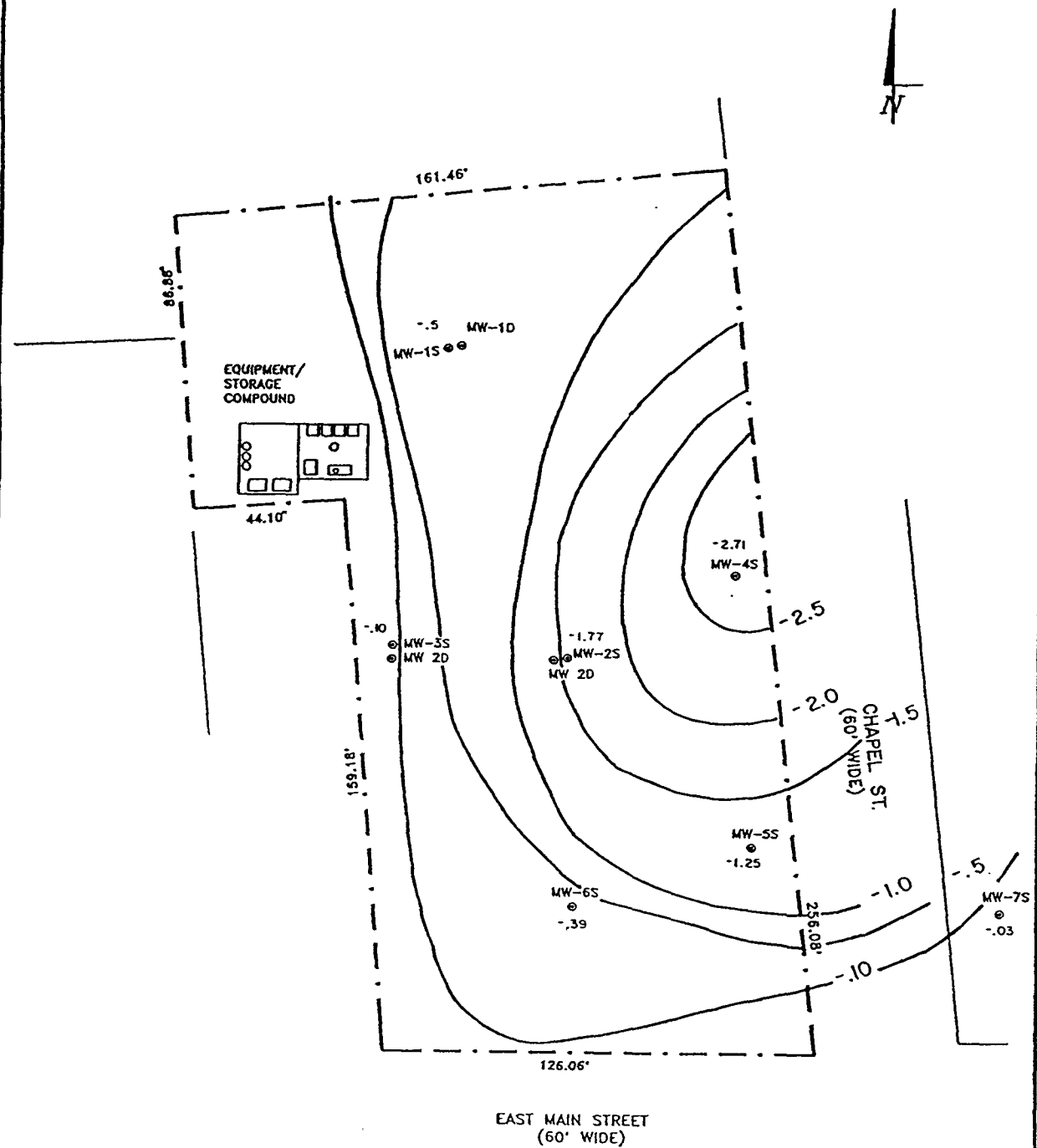
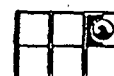


Figure 12

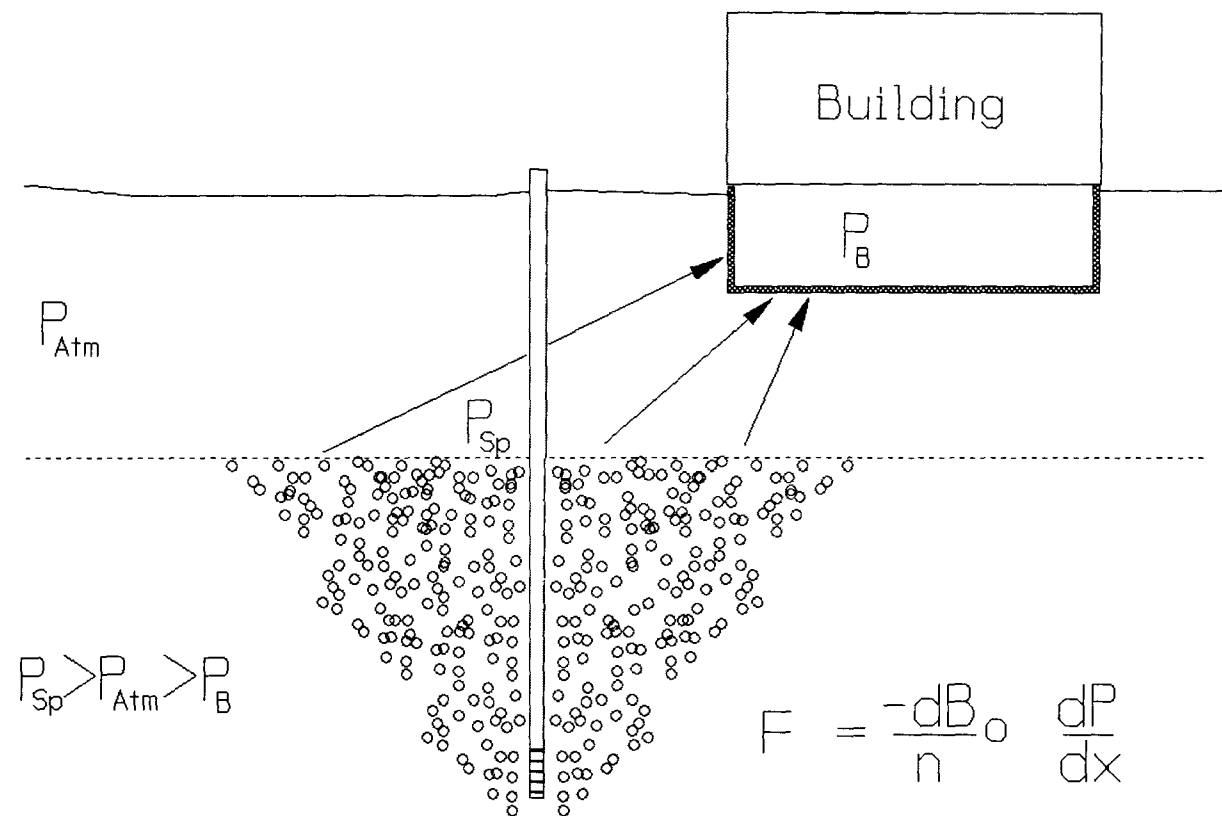
COLLAPSE IN WATER TABLE
15 MINUTES AFTER CENSATION OF SPARGING

0 30 FEET
GRAPHIC SCALE



GROUNDWATER
TECHNOLOGY, INC.

Figure 13: Enhanced Vapor Travel due to Pressure Gradient



P_B = Basement Pressure (low)

P_{Atm} = Atmospheric Pressure

P_{Sp} = Sparge Pressure (high)

$$F = -\frac{dB_0}{n} \frac{dP}{dx}$$

F = Vapor Flux

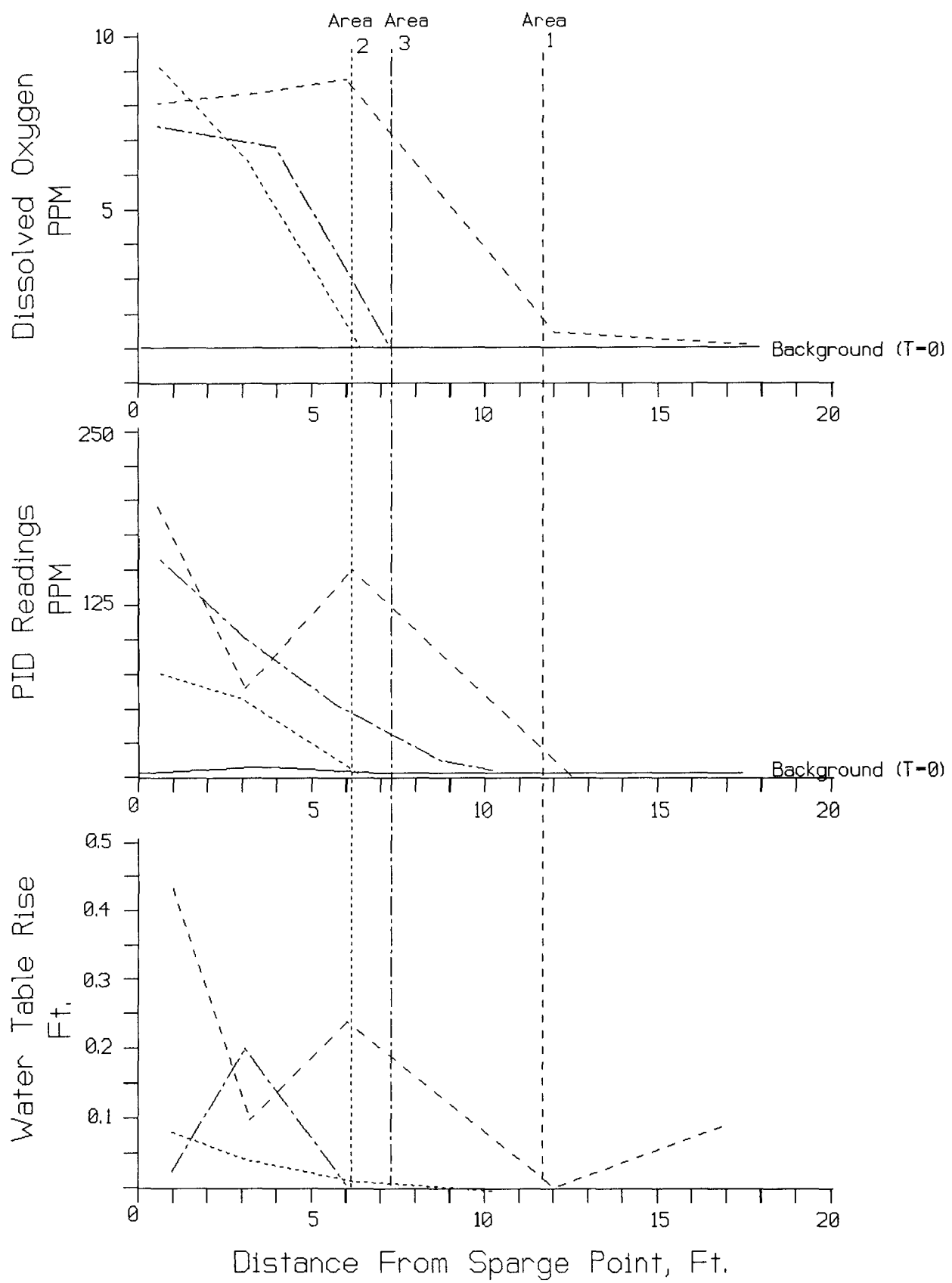
d = Vapor Density

n = Vapor Viscosity

B_0 = Permeability

$\frac{dP}{dx}$ = Pressure Gradient

Figure 14: Correlation Between Sparge Parameters and Radius of Influence



COMMERCIAL VAPOR TREATMENT PROCESSES

F.A.M. BUCK AND E.L. SEIDER

King, Buck & Associates, Inc.
2384 San Diego Avenue, Suite 2
San Diego, CA 92110

Vapor extraction, also referred to as soil venting, is a remedial technique that grew rapidly in the early- to mid-1980s. In simplest application, the suction port of a vacuum blower is connected to one or more extraction wells installed to penetrate the contaminant plume in the soil, and a mixture of air and the volatile contaminant is sucked out of the ground and discharged into the air. This simple process is often the most effective way of reducing soil contamination and protecting groundwater. However, as demonstrated by several papers at this symposium, the design of a collection system that cleans up the contaminated site in minimum time and at minimum cost is dependent upon the skills of earth scientists, hydrogeologists, or others.

Vapor extraction equipment has been developed to handle a wide range of vapor extraction rates, to greater than 28 m³/min (1000 scfm). Early equipment usually had low capacities of about 0.3 m³/min (10 scfm), but lengthy cleanup times inspired the development of equipment capable of higher extraction rates. However, with the higher extraction rates come potentially higher emission rates of VOCs to the atmosphere. This led to more concern over air quality effects.

Many agencies responsible for controlling air pollution have mandated treatment of the recovered vapors. Air pollution control districts in southern California have been in the forefront with strict regulations controlling the processes of soil venting. The South Coast Air Quality Management District, El Monte, California, issued Rule 1166, "Volatile Organic Compound Emissions from Decontamination of Soil," in August 1988. The applicability is to "limit the emissions of VOC" from soil contaminated with VOCs, and the regulation contains requirements that control VOC emissions during any type of mitigation measure, including extraction.

EMISSION CONTROL SYSTEMS

Several potential treatment processes are available to meet pollution control standards using vapor extraction. These methods include the following:

1. Refrigerated condensation to recover VOCs as liquids.
2. Adsorption of VOCs activated charcoal.
3. Burning (oxidation) of VOCs by thermal oxidation, catalytic oxidation, or by two-staged thermal and catalytic oxidation. Examples of two-stage oxidation are an

internal combustion engine with a catalytic converter on the exhaust; or, a system that uses thermal oxidation when the VOC content of the extracted vapor is high, and a catalytic oxidizer when the VOC content is moderate to low (Figure 1).

If the VOCs are hydrocarbons with combustion products not containing appreciable amounts of corrosive or noxious compounds such as HCl, burning of the extracted vapor (by thermal or catalytic oxidation) is usually the process preferred economically.

A few process characteristics are offered supporting the general conclusion that oxidation processes are the preferred choice. The product recovered by refrigerated condensation would be gummy, partially oxidized VOCs that present a disposal problem would be better to burn them in a vapor form without using a costly refrigeration process as an intermediate step.

As for adsorption on activated charcoal, the process has competitive economics only at very low VOC concentrations in the extracted vapor (1).

Burning the VOC in an ICE, may seem to be attractive, but problems arise from some basic characteristics of ICEs. First, the modern ICE is a complex, finely tuned machine that requires highly refined fuels and lubricants that meet stringent specifications. Purity specifications rule out materials that would form gums or lacquers in the carburetor, on valves, etc., but the soil vent vapor is just such a reactive, gummy fuel. Moreover, the combustion process must be completed efficiently in a fraction of a second. Experience has shown that extracted vapor has large variations in combustion properties. Not only does the VOC content vary but, as shown by analyses, carbon dioxide content may range to 6 percent or more, and oxygen may be much lower than the twenty-one percent by volume expected in fresh air. Extracted vapor with such composition has a significantly different flame propagation speed than normal fuel air mixtures. Operating conditions of thermal oxidizers have to be modified to burn process gas efficiently if it has high CO₂ and low O₂ concentrations. The problems are magnified in an ICE, especially if power output is a consideration.

EMISSION CONTROL BY OXIDATION

VOCs in the extracted air can be oxidized efficiently in properly designed burners. With simple VOCs such as gasoline components the process is generally called "thermal oxidation", to distinguish it from "incineration," a term usually applied to the combustion of various noxious materials under carefully controlled, high temperatures at a destruction efficiency of 99.9% and higher.

This discussion will refer to one type of thermal oxidizer, the pre-mix type (a laboratory Bunsen burner is a pre-mix burner) because, though simple, the pre-mix burner illustrates several principles of combustion technology. In a burner of this type, VOCs in the extracted air can be oxidized efficiently if the concentration of combustibles is above their lower flammability limit (LFL) in air. At VOC concentrations below the LFL, enrichment fuel (e.g. natural gas or propane) must be added to maintain efficient combustion. There is no lower limit on VOC concentration below which thermal oxidation will not effectively destroy the VOC; the requirement is merely to add enough enrichment fuel to maintain a stable, efficiently burning flame. Experience has shown that a premix of air and propane or natural gas will burn efficiently at a fuel content 20 to 50 percent above the LFL. This permits an estimation of the maximum fuel consumption for a premix-type thermal oxidizer in an idealized case. For example, the fuel required for an efficient flame with 100

would be 2.8 scfm, or 4.6 gal/h. VOCs in the extracted vapor will reduce the fuel requirement below the “fresh air” case but, as mentioned earlier, other factors such as the concentrations of oxygen, carbon dioxide, and water vapor will affect the combustion process. It is not always accurate to estimate the supplementary fuel consumption by considering only the VOC content of the extracted vapor.

At VOC levels at or below about 30 percent of the LFL, oxidation over catalysts can be used for efficient VOC destruction. There are two boundary limits to the catalytic process: (1) if the VOC concentration is too high, the heat released during oxidation will cause high-temperature destruction of the catalytic oxidizer, or (2) if the VOC concentration is too low, not enough heat is released to maintain the catalyst at a temperature needed for efficient oxidation.

In the first situation, where the exotherm (heat released during oxidation of the VOC) is too large for the system, it is obvious that dilution air can be admitted to the suction of the vacuum/compressor unit to dilute the VOC content and lower the exotherm. There is an unwanted result of this dilution, however. The system capacity is set by one or more limitations on the system, e.g., by the capacity of the vacuum pump, or by the design space velocity of the process gas across the catalyst. At the maximum flow rate of the process gas, dilution of the extracted vapor with fresh air (to contain the exotherm) means that the rate of extraction of vapor from the soil must be reduced. Therefore, this reduction will add to the time and cost required for site remediation. To avoid reducing the extraction rate of vent gas, it is desirable to oxidize high-VOC-content vapor in a thermal oxidizer and to use the catalytic oxidizer with vapor of lower VOC content that has an exotherm compatible with the catalytic system.

The second operating limit on VOC concentration leads naturally to some type of preheater for the process gas before it enters the catalyst bed(s). Usually, a preheat system is controlled by a process controller reading the temperature of one or more thermocouples in the catalytic reactor. For efficient oxidation of most VOCs, the minimum temperature at catalyst entry will be set between 315 and 370°C (600 to 700°F). Energy conservation in a catalytic oxidizer is standard. Usually a product-to-feed gas heat exchanger recaptures 50 percent or more of the sensible heat of the effluent gas from the catalytic reactor before the effluent is discharged to the atmosphere.

An isometric block diagram of a two-stage thermal/catalytic oxidation system is shown by Figure 1.

OPERATING DATA

Efficiency of the emission control system is calculated by measuring total hydrocarbons (THCs) in the effluent from the treatment system and comparing the result to THCs in the extracted vapor. From the point of view of the emission control system, the latter stream is called the influent. THCs can be determined by laboratory analyses of gas samples taken at the operating site, or by continuous, on-line analysis of the influent and effluent. A variety of flame ionization detectors (F.I.D.) are available commercially that have proven to be satisfactory for measuring THCs.

Typically, when an emission control system has been permitted by a local air quality control agency, a condition of the permit requires that a formal performance test be made, often by a third party testing laboratory. The performance test must demonstrate that the equipment is controlling emissions below the limits specified in the agency's permit.

The data reported in Tables 1 and 2 are representative of the emission control efficiencies that are obtained with thermal and catalytic oxidizers, respectively. The data were from tests by testing laboratories pre-approved by the South Coast Air Quality Management District (AQMD) in 1987 and 1988.

The declines in the VOC concentrations at three soil venting sites are shown in Figure 2. In all cases, the vapor extraction rates were about 100 scfm. The so-called "Site A" data were observed by the authors; the data from the two other curves are from cited references. In our experience these decline curves are typical of soil venting projects that do not have special features. To summarize, it is typical for VOC concentrations to decline from about 20,000 ppmv (i.e. above the LFL for gasoline/air mixtures) to less than 1000 ppmv in 200 days or so.

To estimate the amount of VOC potentially emitted to the atmosphere during vapor extraction, refer to Figure 3. In this chart, the conversion from concentration of gasoline vapor to emissions in pounds per day is based on computed physical properties of a surrogate gasoline. The surrogate gasoline was taken to be one-third each of isooctane, methylcyclohexane, and toluene (i.e., a mixture of equal volumes of an alkane, a cycloalkane, and an aromatic). It is assumed to be representative of the weathered gasolines typically encountered in vapor extraction projects. The surrogate gasoline has a vapor density, under standard conditions, of 0.25 lb/ft³.

From the lower curve of Figure 2, and the correlation of Figure 3, it is calculated that vapor extraction at 100 scfm would have emitted 15,800 lb (2400 gal) of gasoline vapors over the 240-day period. Emission control, at a minimum 95 percent destruction efficiency of THCs, therefore reduced atmospheric emissions by 15,000 lb or about 2300 gal. Again, in our opinion, this would be typical.

HALOGENATED VOC

All the preceding discussion has referred to treatment processes for VOC that are hydrocarbons (e.g. gasoline components) or are oxygenates (e.g. alcohols, ethers). Until recently, there were no simple acceptable oxidative treatment processes for halogenated VOC (e.g. trichloroethylene). Burning trichloroethylene (TCE) in a thermal oxidizer would produce two unwanted problems: (1) it would be expensive to neutralize the product HCl in the high temperature thermal exhaust gas, and (2) there is great concern that the interactive oxidation of TCE and hydrocarbons may form toxic PICs (products of incomplete combustion) such as dioxins. Oxidizing TCE catalytically at lower temperature would solve the preceding two problems, but until recently a suitable catalyst for a simple fixed bed oxidation process was not available.

The development of an active, stable catalyst for fixed-bed processing of halogenated VOC has been described by Lester (1989). In this paper data from the first commercial application of the new catalyst will be given. The system is called HD CatOx™, a trade acronym for the term halohydrocarbon destruct catalytic oxidation system.

The prototype HD CatOx system has a nominal capacity of 200 scfm and was initially treating a chlorinated VOC concentration of 3500 ppm. The vapor extraction system, i.e., the vapor extraction wells, the vapor/liquid separator, and the vacuum/compressor unit is similar to conventional systems used for hydrocarbon

recovery. Electrical resistance heaters heat the process stream up to 750°F before the new “H.D.” catalyst converts the TCE to carbon dioxide, water, and hydrochloric acid. The hot gas from the catalytic reactor is cooled in a special quench section and passes through a scrubber tower where the hydrochloric acid is neutralized to sodium chloride. An ancillary refrigeration system maintains the system temperature. The effluents discharged are carbon dioxide and an aqueous solution of sodium chloride and sodium bicarbonate. Destruction efficiency of TCE, at the design operating conditions for the unit, was over 95%; a longer term average destruction efficiency is not available because, as one would expect, the operating conditions of this prototype have been changed frequently. Figure 4 shows the decline of TCE concentrations over time as well as the cumulative amount of TCE treated. After 160 operating days, the weight of TCE recovered from the contaminated site exceeds 20,000 pounds.

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**Table 1. Performance of a Thermal Oxidizer, during Soil Venting of a Gasoline-Contaminated Site.
(W.W. Irwin, Inc., 1989)**

	<u>Influent</u>	<u>Effluent</u>
Flow rate, air+VOC, scfm	71	170
O ₂ , %		7.2 7.6
CO ₂ , %		7.5 8.8
NOX, ppm		-- 30
CO, ppm		3.0 2.7
Hydrocarbons, NMHC as Cl, ppm	92,410	3
NMHC, lb/hr	16.6	0013
Benzene, ppb	82,100	ND (<10)
Benzene, lb/hr	0.72	<.0003
Hydrocarbon destruction efficiency, %		99.9+

**Table 2. Performance of a Catalytic Oxidizer, during Soil Venting of a Gasoline-Contaminated Site.
(W.W. Irwin, Inc., 1989)**

	<u>CatOx Inlet</u>	<u>CatOx Outlet</u>
Flow rate, dscfm	72	--
NOX, ppm	<15	<15
CO, ppm	<15	<10
Hydrocarbons:		
CH ₄ , ppm	--	30
Nonmethane, ppm as Cl	14,400	573
Hydrocarbon destruction efficiency, %		95.8

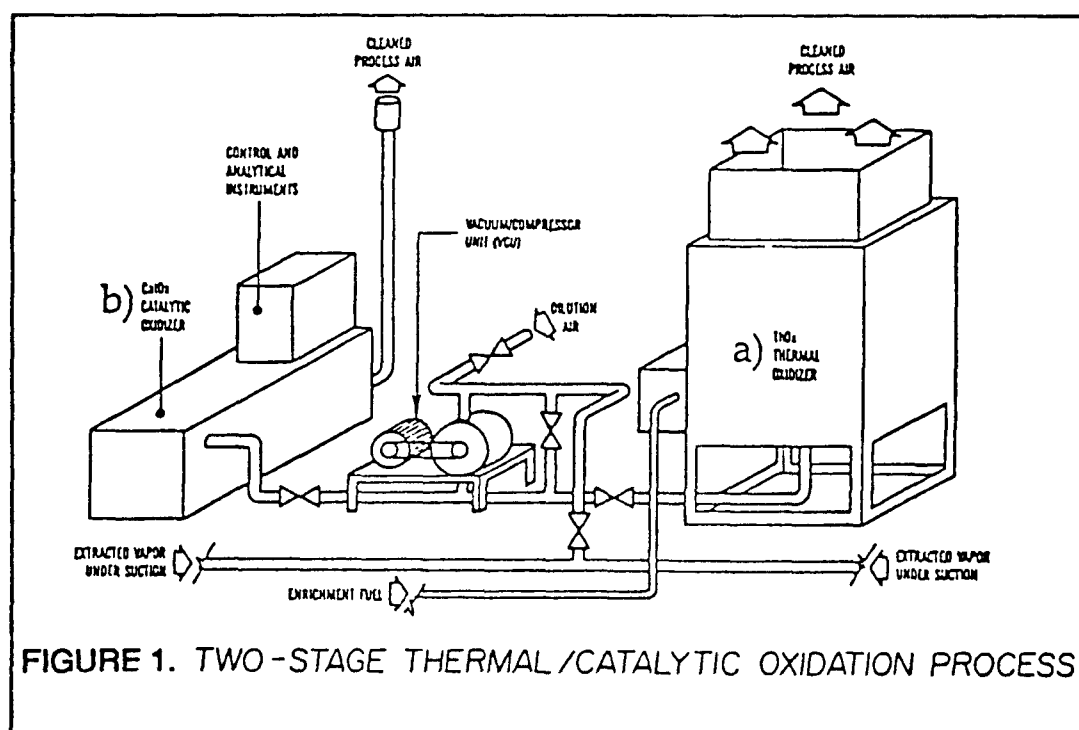
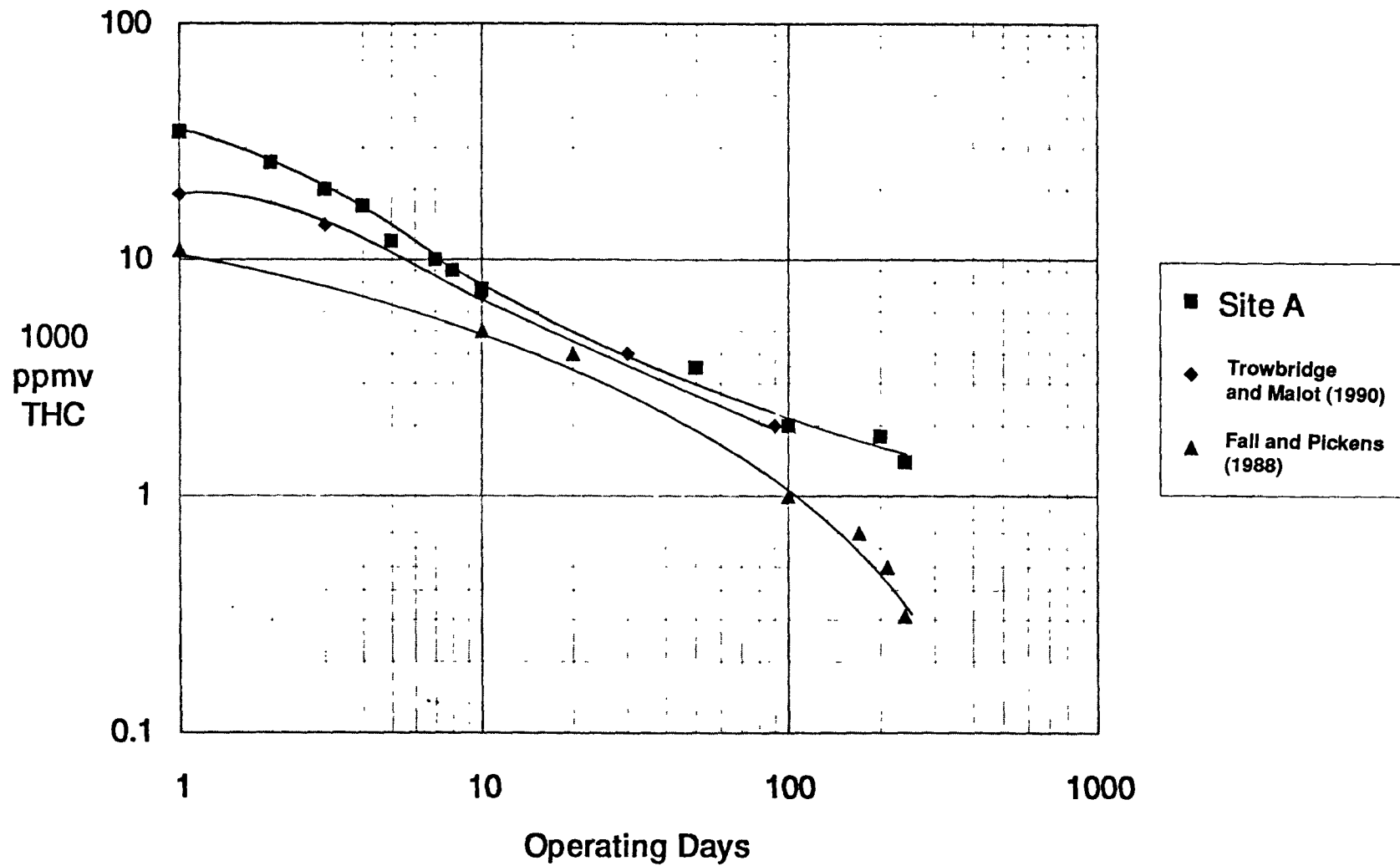
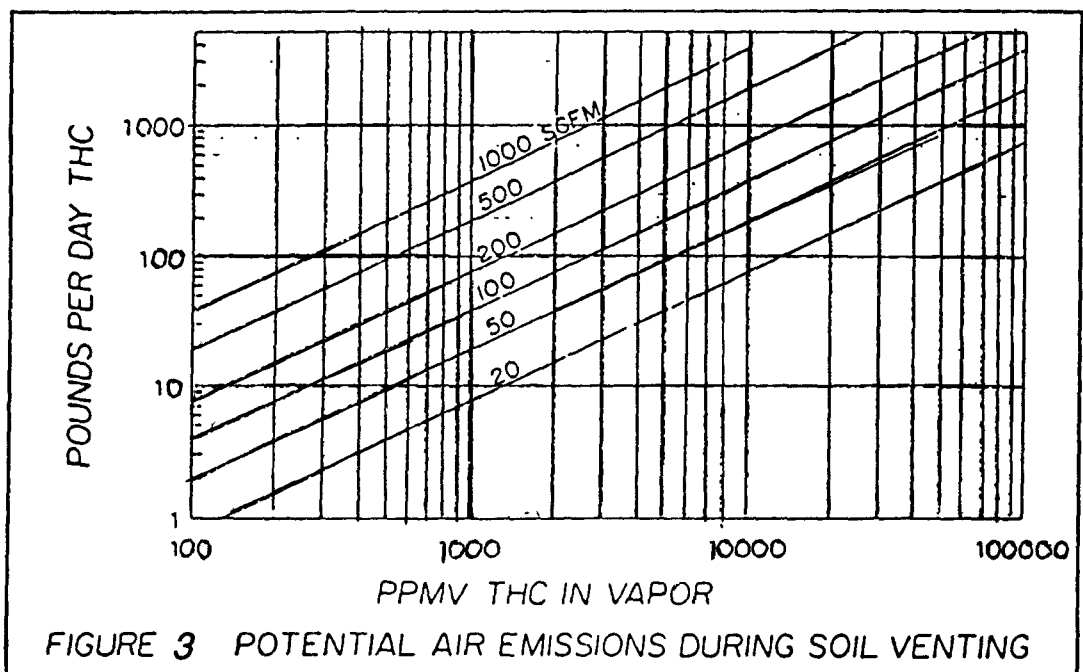


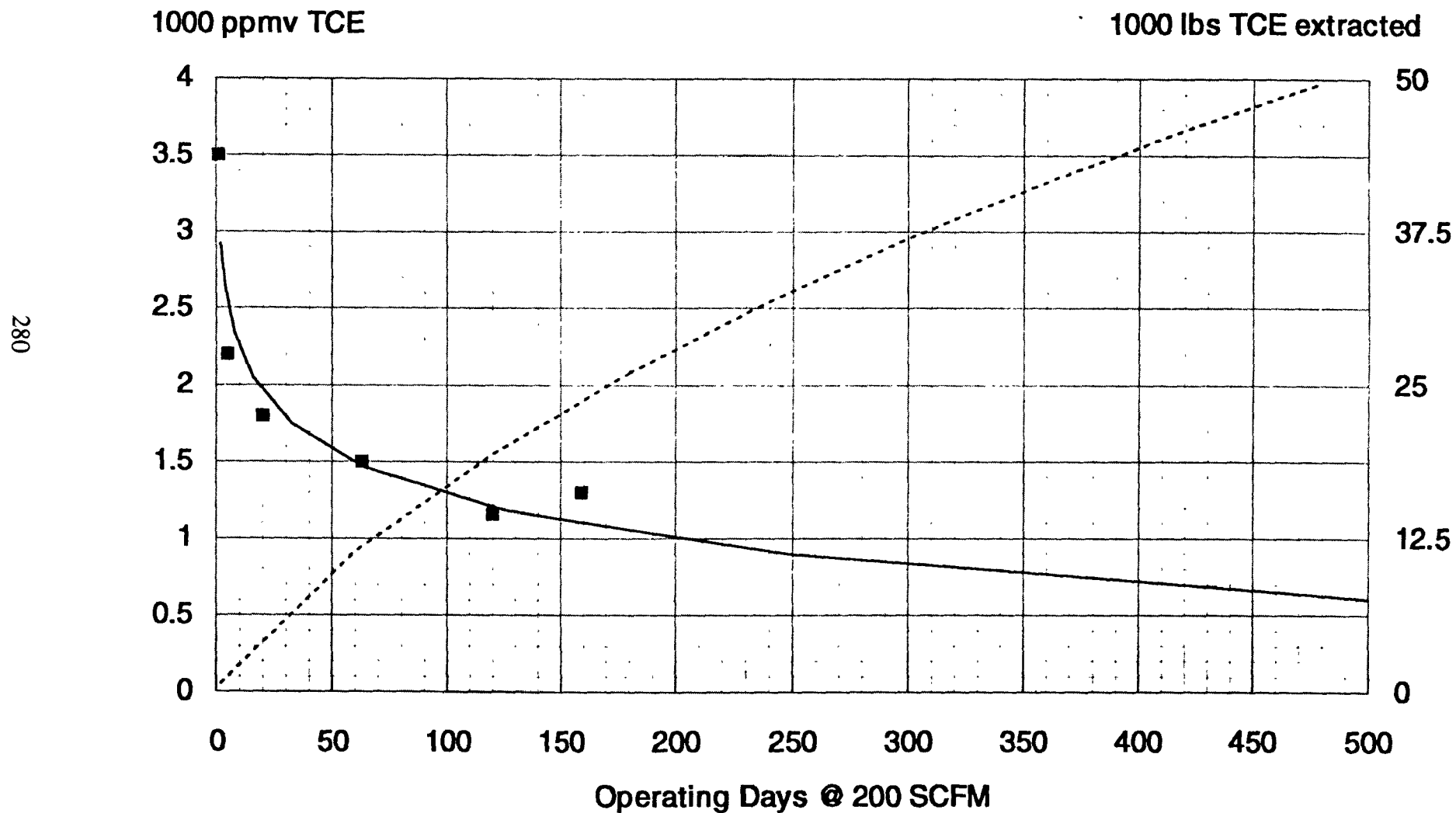
FIGURE 1. TWO-STAGE THERMAL/CATALYTIC OXIDATION PROCESS

FIGURE 2. Soil Venting VOC Decline Curves





**FIGURE 4. Soil Vapor Extraction System, SC AQMD Site
TCE Decline Rate**



CATALYTIC DESTRUCTION OF HAZARDOUS HALOGENATED ORGANIC CHEMICALS

GEORGE R. LESTER

Allied Signal, Inc.

Research and Technology

Des Plains, Illinois

ABSTRACT

A family of catalysts has been developed which appear to be clearly superior to those previously described for the destruction of highly toxic or hazardous volatile halogenated compounds including chlorohydrocarbons such as polychlorinated aromatic hydrocarbons and C_1 and C_2 chlorohydrocarbons and chlorofluorohydrocarbons. Applications for these catalysts include the destruction of hazardous chlorinated and/or fluorinated hydrocarbons in vent gases in the chemical process industry, and the purification of the discharge air from ground water and soil stripping processes. The new catalysts have demonstrated stable operation for over 1600 hours at greater than 99 percent destruction of carbon tetrachloride (CCl_4) in moist air at 375 degrees Celsius and $15,000 \text{ hr}^{-1}$ GHSV(STP). The effectiveness of these catalysts for destroying chloro- and fluoro-aromatics and other fluorohydrocarbons will also be described. It will be shown that the new catalysts are capable of operating at lower temperatures and/or shorter residence times than previously known catalysts. Results will be shown for the catalysts in the form of monolithic honeycombs and extruded pellets.

BIOVENTING FOR IN SITU REMEDIATION OF PETROLEUM HYDROCARBONS

ROBERT E. HINCHEE

Battelle Memorial Institute
Columbus, Ohio 43201

ROSS N. MILLER

Major, USAF
HSD/YAQE
Brooks Air Force Base, Texas 78235

Biodegradation of hydrocarbons in unsaturated zones through forced aeration has been observed at several field sites. Data are presented from two sites, one located at Hill Air Force Base in Utah and one at Tyndall Air Force Base in Florida where field demonstrations of this technology are ongoing.

INTRODUCTION

As a result of regulations requiring investigation of underground storage tanks as well as other surface and subsurface spills, literally thousands of sites have been identified as contaminated with petroleum hydrocarbons. To date, much attention has been given to pump-and-treat remedial technologies, but this technique leaves a substantial fuel residue in the capillary fringe or vadose zone that continues to contaminate groundwater. Methods of uniformly degrading fuel hydrocarbons in situ, without excessive groundwater pumping or toxic releases to the atmosphere, need to be developed. This paper focuses on one such emerging technology.

Petroleum distillate fuel hydrocarbons are generally biodegradable if naturally occurring microorganisms are provided an adequate supply of oxygen and basic nutrients (1). Natural biodegradation does occur and at many sites may eventually mineralize most fuel contamination. However, the process is dependent upon natural oxygen diffusion rates (11) and as a result is frequently too slow to prevent the spread of contamination. Such sites may require remediation of the contaminant source to protect sensitive aquifers. At these sites, an acceleration or enhancement of the natural biodegradation process may prove the most effective remediation.

Important in any in situ remediation is an understanding of the distribution of contaminants. Much of the residue of hydrocarbons at a fuel contaminated site is found in the unsaturated zone soils, in the capillary fringe, and immediately below the water table. Typically, seasonal water table fluctuations spread residues in the area immediately above and below the water table. Any successful bioremediation effort must treat these areas.

CONVENTIONAL ENHANCED BIODEGRADATION

Over the past two decades the practice of enhanced biodegradation has increased, particularly for treating soluble fuel components in groundwater (8). Less emphasis has been given to enhancing

biodegradation in the unsaturated zone. The current conventional enhanced bioreclamation process uses water to carry the oxygen or an alternative electron acceptor to the contamination, whether it occurs in the groundwater or unsaturated zone.

A recent field experiment at a jet fuel contaminated site using infiltration galleries and spray irrigation to introduce oxygen (as hydrogen peroxide), nitrogen, and phosphorus to unsaturated, sandy soils was unsuccessful because of rapid hydrogen peroxide decomposition and resulting poor oxygen distribution (6). A study being conducted by the U.S. Environmental Protection Agency and the U.S. Coast Guard at Traverse City, Michigan, uses deep well injection to raise the water table in order to supply oxygen-enriched water to the contaminated soils. Pure oxygen and hydrogen peroxide have been used as oxygen sources, and recently nitrate has been added as an alternative to oxygen. Although results indicate better hydrogen peroxide stability than achieved by Hinchee et al. (6), it was concluded that much of the hydrogen peroxide decomposed rapidly and was lost as bubbles (7). Some degradation of aromatic hydrocarbons appears to have occurred; however, no change in total hydrocarbon contamination levels was detected in the soils (14).

In most cases where water is used as the oxygen carrier, oxygen is the limiting factor for biodegradation. If pure oxygen is utilized and 40 mg/l of dissolved oxygen is achieved, approximately 80,000 kg of water must be delivered to the formation to degrade a single kg of hydrocarbon. If 500 mg/l of hydrogen peroxide is successfully delivered, then approximately 13,000 kg of water are necessary. As a result, even if hydrogen peroxide can be successfully used, substantial volumes of water must be pumped through the contaminated formation to deliver sufficient oxygen.

ENHANCED BIODEGRADATION THROUGH VACUUM EXTRACTION

A system engineered to increase the microbial biodegradation of fuel hydrocarbons in the vadose zone using forced air as the oxygen source is a cost-effective alternative to conventional systems. This process stimulates soil-indigenous microorganisms to aerobically metabolize fuel hydrocarbons in unsaturated soils. Depending on air flow rates, volatile compounds may be simultaneously removed from contaminated soils.

By using air as an oxygen source, the minimum ratio (based on stoichiometry) of air to hydrocarbon on a mass basis is approximately 13 to 1. This compares with over 10,000 to 1, water to hydrocarbon, for a conventional waterborne enhanced bioreclamation process. An additional advantage of using an airborne process is that gases have greater diffusivity than liquids. At many sites, geological heterogeneities present an added problem with a waterborne oxygen source because fluid pumped through the formation is channelled into the more permeable pathways. For example, in an alluvial soil with interbedded sand and clay, virtually all of the fluid flow will take place in the sand. As a result, oxygen must be delivered to the less permeable clay lenses through diffusion. In a gaseous system this diffusion can be expected to take place at a rate several orders of magnitude greater than in a liquid system. Although it is not realistic to expect diffusion to aid significantly in water-based bioreclamation, in an air-based application, diffusion may be a significant mechanism for oxygen delivery to less permeable zones.

The first documented evidence of unsaturated zone biodegradation resulting from forced aeration was reported by the Texas Research Institute, Inc., in a study for the American Petroleum

Institute. A large-scale model experiment was conducted to test the effectiveness of a surfactant treatment to enhance recovery of spilled gasoline. The experiment accounted for only 30 liters of the 250 liters originally spilled and raised questions about the fate of the gasoline. A subsequent column study was conducted to determine a diffusion coefficient for soil venting. This column study evolved into a biodegradation study in which it was concluded that as much as 38 percent of the fuel hydrocarbon was biologically mineralized. Researchers concluded that venting would not only remove gasoline by physical means, but also could enhance microbial activity (12,13).

Wilson and Ward (15) suggested that using air as a carrier for oxygen could be 1,000 times more efficient than transferring it to water, especially in deep, hard-to-flood unsaturated zones. They made the connection between soil venting and biodegradation by observing that "soil venting uses the same principle to remove volatile components of the hydrocarbon." In a general overview of the soil venting process, Bennedsen (2) concluded that soil venting provides large quantities of oxygen to the vadose zone, possibly stimulating aerobic degradation. He suggested that water and nutrients would also be required for significant degradation and encouraged additional investigation into this area.

Biodegradation enhanced by soil venting has been observed at several field sites. Investigators at a soil venting site for remediation of gasoline contaminated soil claim significant biodegradation as measured by a temperature rise when air was supplied. Investigators pulsed pumped air through a pile of excavated soil and observed a consistent temperature rise that they attributed to biodegradation. They claimed that the pile was cleaned up during the summer primarily by biodegradation (3). However, they did not control for natural volatilization from the aboveground pile, and not enough data were published to review the biodegradation claim critically.

Researchers at Traverse City, Michigan, measured toluene concentration in vadose zone soil gas as an indicator of fuel contamination in the vadose zone. They assumed absence of advection and attributed toluene loss to biodegradation. The investigators concluded that, because toluene concentrations decayed near the oxygenated ground surface, soil venting is an attractive remediation alternative for biodegrading light volatile hydrocarbon spills (11).

Ely and Heffner (5) of the Chevron Research Company patented a process for the in situ biodegradation of spilled hydrocarbons using soil venting. Experimental design and data are not provided, but findings are presented graphically. At a gasoline and diesel oil contaminated site, slightly higher removal through biodegradation than through evaporation was observed. At a gasoline contaminated site, results indicated that about 2/3 of the hydrocarbon removal was by volatilization and 1/3 by biodegradation. At a site containing only fuel oils, approximately 75 liters/well/day were biodegraded, while vapor pressures were too low for removal by volatilization. Ely and Heffner (5) claimed that the process is more advantageous than strict soil venting because removal is not dependent only on vapor pressure. In the examples stated in the patent, CO₂ was maintained between 6.8 percent and 11 percent and O₂ between 2.3 percent and 11 percent in vented air. The patent suggests that the addition of water and nutrients may not be acceptable because of flushing to the water table, but nutrient addition is claimed as part of the patent. The patent recommends flow rates between 50 and 420 m³/min per well and states that air flows higher than those required for volatilization may be optimum for biodegradation.

APPLICATIONS

The use of an air-based oxygen supply for enhancing biodegradation relies on air flow through hydrocarbon-contaminated soils at rates and configurations that will ensure adequate oxygenation of aerobic biodegradation and minimize or eliminate the production of a hydrocarbon-contaminated offgas. The addition of nutrients and moisture may be desirable to increase biodegradation rates. Figures 1 and 2 illustrate possible air injection/withdrawal configurations. Dewatering is illustrated in Figure 1, but this may not always be necessary depending upon the distribution of contaminants relative to the water table. However, it is required at many fuel hydrocarbon-contaminated sites. A key feature not illustrated is the narrowly screened soil gas monitoring points that sample only a short vertical section of the soil. These points are required to determine local oxygen concentrations. Measurements of oxygen levels in the vent are not representative of local conditions. Nutrient and moisture addition typically may take any of a variety of configurations.

A conventional soil venting installation where air is drawn from a vent well in the area of greatest contamination is possible. The advantage of this configuration is that it generally requires the least air pumping; the disadvantage is that hydrocarbon offgas concentration is probably maximized and all of the capillary fringe contamination may not be treated. Figure 1 involves air injection only. This is the lowest cost configuration; however, monitoring must assure that surface emissions do not exceed acceptance levels, and monitoring and/or protection of subsurface structures may be required. Figure 2 illustrates a configuration in which air is injected into the contaminated zone and withdrawn from clean soils. This configuration allows the more volatile hydrocarbons to degrade prior to being withdrawn and thereby eliminates contaminated offgases. The optimal configuration for any given site will, of course, depend upon site-specific conditions and remedial objectives.

The significant features of this technology include the following:

- Optimizing air flow to reduce volatilization, while maintaining aerobic conditions for biodegradation
- Monitoring local soil gas conditions to assure aerobic conditions, not just monitoring vent gas composition
- Adding moisture and nutrients as required to increase biodegradation rates
- Manipulating the water table as required for air/contaminant contact.

HILL AIR FORCE BASE SITE

A spill of approximately 100,000 liters of JP-4 jet fuel occurred when an automatic overflow device failed at Hill Air Force Base near Ogden, Utah. The contamination is primarily found in the upper 20 meters of a delta outwash of the Weber River. This surficial formation extends from the surface to a depth of approximately 20 meters and is composed of mixed sand and gravel with occasional clay stingers. Depth to regional groundwater is approximately 200 meters, however, water may occasionally be found in discontinuous perched zones. Soil moisture averaged less than 6 percent in the contaminated soils.

FIGURE 1. CONCEPTUAL LAYOUT OF LOW INTENSITY BIORECLAMATION TECHNOLOGY

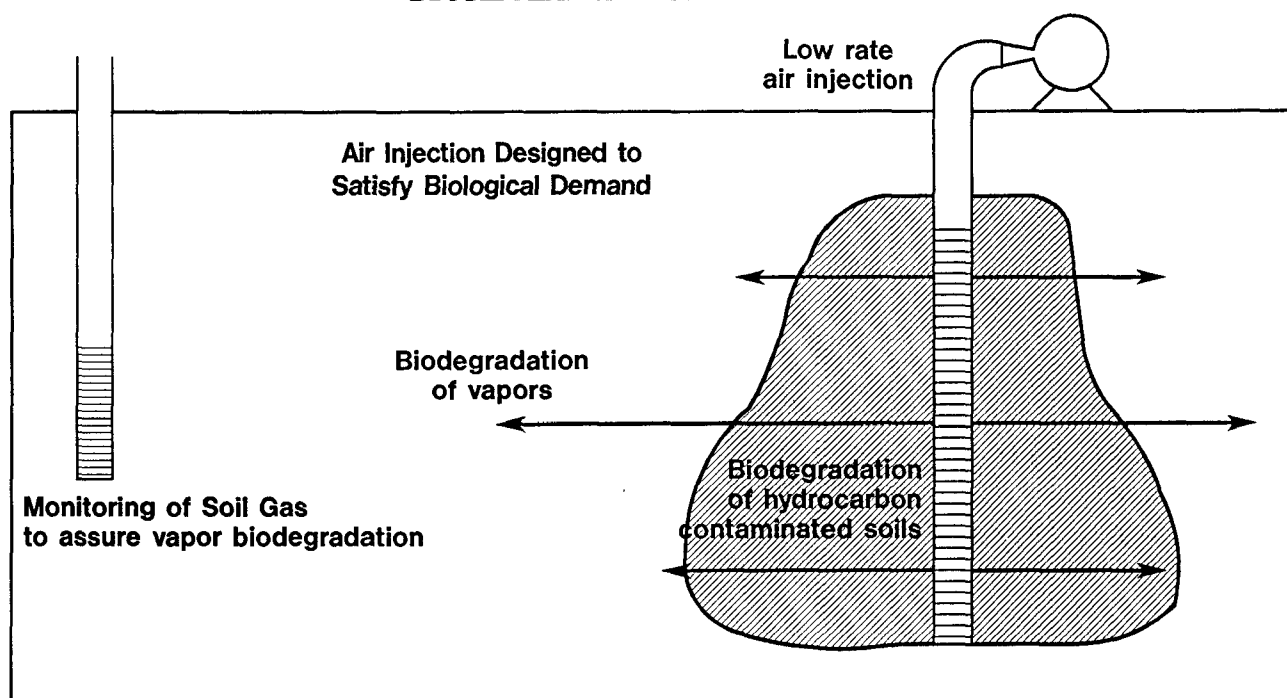
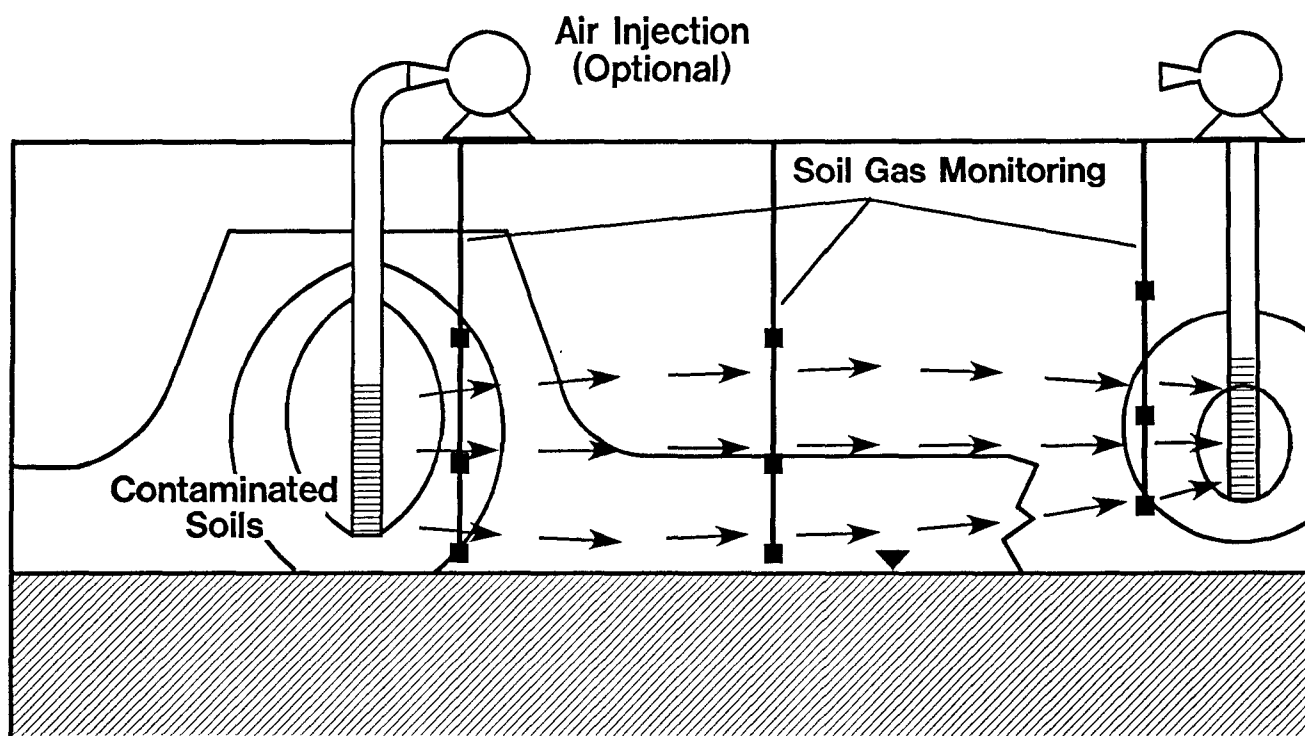


FIGURE 2. POTENTIAL CONFIGURATION FOR ENHANCED BIORECLAMATION THROUGH SOIL VENTING (AIR WITHDRAWN FROM CLEAN SOIL)



Soil samples that were collected indicated JP-4 concentrations up to 20,000 mg/kg, with an average concentration of approximately 400 mg/kg (10). Contaminants were unevenly distributed to depths of 20 meters. Vent wells were drilled to approximately 20 meters below the ground surface and screened from 3 to 18 meters below the surface. A background vent was installed in an uncontaminated location in the same geological formation approximately 200 meters north of the site.

Venting was initiated in December 1988 at a rate of approximately 45 m³/hr. The offgas was treated by catalytic incineration, and it was initially necessary to dilute the highly concentrated gas to remain below explosive limits and within the incinerator's hydrocarbon operating limits. The venting rate was gradually increased to approximately 2,500 m³/hr as hydrocarbon concentration levels dropped (10). During the period between December 1988 and November 1990, more than 10,000,000 m³ of soil gas were extracted from the site. In November 1989, ventilation rates were reduced to approximately 500 to 1,000 m³/hr to provide aeration for bioremediation but to reduce volatilization. This resulted in removal of the catalytic incinerator, saving approximately \$6,000 per month. Oxygen and hydrocarbon concentrations were measured in the offgas during extraction. To quantify the extent of biodegradation at the site, the oxygen was converted to an equivalent basis. This was based upon the stoichiometric oxygen requirement for hexane mineralization. JP-4 was determined based on direct readings of a total hydrocarbon analyzer calibrated to hexane.

Based upon these calculations, the mass of JP-4 as carbon removed and degraded was approximately 53,000 kg volatilized and 42,000 kg biodegraded. Figures 3 and 4 illustrate these results. Further details of this study are reported in Dupont et al. (4).

TYNDALL AIR FORCE BASE SITE

As a follow-up to the Hill Air Force Base (AFB) research, a more controlled study was designed. The experimental area at Tyndall AFB was located at a site where past JP-4 storage had resulted in contaminated soils. The nature and volume of fuel spilled or leaked is unknown. Initial site characterization indicated soil hydrocarbon levels up to 20,000 mg/kg. The site soils are a fine to medium grained quartz sand and depth to groundwater is 0.5 to 1.0 meters. Four test cells were constructed to allow control of gas flow, water flow, and nutrient addition. Two of the test cells were installed in the hydrocarbon contaminated zone and two in uncontaminated soils. The contaminated area was dewatered and hydraulic control was maintained to keep the depth to water at approximately 1.6 meters. This exposed more of the contaminated soil to aeration. During normal operation, air flow rates were maintained at approximately 1 air-filled void volume exchange per day. Biodegradation and volatilization rates were much higher than those observed at Hill AFB; this was likely due to higher average levels of contamination, warmer temperatures, and moisture conditions. As illustrated in Figure 5, at 120 days of aeration in one treatment cell approximately 50 kg of hydrocarbons had volatilized and 50 kg biodegraded. This represents an average hydrocarbon reduction of approximately 3,000 mg/kg in the treated soils. Biodegradation rates measured here appeared to be initially high and then declined substantially. The causes of this are unclear; however, they did not appear to be related to hydrocarbon disappearance--biodegradation rates dropped substantially before 20 percent of the hydrocarbon was removed. This study concluded that at this site nutrient and moisture addition did not result in higher rates of biodegradation. More complete results are found in Miller et al. (9).

FIGURE 3. CUMULATIVE HYDROCARBON REMOVAL FROM THE HILL AFB SOIL VENTING SITE

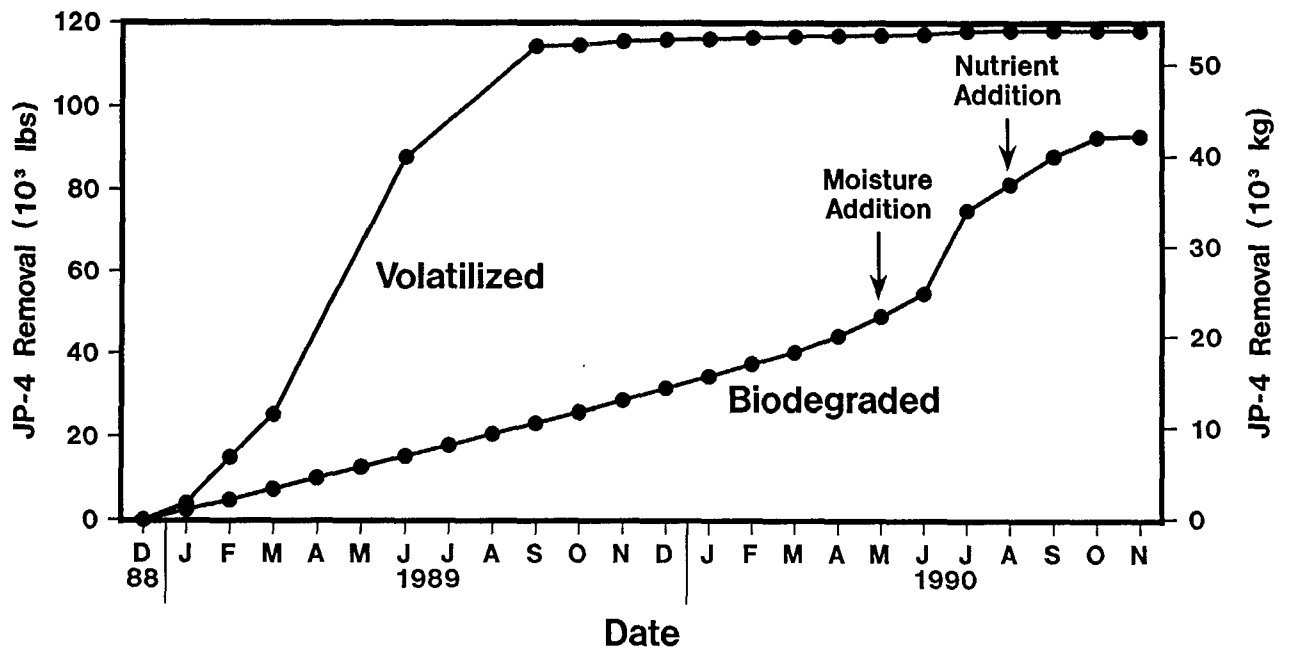


FIGURE 4. RESULTS OF SOIL ANALYSIS AT HILL AFB BEFORE AND AFTER VENTING (EACH BAR IS THE AVERAGE OF 14 OR MORE SAMPLES)

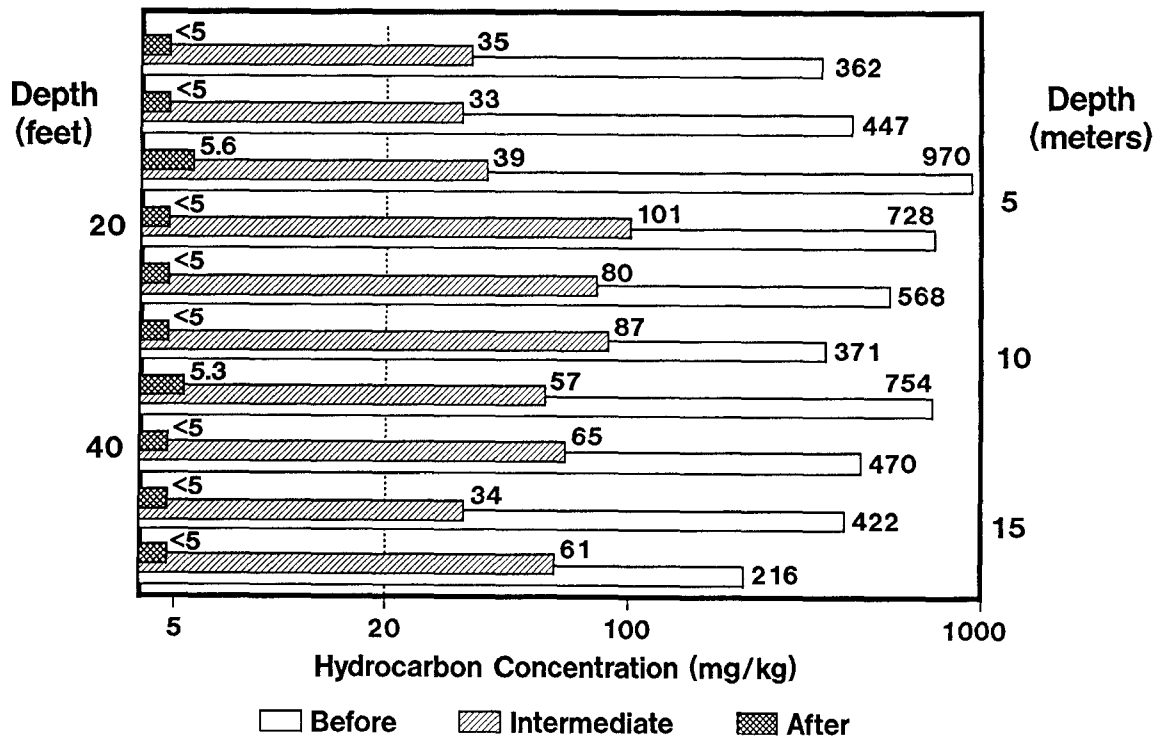
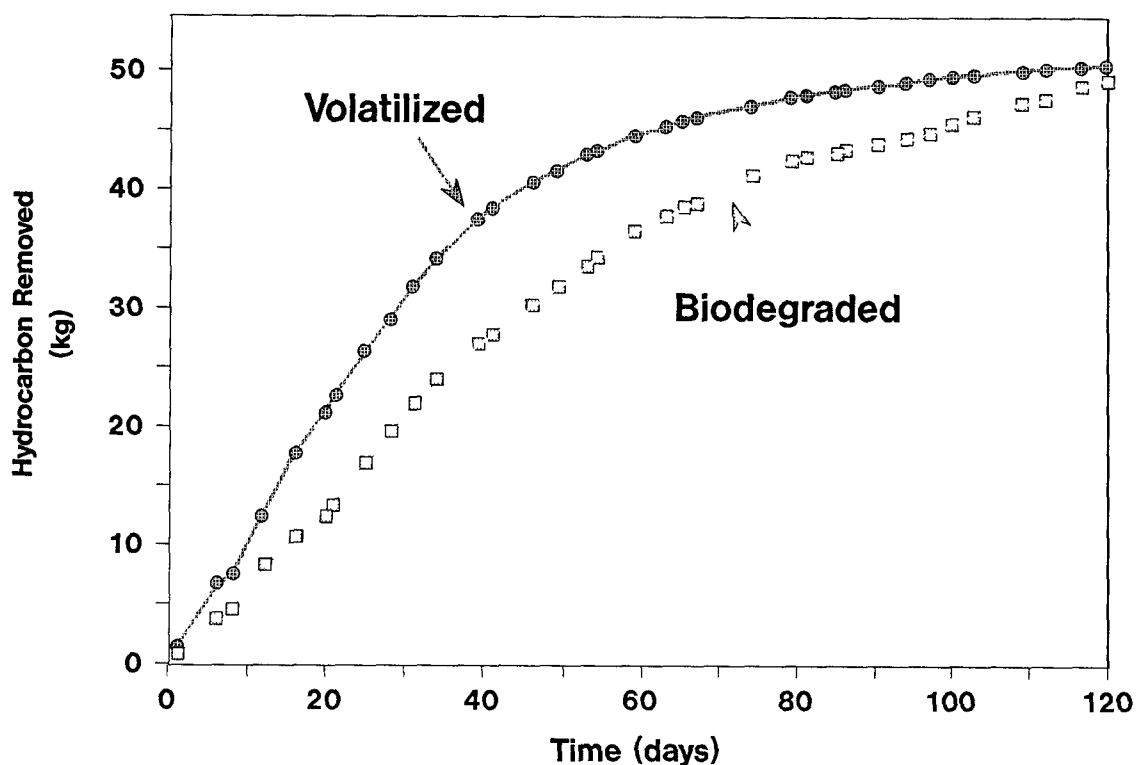


FIGURE 5. CUMULATIVE HYDROCARBON REMOVAL IN TREATMENT PLOT V1 AT TYNDALL AFB



RECOMMENDATIONS

Using air as the oxygen source is a cost-effective way to increase the microbial degradation of fuel hydrocarbons in unsaturated soil. Soil venting alone, with no nutrient or moisture addition, typically results in some stimulation of in situ biodegradation. The following recommendations are made for documenting biodegradation when conducting conventional soil venting of fuel hydrocarbon contaminated soils:

1. Prior to venting, determine soil gas hydrocarbon, CO_2 , and O_2 profiles.
2. Measure hydrocarbon, CO_2 , and O_2 in the offgas. This information can be used to document biodegradation and may help determine the end point for venting. A mixed hydrocarbon fuel such as JP-4 has a fraction too heavy to volatilize, and it is possible that biodegradation may continue after the light end has volatilized. This information is essential to complete a mass balance of spilled hydrocarbons and to estimate the extent of cleanup.
3. Develop an estimate of noncontaminant respiration. This may be accomplished either through background measurements of CO_2 and O_2 in an uncontaminated location or by means of carbon isotopic analysis.

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A FIELD SCALE INVESTIGATION OF SOIL VENTING ENHANCED PETROLEUM HYDROCARBON

BIODEGRADATION IN THE VADOSE-ZONE AT TYNDALL AFB, FLORIDA

MAJOR ROSS N. MILLER, PH.D, PE, CIH

U. S. Air Force, HSD/YAQE
Brooks Air Force Base, Texas

ROBERT E. HINCHEE, PH.D, PE

Battelle Memorial Institute
Columbus, Ohio

CAPTAIN CATHERINE M. VOGEL

U. S. Air Force, AFESC/RDVW
Tyndall Air Force Base, Florida

ABSTRACT

Soil venting is effective for the physical removal of volatile hydrocarbons from unsaturated soils, and is also effective as a source of oxygen for biological degradation of the volatile and non-volatile fractions of hydrocarbons in contaminated soil. Treatment of soil venting off-gas is expensive, constituting a minimum of 50% of soil venting remediation costs. In this research, methods for enhancing biodegradation through soil venting were investigated, with the goal of eliminating the need for expensive off-gas treatment.

A seven-month field investigation was conducted at Tyndall Air Force Base (AFB), Florida, where past jet fuel storage had resulted in contamination of a sandy soil. The contaminated area was dewatered to maintain approximately 1.6 meters of unsaturated soil. Soil hydrocarbon concentrations ranged from 30 to 23,000 mg/kg. Contaminated and uncontaminated test plots were vented for 188 days. Venting was interrupted five times during operation to allow for measurement of biological activity (CO_2 production and O_2 consumption) under varying moisture and nutrient conditions.

Moisture addition had no significant effect on soil moisture content or biodegradation rate. Soil moisture content ranged from 6.5 to 9.8%, by weight, throughout the field test. Nutrient addition was also shown to have no statistically significant effect on biodegradation rate. Initial soil sampling results indicated that naturally occurring nutrients were adequate for the amount of biodegradation observed. Acetylene reduction studies, conducted in the laboratory, indicated a biological nitrogen fixation potential capable of fixing the organic nitrogen, observed in initial soil samples, in five to eight years under anaerobic conditions. Biodegradation rate constants were shown to be effected by soil temperature and followed predicted values based on the van't Hoff-Arrhenius Equation.

In one treatment cell, approximately 26 kg of hydrocarbons volatilized and 32 kg biodegraded over the seven-month field test. Although this equates to 55% removal attributed to biodegradation, a series of flow rate tests showed that biodegradation could be increased to 85% by managing air flow rate. Off-gas from one treatment cell was injected into clean soil to assess the potential for complete biological remediation. Based on biodegradation rate data collected at this field site, a soil volume ratio of approximately 4 to 1, uncontaminated to contaminated soil, would have been required to completely biodegrade the off-gas from the contaminated soil.

This research indicates that proper ratios of uncontaminated to contaminated soil and air flow management are important factors in influencing total biodegradation of jet fuel, substantially reducing remediation costs associated with treatment of soil venting off-gas.

MATERIALS AND METHODS

Site Description

An *in situ* field demonstration of enhanced biodegradation through soil venting was conducted at the site of an abandoned tank farm located on Tyndall AFB, Florida. The site is contaminated with fuel, primarily JP-4, and free product has been observed floating on the shallow ground water table. Tyndall AFB is located on a peninsula that extends along the shoreline of the Gulf of Mexico in the central part of the Florida Panhandle. The highest ground on the peninsula is 7.6 to 9.1 m (25 to 30 ft) above mean sea level. The uppermost sediments, at Tyndall AFB, are sands and gravels of Pleistocene to Holocene age (2). Soils at the site are best described by the Mandarin series consisting of somewhat poorly drained, moderately permeable soils that formed in thick beds of sandy material (5).

The climate at the site is sub-tropical with an annual average temperature of 20.5° C (69°F). Average daily maximum and minimum temperatures are 25°C and 16°C (77°F and 61°F), respectively. Temperatures of 32°C (90°F) or higher are frequently reached during summer months, but temperatures above 38°C (100°F) are reached only rarely. Average annual rainfall at Tyndall AFB is 140 cm (55.2 inches) with approximately 125 days of recordable precipitation during the year. The depth to ground water on Tyndall AFB varies from about 0.3 to 3.0 m (1 to 10 ft). The water-table elevation rises during periods of heavy rainfall and declines during periods of low rainfall. Yearly fluctuations in ground water elevations of approximately 1.5 m (5 ft) are typical (2). Prior to dewatering at the site, the water table was observed to be as shallow as 46 cm (1.5 ft).

Field Testing Objectives

A seven month field study (October, 1989, to May, 1990) was designed to address the following areas:

1. Does soil venting enhance biodegradation of JP-4 at this site?
2. Does moisture addition coupled with soil venting enhance biodegradation at this site?

3. Does nutrient addition coupled with soil venting and moisture addition enhance biodegradation at this site?
4. Will the hydrocarbons in the off-gas biodegrade when passed through uncontaminated soil?
5. Evaluation of ventilation rate manipulation to maximize biodegradation and minimize volatilization.
6. Calculation of specific biodegradation rate constants from a series of respiration tests conducted during shutdown of the air extraction system.
7. Determination of the effects of biodegradation and volatilization on a subset of selected JP-4 components.
8. Determination of the potential for nitrogen fixation under aerobic and anaerobic conditions.
9. Evaluation of alternative vent placement and vent configuration to maximize biodegradation and minimize volatilization.

Test Plot Design and Operation

In order to accomplish project objectives, two treatment plots and two background plots were constructed and operated in the following manner:

1. Contaminated Treatment Plot 1 (V1) - Venting only for approximately 8 weeks, followed by moisture addition for approximately 14 weeks, followed by moisture and nutrient addition for approximately 7 weeks.
2. Contaminated Treatment Plot 2 (V2) - Venting coupled with moisture and nutrient addition for 29 weeks.
3. Background Plot 3 (V3) - Venting with moisture and nutrient addition at rates similar to V2, with injection of hydrocarbon contaminated off-gas from V1.
4. Background Plot 4 (V4) - Venting with moisture and nutrient addition at rates similar to Vent 2.

Air Flow

Air flow was maintained throughout the field test duration except during in situ respiration tests. Flow rates were adjusted to maintain aerobic conditions in treatment plots, and background plots were operated at similar air retention times. Off-gas treatment experiments in one background plot (V3) involved operation at a series of flow rates and retention times. Soil gas was withdrawn from the center monitoring well in V1 and V2 and from the only monitoring well in V3 and V4. This configuration was selected to minimize leakage of outside air observed when air was withdrawn from the ends of the plots. In all but one plot, V3, atmospheric air was allowed to passively enter at both ends. Off-gas from V1 was pumped back to the upstream ends of V3. Flow rates through all test plots were measured with calibrated rotameters.

Water Flow

To allow control of soil moisture, tap water was applied to the surface of the treatment plots. The design flow rates allowed variation from 10 to 100 mL/min in the contaminated treatment plots, and 2.5 to 25 mL/min in the background vents. This corresponds to an average annual surface application rate of 43 to 430 cm (17 to 170 in). Based on vacuum and oxygen measurements in the soil gas monitoring probes, it was determined that a flow rate of 100 mL/min in the Treatment Plots inhibited air flow and oxygen transfer. Using the same technique, a flow rate of 50 mL/min (215 cm/yr surface application rate) was selected as the final water application rate. This rate did not appear to inhibit oxygen transfer to the soil gas monitoring points.

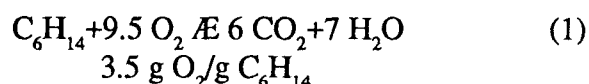
Nutrient Addition

The objective of nutrient addition was to apply sufficient inorganic nitrogen (N), phosphorus (P), and potassium (K) to ensure, as far as possible, that these nutrients would not become limiting during the biodegradation of fuel hydrocarbons in the test plots. Optimizing nutrient addition rates was not the primary objective of this phase of the study. Sodium trimetaphosphate (Na-TMP), ammonium chloride (NH₄Cl), and potassium nitrate (KNO₃) were used as sources of P, N, and K, respectively.

RESULTS AND DISCUSSION

Operational Monitoring of Treatment Plots V1 and V2

Treatment plots were operated for 188 days between October 4, 1989 and April 24, 1990. Operation was interrupted only for scheduled respiration tests. Discharge gases were monitored for oxygen, carbon dioxide, and total hydrocarbons throughout the operational period. The biodegradation component was calculated using the stoichiometric oxidation of hexane (Equation 1).



Oxygen consumption was calculated as the difference between oxygen in Background Plot V4 and oxygen in the treatment plots. Using the oxygen concentration in the background plot, rather than atmospheric oxygen concentration, the natural biodegradation of organic carbon in uncontaminated soil was accounted for. This method ensured that the biodegradation of fuel hydrocarbons was not overestimated. Biodegradation based on carbon dioxide production was similarly calculated. Hydrocarbon removal rates attributed to volatilization and biodegradation are presented in Figures 1 and 2, respectively, for Treatment Plots V1 and V2. Removal rates are expressed in mg/(kg day) and are based on an estimated soil bulk density of 1440 kg/m³ (90 lb/ft³) and a treatment volume of 20 m³ (704 ft³).

As the more volatile compounds are stripped from the soil, biodegradation becomes increasingly important over time as the primary hydrocarbon removal mechanism as illustrated in Figures 3 and 4 for Treatment Plots V1 and V2, respectively. Percentages of combined volatilization and biodegradation removal rates attributable to biodegradation are compared in Figure 5 for Treatment Plots V1 and V2.

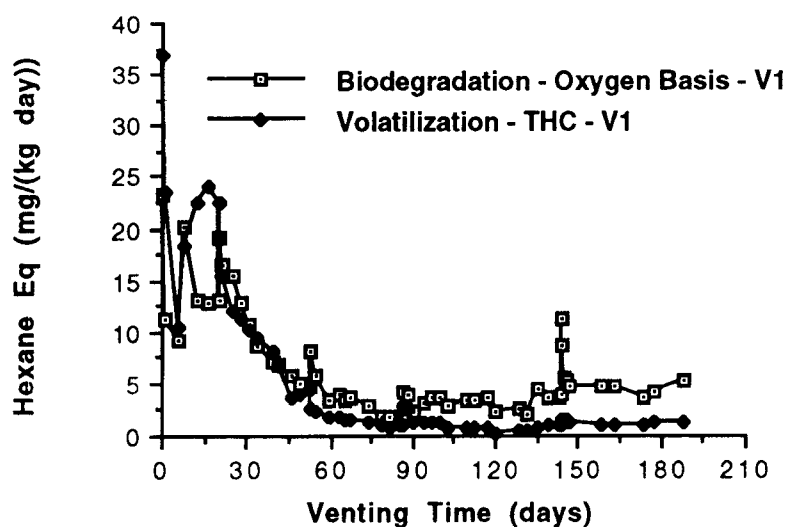


Figure 1. Hydrocarbon removal rate attributed to volatilization and biodegradation (oxygen basis) in treatment plot V1 during the field study.

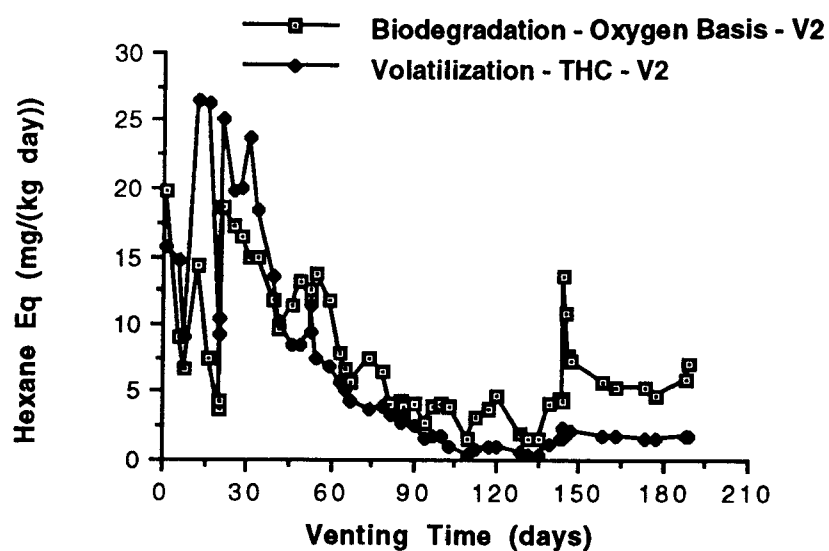


Figure 2. Hydrocarbon removal rate attributed to volatilization and biodegradation (oxygen basis) in treatment plot V2 during the field study.

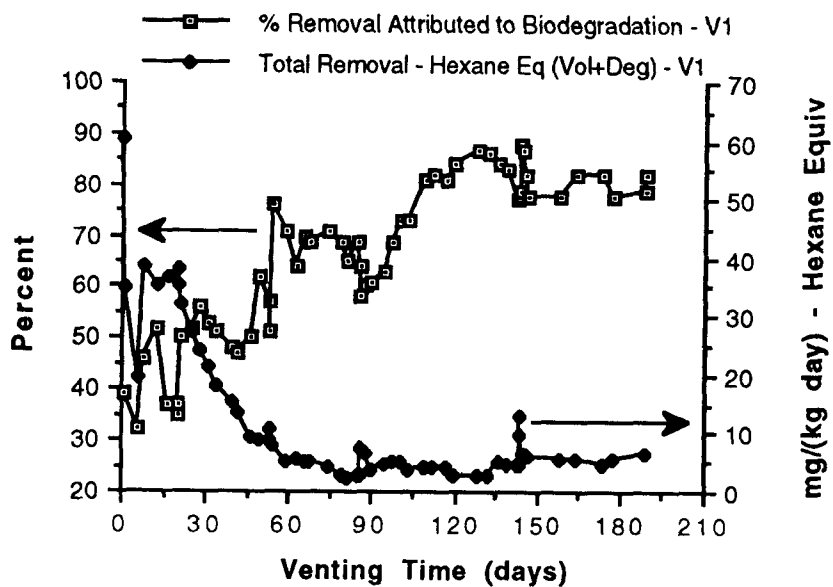


Figure 3. Comparison of the combined volatilization and biodegradation removal rates and the percent of removal rate attributed to biodegradation (oxygen basis) in Treatment Plot V1 during the field study.

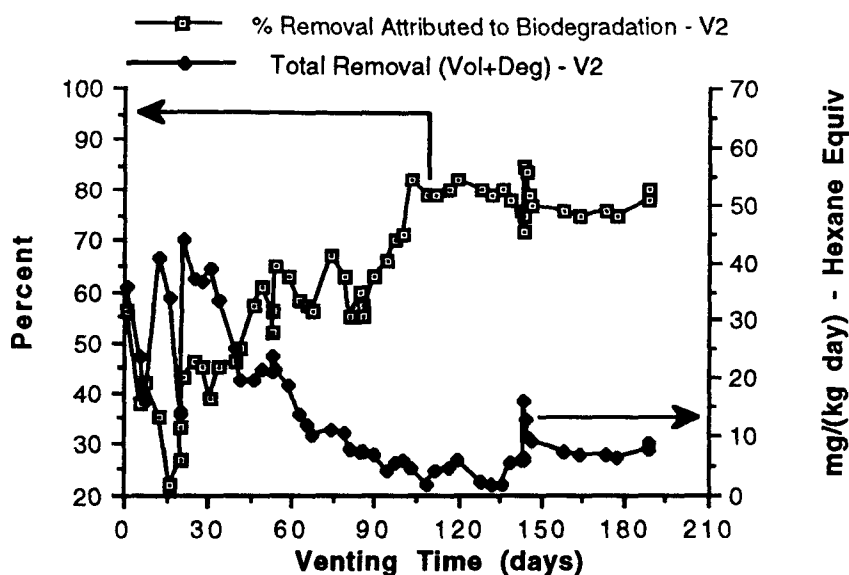


Figure 4. Comparison of the combined volatilization and biodegradation removal rates and the percent of removal rate attributed to biodegradation (oxygen basis) in Treatment Plot V2 during the field study.

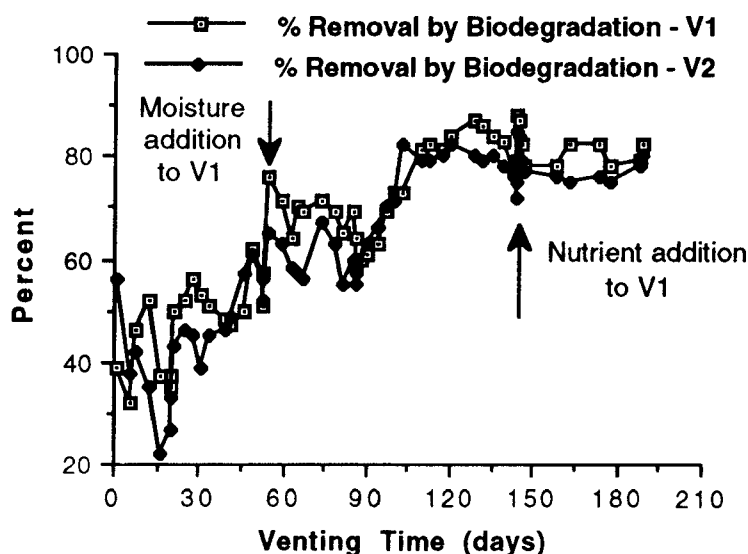


Figure 5. Comparison of the percent of combined volatilization and biodegradation hydrocarbon removal rates attributed to biodegradation (oxygen basis) in Treatment Plots V1 and V2 during the field study.

Operational data for the treatment plots are remarkably similar considering that Treatment Plot V2 received moisture and nutrients throughout the experimental period and Treatment Plot V1 received moisture after eight weeks of operation and nutrients after 22 weeks of operation. The relationships demonstrated above indicate that moisture and nutrients were not a limiting factor in hydrocarbon biodegradation removal rate.

Flow Rate vs Total Hydrocarbon Removal Rate and Percent Biodegradation In Treatment Plots

Rate constants (k) for oxygen consumption and carbon dioxide production have been shown, through respiration tests in this research (Miller, 1990), to follow zero order kinetics for oxygen concentrations above 1%. Therefore, lower flow rates, resulting in longer retention times should result in higher percentages of hydrocarbon removal by biodegradation.

An experiment was conducted to evaluate the relationship between air flow rate, total hydrocarbon removal rate, and percent of total removal attributed to biodegradation following the period of high volatilization removal (after approximately 75 days of venting). Beginning at Day 89, air flow rates in Treatment Plots V1 and V2 were varied over a seven week period from January 8, 1990, to February 28, 1990. Flow rates were approximately 8, 4, 2, and 1 l/min which equate to approximately 2, 1, 0.5, and 0.25 air filled void volumes per day, respectively. Oxygen, carbon dioxide, and hydrocarbon concentrations were allowed to stabilize at each air flow rate. Figures 6 and 7 illustrate the data for Treatment Plots V1 and V2, respectively, using oxygen and total hydrocarbon concentrations in the discharge gas streams as the basis for calculating percent removal by biodegradation. Figures 6 and 7 reveal a trade-off between maximizing the percent of hydrocarbon removed by biodegradation and maximizing the overall hydrocarbon removal rate, thereby minimizing the operational time required to remediate a contaminated site. Using the data illustrated in

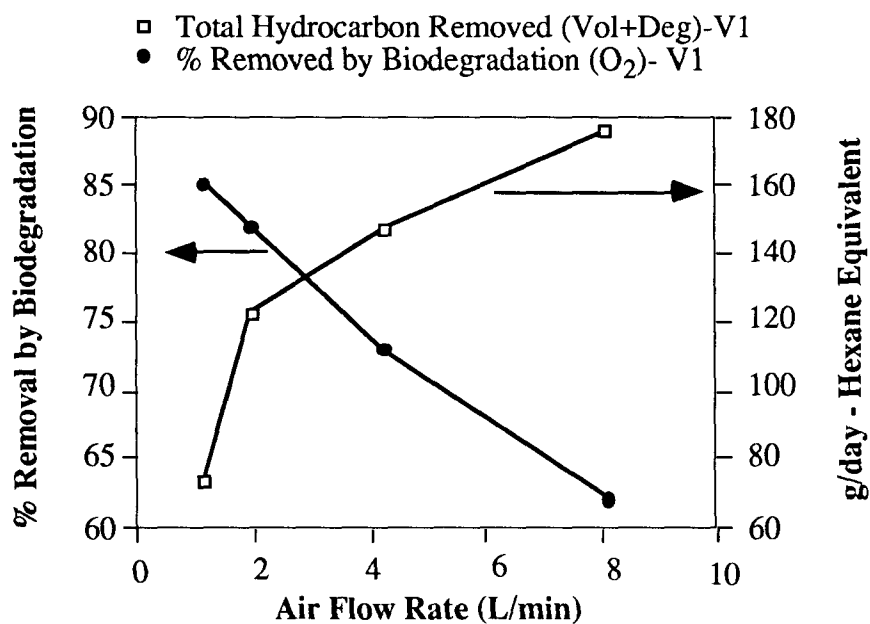


Figure 6. Comparison of air flow rate versus total hydrocarbon removal and percent of total removal attributed to biodegradation in Treatment Plot V1 (O₂ basis) during the variable air flow rate study.

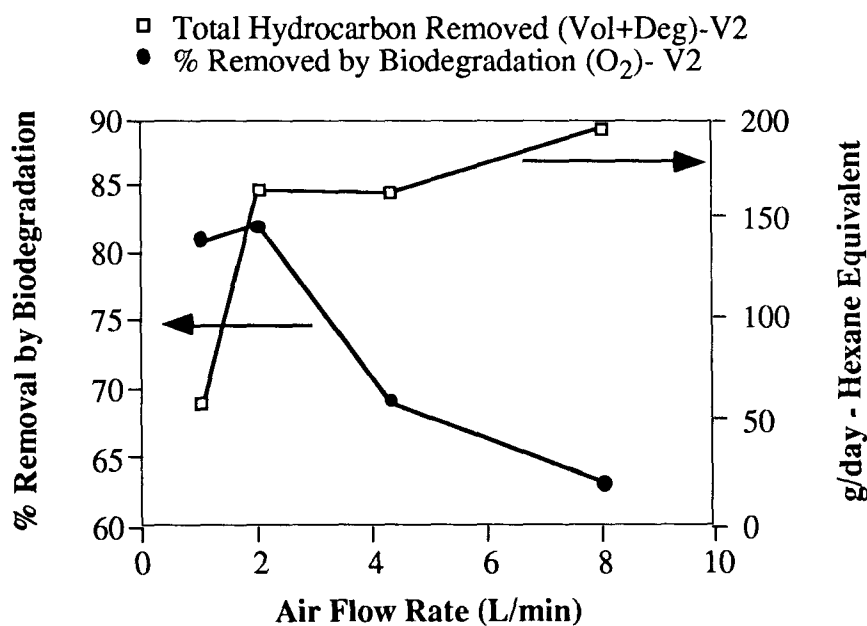


Figure 7. Comparison of air flow rate versus total hydrocarbon removal and percent of total removal attributed to biodegradation in Treatment Plot V2 (O₂ basis) during the variable air flow rate study.

Figure 6 for Treatment Plot V1 and assuming that 100,000 g (3500 mg/kg) of hydrocarbons must be removed, a hypothetical case can be evaluated. If 62% biodegradation is desired, then 8 l/min (two air void volumes per day) would be selected with an expected operational time of 571 days. However, if 85% biodegradation were desired, then 1 l/min (0.25 air void volumes per day) would be selected with an expected operational time of 1370 days. Although operational time is increased by a factor of 2.4, total air requirement actually decreases from 6.6 to 2.2 million L. Optimal air flow conditions in V1 appear to be 2 l/min (0.5 air void volumes per day) where 82% biodegradation is achieved. Although 85% biodegradation is achieved at 1 l/min in V1, hydrocarbon removal rate is greatly reduced. Operating at 2 l/min in V1, expected operation time is 820 days (1.4 times that required at 8 l/min) and the total air requirement is only 2.3 million L. It is emphasized that operational times in this case are merely hypothetical as relationships between air flow and removal rate are applicable only over the seven week field test period. However, it is likely that similar relationships would exist throughout the remediation period although the magnitude of removal rates vary widely.

This research has documented that decreasing air flow rates will increase the percent of hydrocarbon removal by biodegradation and decrease the percent of hydrocarbon removal by volatilization.

Respiration Tests

Respiration Tests, 1 through 5, were conducted October 24 through 26; November 28 through December 1, 1989; January 3 through 8; March 3 through 11; and April 24 through 26, 1990, respectively. In addition, two limited respiration tests, 3A and 4A, were conducted from January 25 through 26, and March 9 through 12, 1990. The respiration tests were designed to determine the order and rate of hydrocarbon biodegradation kinetics under varying conditions of moisture and nutrient addition. Treatment Plot V2 received moisture and nutrients throughout the experimental period and therefore served as a control for kinetic changes due to soil temperature and other factors not related to moisture and nutrients. The respiration tests were conducted by first shutting down the air delivery system to both the treatment and background plots, followed by measurement of oxygen consumption and carbon dioxide production over time. Biological respiration in Treatment Plots V1 and V2 was most consistently modeled by zero order kinetics during all respiration tests (Miller, 1990). In a system not limited by substrate, such as fuel contaminated soil, biodegradation is likely to be best modeled by zero-order kinetics (4).

Oxygen and carbon dioxide concentrations, measured in the vapor monitoring wells prior to initiating the respiration tests, were highly variable. Regardless of initial concentration, however, oxygen consumption and carbon dioxide production rates were relatively consistent. For this reason, the data were normalized by dividing oxygen concentration data measured in each vapor monitoring well by the initial oxygen concentration at each location. A regression of the normalized data versus time for each plot and each respiration test yielded a normalized zero order rate constant, that when multiplied by the initial average oxygen concentration in the plot, yielded the actual zero order rate constant ($k = \%/min$).

The normalized regression and 95% confidence interval band for Treatment Plot V1 is illustrated in Figure 8 for Respiration Test 4. Figure 8 is typical of all respiration tests conducted in Treatment Plots V1 and V2.

A summary of the zero order rate constant data obtained from the respiration tests is graphically illustrated in Figure 9. In Treatment Plot V1 the rate constant showed a significant drop between Test 1 and Test 2 and between Test 2 and Test 3. The rate constant significantly increased between Test 3 and Test 4 in Treatment

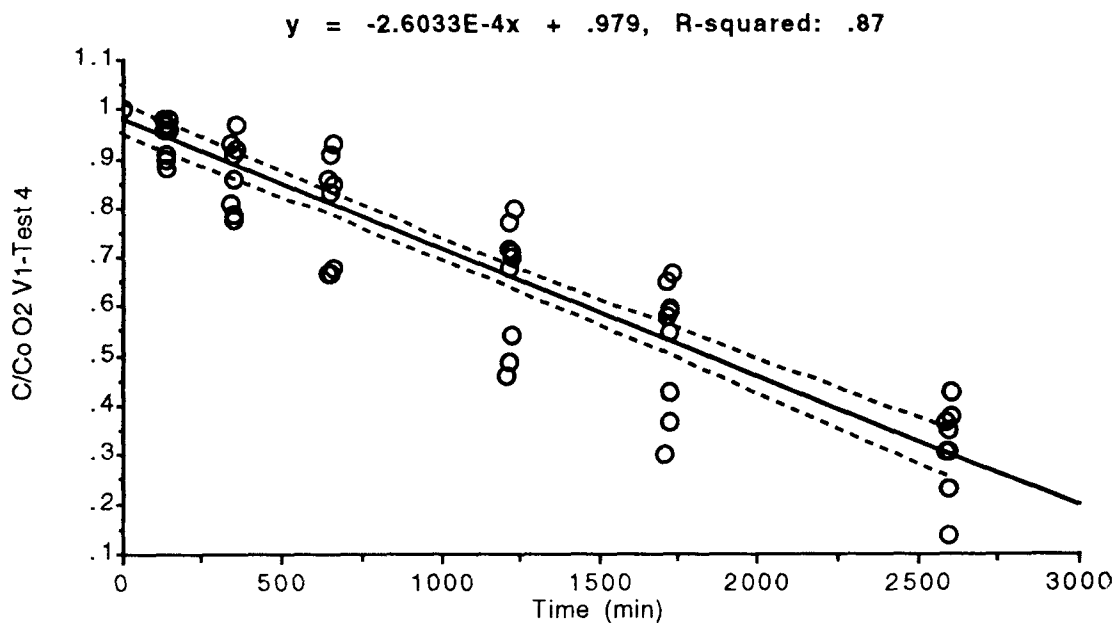


Figure 8. Regression of normalized data and 95% confidence band for Treatment Plot V1 and Respiration Test 4.

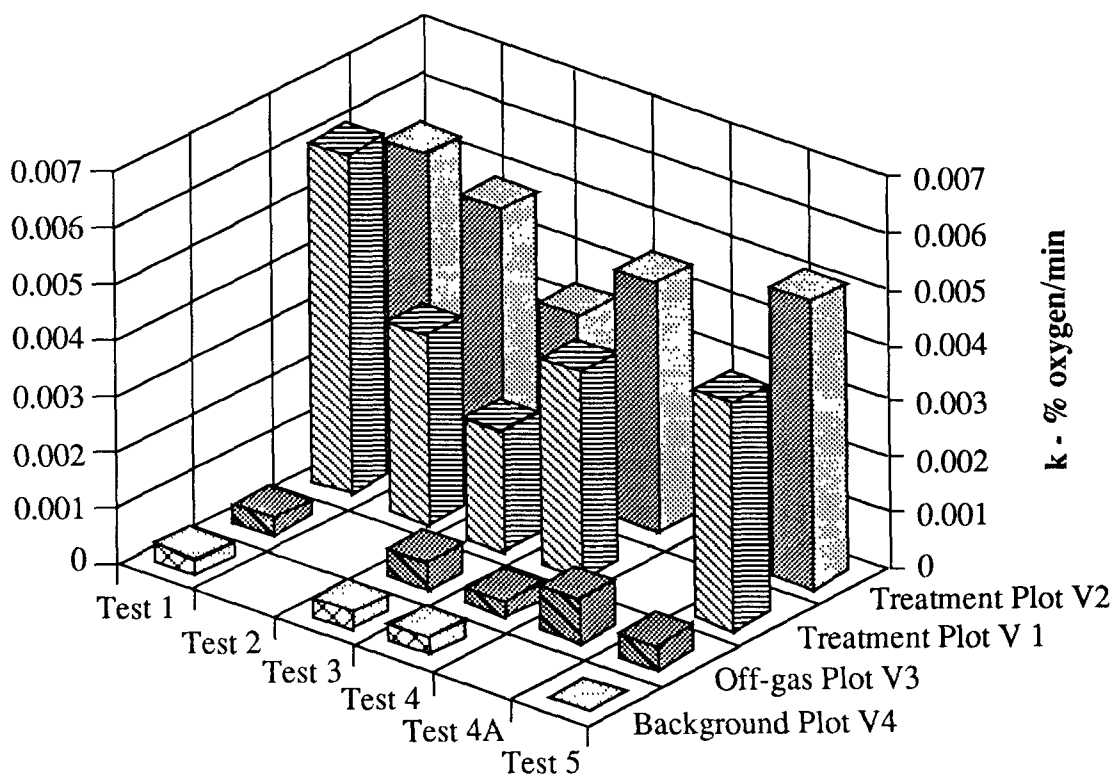


Figure 9. Average zero order rate constants determined by respiration tests.

Plot V1 but did not significantly increase between Tests 4 and 5. Since moisture was added to Treatment Plot V1 after Test 2 and nutrients after Test 4 their addition would seem without further analysis to be of no benefit and even detrimental in the case of moisture addition. In Treatment Plot V2 there was a statistically significant drop in the rate constant from Test 2 to Test 3 and a statistically significant increase in the rate constant between Test 3 and Test 4. Although a depression appears in the rate constant data there were no other statistically significant differences in Treatment Plot V2 rate constants.

Statistically significant differences in respiration rate between Treatment Plots V1 and V2 and the Background Plot V4 on all tests and between Off-Gas Treatment Plot V3 and Background Plot V4 on Tests 3, 4A, and 5 are illustrated in Figure 9. From the data presented it was concluded that biodegradation of jet fuel in contaminated soil and biodegradation of hydrocarbon off-gas resulted in statistically significant increases in respiration over that observed in uncontaminated soil.

Potential Temperature Effects on Respiration Tests

As described above, hydrocarbon biodegradation rates appear to have been unaffected by moisture and nutrient addition. This conclusion was based on insignificant differences in biodegradation rates in Treatment Plots V1 and V2 even though the treatment plots were operated under different moisture and nutrient conditions. Although biodegradation rates in the treatment plots were similar there was a general decline in hydrocarbon removal rates from initiation of the field study; reaching minimum values near the middle of the experimental period; followed by a general increase in hydrocarbon removal rates through the completion of the field study. Since the treatment plots appeared unaffected by moisture and nutrient addition soil temperature was investigated as the potential cause of the depression in biodegradation rates.

Soil temperature at this field site was related to ambient air temperature because air was continually drawn through the soil. More importantly, the moisture provided to the treatment plots affected soil temperature as the applied water temperature was a function of air temperature because this water was temporarily stored in the site building prior to delivery to the treatment plots. Local ambient temperature data were obtained from a weather station located near the field site. The 10 day moving average above ground air temperature data are compared with soil temperature in Figure 10. Soil temperature data before January 5, 1990, were not collected at the field site. Therefore, the relationship between ambient temperature and soil temperature was used to estimate soil temperatures prior to this date. Comparison of average soil temperature (Figure 10) to oxygen consumption rate (Figure 9) during respiration tests in Treatment Plots V1 and V2 imply a relationship between soil temperature and biological activity. It appears from the respiration data presented, that soil temperature had a much more significant effect on the rate of hydrocarbon biodegradation than moisture and nutrient addition.

To evaluate the effect of moisture and nutrient addition on biological activity in Treatment Plot V1, the effect of temperature must be understood. Treatment Plot V2 received moisture and nutrients throughout the experimental period and should be a control on temperature and other unmeasured variables. Therefore, a model that eliminates the effect of temperature on the oxygen consumption rate constants (Figure 9) in Treatment Plot V2 should be adequate for temperature correcting rate constants measured in Treatment Plot V1, thereby allowing an assessment of the effect of moisture and nutrient addition in Treatment Plot V1.

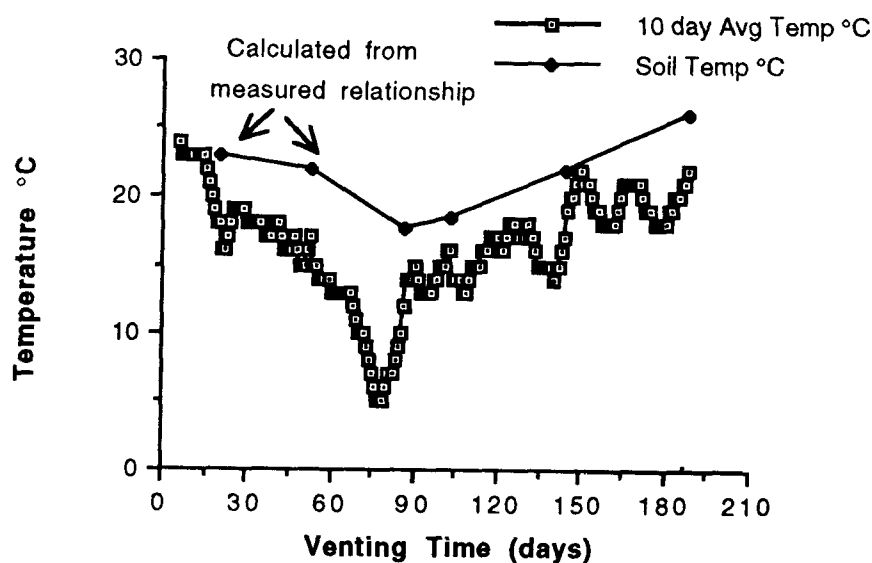


Figure 10. Comparison of the 10 day moving average of the mean ambient above ground air temperature and corresponding measured and estimated soil temperature.

In aquatic systems, the van't Hoff-Arrhenius equation predicts a doubling of the rate constant with each temperature increase of 10°C, assuming typical activation energy values (1). Figure 11 is the Arrhenius Plot for determining activation energy using measured soil temperature and rate constant relationships from Tests 3, 4, and 5 for Treatment Plots V1 and V2. Using the Arrhenius constants determined from the plots in Figure 11, the rate constants for Treatment Plots V1 and V2 were corrected to 23°C, the soil temperature of Test 1. The Arrhenius model for temperature correction resulted in insignificant rate constant differences between Tests 2, 3, 4, and 5 in Treatment Plot V2 (Figure 12). Therefore, the Arrhenius equation adequately modeled the effects of temperature on hydrocarbon biodegradation rate. Using the same model, the oxygen consumption rate constants in Treatment Plot V1 were corrected for temperature (Figure 13). Although statistically significant differences in rate constants remained between Test 3 and Tests 2 and 4 in Treatment Plot V1, the magnitude of the differences are not important from a practical application standpoint. Test 1 in both treatment plots was not considered because it was conducted when hydrocarbon concentrations in the soil gas were still very high.

Moisture was added to Treatment Plot V1 following Respiration Test 2 and nutrients were added following Respiration Test 4. Temperature corrected rate constants (Figure 13), were not significantly increased between Tests 2 and 3, and between Tests 4 and 5. Therefore, it can be concluded that moisture and nutrient addition were of insignificant benefit to the rate of hydrocarbon biodegradation in Treatment Plot V1. Although moisture and nutrient addition did not effect biodegradation rates, the data indicate that soil temperature likely did.

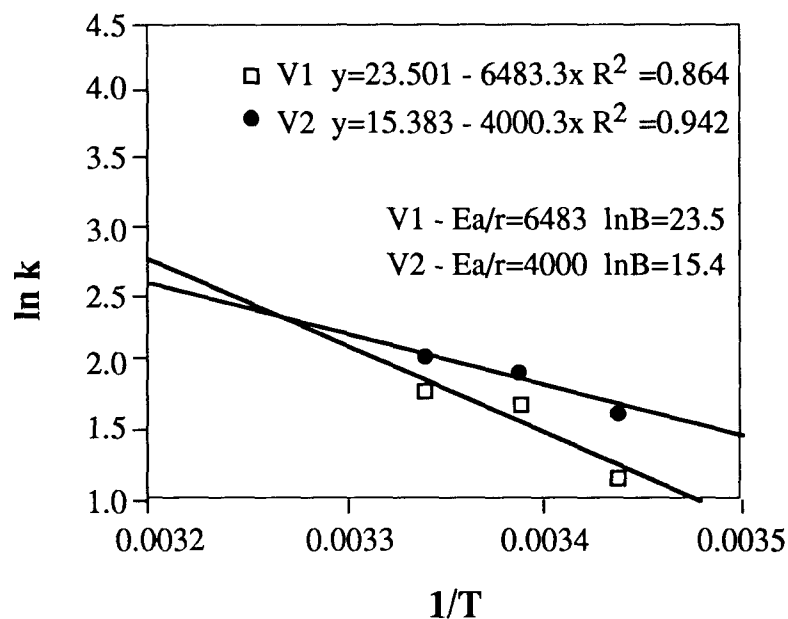


Figure 11. Arrhenius Plot for determining activation energy using measured soil temperature and rate constant relationships from Tests 3, 4, and 5 for Treatment Plots V1 and V2.

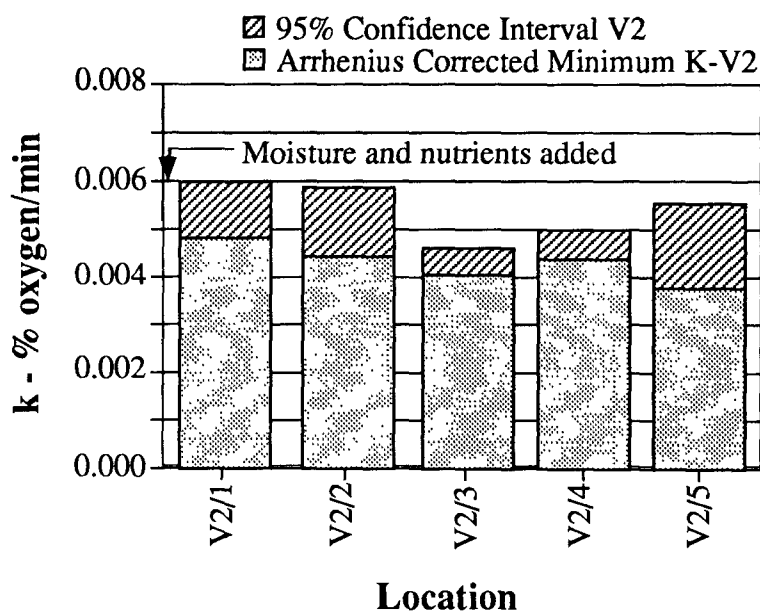


Figure 12. Temperature corrected (23°C based on Arrhenius Plot) oxygen consumption rate constants determined by respiration tests for Treatment Plot V2. Mean k is at the center of the 95% confidence interval.

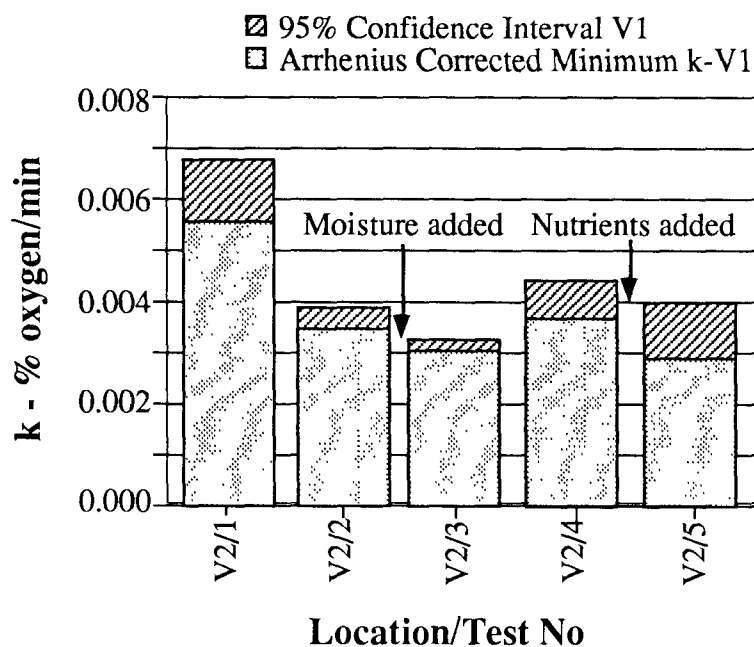


Figure 13. Temperature corrected (23°C based on Arrhenius Plot) oxygen consumption rate constants (k) determined by respiration tests for Treatment Plot V1. Mean k is at the center of the 95% confidence interval.

CONCLUSIONS

This field scale investigation has demonstrated that soil venting is an effective source of oxygen for enhanced aerobic biodegradation of petroleum hydrocarbons (jet fuel) in the vadose-zone. Specific conclusions are:

1. Operational data and respiration tests indicated that moisture (6.5 to 9.8% by weight) and nutrients were not a limiting factor in hydrocarbon biodegradation. Oil and water samples indicated that nutrients were delivered to the treatment plots and passed through the vadose-zone to the ground water.
2. Air flow tests documented that decreasing flow rates increased the percent of hydrocarbon removal by biodegradation and decreased the percent of hydrocarbon removal by volatilization. Under optimal air flow conditions (0.5 air void volumes per day) 82% of hydrocarbon removal was biodegraded and 18% volatilized. Biodegradation removal rates ranged from approximately 2 to 20 mg/(kg day), but stabilized values averaged about 5 mg/(kg day). The effect of soil temperature on biodegradation rates was shown to approximate effects predicted by the van't Hoff-Arrhenius equation.
3. Off-gas treatment studies (3) documented that uncontaminated soil at this test site could be successfully used as a biological reactor for the mineralization of hydrocarbon vapors (off-gas) generated during remediation of fuel contaminated soil using the enhanced biodegradation through soil venting technology investigated in this field study. The average off-gas biodegradation rate was 1.34 (SD \pm 0.83) mg/(kg day), or 1.93 (SD \pm 1.2) g/(m³ day). The percent of off-gas biodegradation

was inversely related to air flow rate (retention time), and was directly related to hydrocarbon loading rate, at the 95% confidence level. Based on data collected at the field site, a soil volume ratio of approximately 4 to 1, uncontaminated to contaminated soil, would be required to completely biodegrade the off-gas from a bioventing system operated similar to this field project. However, if air flow rates in contaminated soil were designed to maximize biodegradation, the ratio of uncontaminated to contaminated soil required would be proportionally less

4. Respiration tests documented that oxygen consumption rates followed zero-order kinetics, and that rates were linear down to about 2 to 4 % oxygen. Therefore, air flow rates can be minimized to maintain oxygen levels between 2 and 4% without inhibiting biodegradation of fuel, with the added benefit that lower air flow rates will increase the percent of removal by biodegradation and decrease the percent of removal by volatilization.
5. Initial soil samples indicated that naturally available nitrogen and phosphorus were adequate for the amount of biodegradation measured, explaining the observation that nutrient addition had an insignificant effect on the rate of biodegradation. Acetylene reduction studies (3) revealed an organic nitrogen fixation potential that could fix the observed organic nitrogen, under anaerobic conditions, in five to eight years.
6. Soil moisture levels did not significantly change during the field study. Soil moisture levels ranged from 6.5 to 7.4%, and 8.5 to 9.8%, by weight, respectively, in Treatment Plots V1 and V2. Neither venting nor moisture addition had a statistically significant effect on soil moisture at this site.

RECOMMENDATIONS FOR FUTURE STUDY

To further pursue the development of an enhanced biodegradation of petroleum hydrocarbons through soil venting technology, the following studies are recommended:

1. Further investigate the relationship between soil temperature and hydrocarbon biodegradation rate.
2. Investigate methods to increase hydrocarbon biodegradation rate by increasing soil temperature with heated air, heated water, or low level radio frequency radiation.
3. Investigate the effect of soil moisture content on biodegradation rate in different soils with and without nutrient addition.
4. Investigate nutrient recycling to determine maximum C:N:P ratios that do not limit biodegradation rates.
5. Investigate different types of uncontaminated soil for use as a reactor for biodegradation of generated hydrocarbon off-gas and determine off-gas biodegradation rates.
6. Investigate gas transport in the vadose-zone to allow adequate design of air delivery systems.

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SUBSURFACE REMEDIATION AT A GASOLINE SPILL SITE USING A BIOVENT APPROACH

DON H. KAMPBELL

U.S. Environmental Protection Agency
Robert S. Kerr Environmental Research Laboratory
P.O. Box 1198
Ada, OK 74820

INTRODUCTION

Soil vapor extraction in combination with biodegradation is a promising remediation technology. Laboratory treatability studies have shown that the process of bioventing should be adaptable to a considerable range of conditions and volatile organics.

An aviation gasoline spill of about 35,000 gallons occurred at an air station in 1969. A major portion of the spill still persists as oily phase residue in the capillary fringe of the subsurface. The vertical profile of the subsurface is a relatively uniform beach sand to below the water table which was near 5 meters.

The objective of the project was to design, install, operate, and evaluate two pilot-scale bioventing systems. Anticipated results were to demonstrate the enhanced feasibility of engineered biological remediation of a subsurface containing retained oily phase gasoline. Performance of the two pilot-scale systems was to demonstrate that surface emissions of fuel are minimum, total fuel hydrocarbons in remediated core material will be less than 100 mg/Kg, final benzene in the underlying groundwater will not exceed 5 µg/L, remediation will be completed in a reasonable time, and the technique is applicable to full-scale reclamation.

EXPERIMENTAL

Prior to design of the bioventing units several laboratory soil microcosm treatability studies were conducted using surface soil from the field site. Aviation gasoline vapor biodegradation was rapid and complete showing curves typical of first-order kinetics.

Degradation occurred at all temperatures within a range of 4 to 37°C. A moisture range of 3.5 to 20 percent did not limit degradation. Reaction rates and active biomass were increased at least four fold in test microcosms receiving a nutrient addition of nitrogen, phosphorus, and potassium. The biodegradation rates obtained from acclimated soil microcosms were more than adequate to consume all vapors in the unsaturated zone at the pilot-scale demonstration site.

DESIGN

The design concept provided subsurface forced aeration to vaporize and transport oily phase components upward to more amiable microbial degradation activity. A surface area above the plume was divided into two adjacent equal plots of 13.7 X 22.9 meters (45 X 75 feet). The north plot shown in Figure 1 was an injection only aeration system. The injection wells were placed in a 3 X 5 grid 3.05 meters apart to a depth of 5.5 meters

which was one meter below the existing water table level. Each well had an outer 5 inch diameter PVC tube with a well screen of 10 vertical slots 1.5 meters long. A depth adjustable inner 4 inch diameter open-end PVC tube 5.8 meter long with a lower rubber packer and an upper rubber collar seal was inside the larger well tube. The above ground portion of the smaller tube was connected to a main forced air transfer line. An injection depth was set to emit air flow over 0.15 meter depth just above the water table. Seven vapor withdrawal wells were similar in construction to the injection wells and placed alternately in the south plot. Extracted air was reinjected to a depth of 4 meters midway between coupled units as shown in Figure 1. A blower flow rate of 5 cfm per plot was used which was equivalent to a calculated forced air residence time of 24 hours.

A nutrient solution of 25, 5, and 2 mg/Kg soil of nitrogen, phosphorus, and potassium was applied throughout the unsaturated zone to sustain microbial activity. A turf grass cover was established and maintained to provide a root zone rhizosphere to complete removal of fuel vapor constituents in surface emissions.

SYSTEM MONITORING

Core material, underlying groundwater, soil gas and air vented air streams were monitored to determine the extent of remediation.

Vertical profile core samples were collected and analyzed for fuel carbon at three month intervals. Groundwater was analyzed monthly for BTEX, dissolved oxygen, and nutrients. Soil gas probes were installed to measure fuel vapor, oxygen, and carbon dioxide on a regularly scheduled basis. Subsurface moisture and temperature was recorded from the meter readings. Soil pore water was collected from different depths for nutrient analysis. Gauge readings were recorded for flow and pressure of the vented air streams. Surface emission samples were collected by cartridge traps for analysis of vapor constituents.

RESULTS & DISCUSSION

The air blowers were turned on during October 1990. They were operated continuously for three months at a subsurface volume flow calculated to be a 24 hour residence time. The systems were shut down for the winter in January. The frost line was then below the turf root zone. Operation will commence again in April 1991 .

Soil gas was monitored at depths of 1,2,3, and 4 meters. Fuel vapor concentrations increased to a maximum the first few days at all depths in both the north and south plots then decreased rapidly until stabilizing in three weeks (Figures 2,3). A combustible gas Threshold Limit Meter (TLV) was used. A response factor near 0.6 was obtained from aviation gasoline vapor when comparing meter readings with standard calibration by butane in ppm (v/v). Initial carbon dioxide in the subsurface soil gas varied from 3.5 to 8.0 percent. During venting, the levels remained at <0.1 percent. Oxygen initially was in the 10 to 14 percent range then increased to 20 percent during venting.

Water from the three monitoring wells was collected at two depths and analyzed as shown in Table 1. Benzene at depths nearest to the water table within the influence of forced air venting was much lower than at depths further down.

Averaged concentrations of fuel carbon over vertical profiles of both the north and south plots showed much greater reductions than in adjacent control locations (Tables 2,3). Although fuel carbon had been reduced considerable, the desired concentration of 100 mg/Kg has not yet been attained as of February 1991. Water table levels at the core sampling times of September 1990 and February 1991 were 472 and 477 cm respectively.

Surface emissions were less than 1 mg fuel hydrocarbons/L soil air (Tables 4). The concentration of fuel hydrocarbons were reduced over 100 fold between the soil surface and at a one meter depth.

CONCLUSION

Operational performance of both venting systems during the first three months of an expected twelve month field project was satisfactory. Oily phase gasoline was reduced in the core profile of both bioventing system plots, particularly in the unsaturated subsurface above the water table. Water quality for benzene has been improved that suggested a beneficial influence from venting aeration. Fuel emissions from the soil surface were minimal indicative of active cleaning action in the turf root rhizosphere.

ACKNOWLEDGEMENTS

Christopher J. Griffin, Project Engineer, with the TraverseGroup, Inc. was the on-site operations manager.

John T. Wilson, Bioremediation Team Leader, with the Robert S. Kerr Environmental Research Laboratory has provided helpful guidance.

Table 1. WATER QUALITY - FEBRUARY 1991

SAMPLE	DEPTH METER	TOTAL AVGAS	BENZENE
		-----µg/l-----	
Upgradient	5.3	3090	182
Upgradient	6.7	415	132
South Plot	5.2	686	<1
South Plot	6.1	1680	19
North Plot	5.1	2790	7
North Plot	6.4	2410	202

Table 2. CORE PROFILE OF FUEL CARBON (mg/kg)

DEPTH (CENTIMETERS)	CONTROL ₁ SEPT. 1990 - FEB. 1991		NORTH PLOT SEPT. 1990 - FEB. 1991	
406	234	97	52	<8
444	461	1080	923	18
462	1030	1000	1253	153
488	701	731	926	972
503	6500	8240	6740	1420
523	5620	3020	5780	2200
538	N.D.	<8	39	53
X	2862	2814	3124	913

(mean value within dashed area)

Table 3. CORE PROFILE OF FUEL CARBON (mg/kg)

DEPTH (CENTIMETERS)	CONTROL ₂ SEPT. 1990 - FEB. 1991		SOUTH PLOT SEPT. 1990 - FEB. 1991	
406	<8	<8	11	<8
444	193	84	144	16
462	238	85	253	70
488	212	140	1970	946
503	549	639	1880	1860
523	34	10	2830	17
538	<8	<8	<8	<8
X	245	192	1415	582
(mean value within dashed area)				

Table 4. SURFACE EMISSIONS Volatile Hydrocarbons

Nov. & Dec	South Plot	North Plot
Canopy	0.24 mg/L	0.52 mg/L
One meter probe	271 mg/L	174 mg/L
Per cent removed	99.9	99.7

314

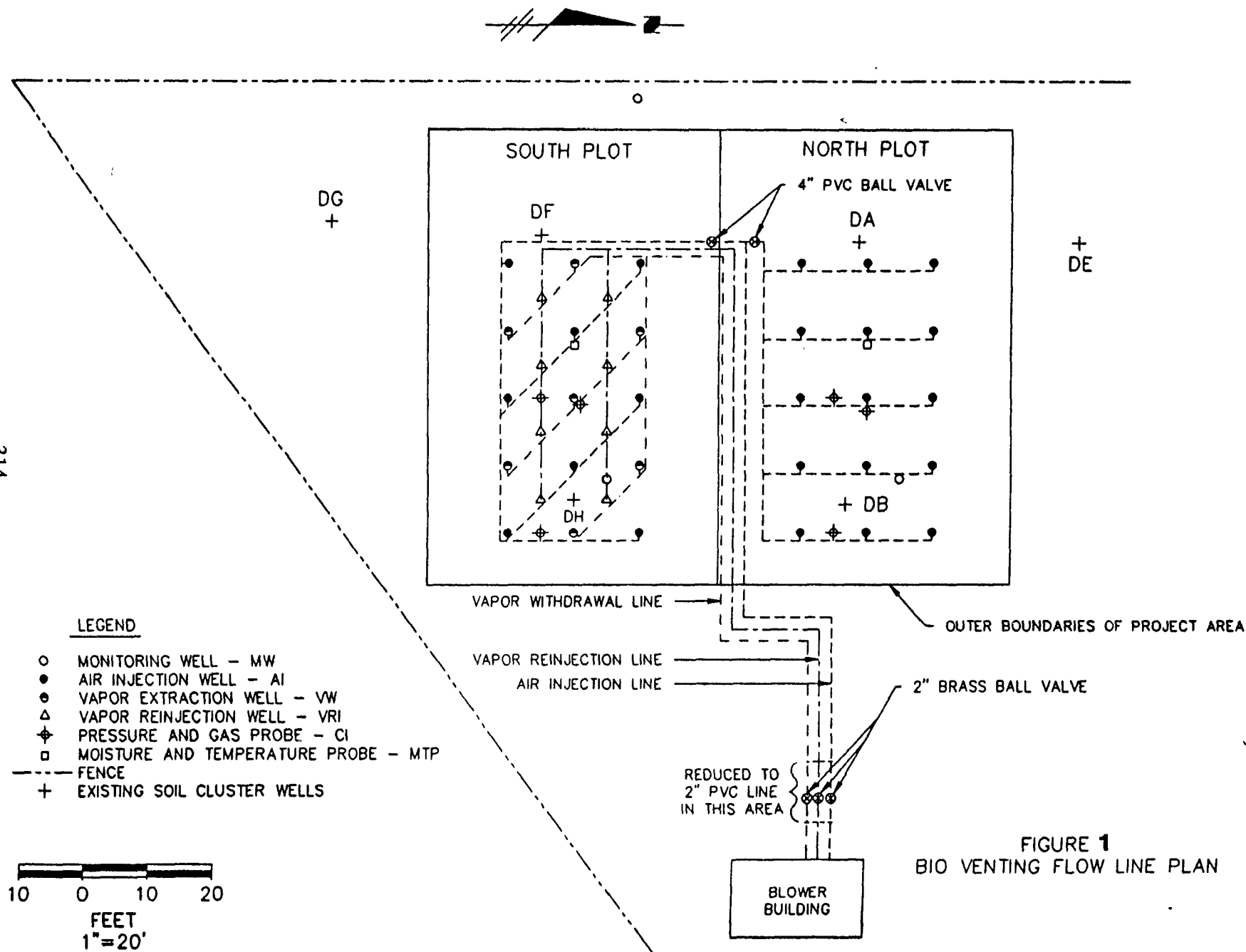


FIGURE 1
BIO VENTING FLOW LINE PLAN

Figure 2
TLV vs. Time for the North Plot

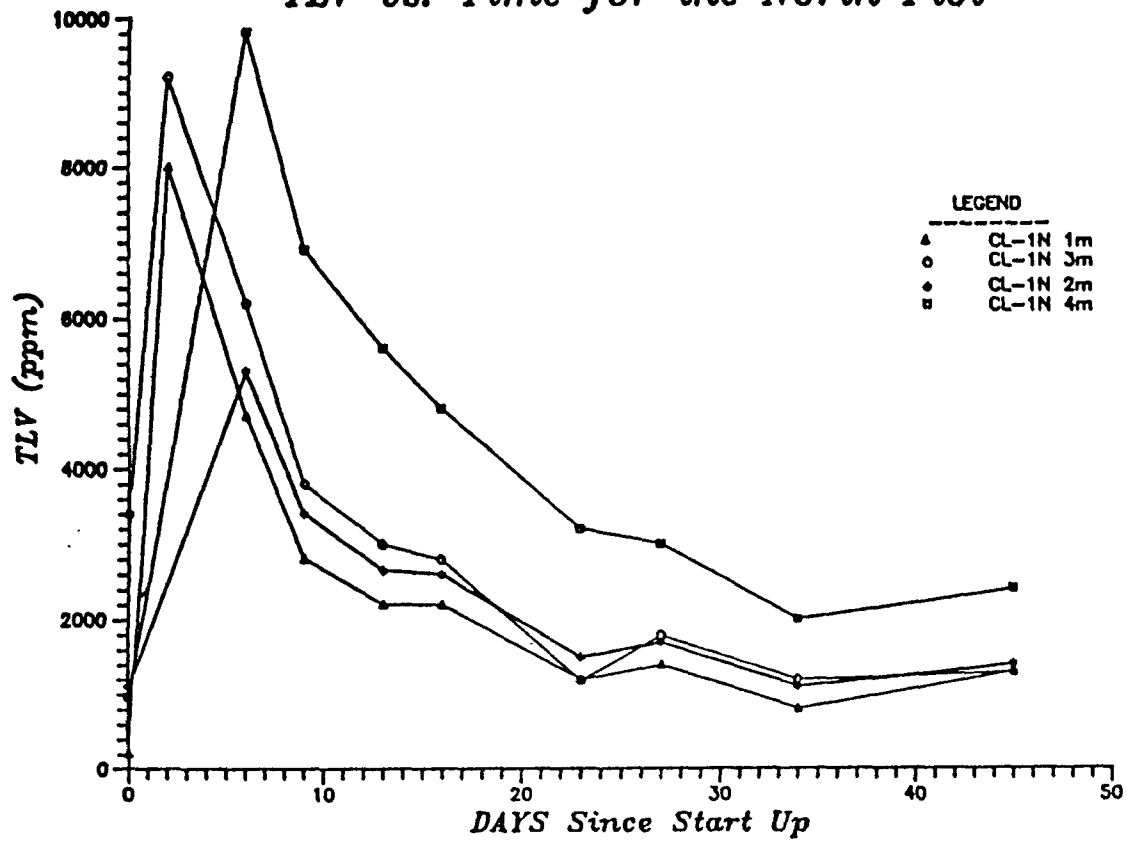
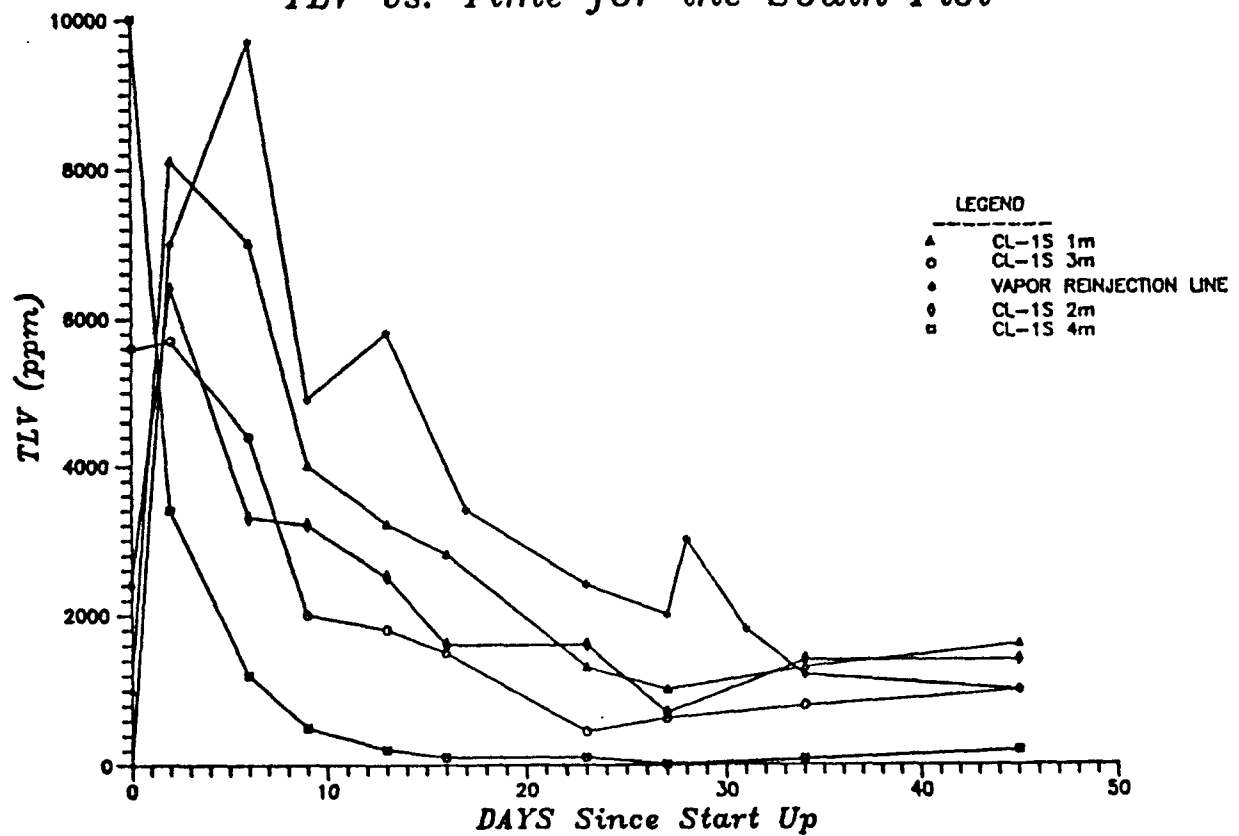


Figure 3
TLV vs. Time for the South Plot



BIOVENTING AN IN SITU REMEDIAL TECHNOLOGY SCOPE AND LIMITATIONS

J. VAN EYK
Delft Geotechnics
P.O. Box 69
2600 AB Delft, The Netherlands

INTRODUCTION

For a variety of reasons, in situ methodologies are not as popular as one might wish. One obvious reason is, that when the decision has been taken that a site has to be cleaned up, the results of the in situ cleanup technique will have to comply with the standards laid down by the authorities with respect to maximum allowable residual levels for soil. If no guarantee can be given with respect to the minimum levels achievable, excavation (if possible) will be the cleanup method of choice. As a result, the development of in situ techniques advances only very slowly. To circumvent this problem and to give the development of in situ methodologies a fair chance, the Dutch Government has decided to support research and development of in situ techniques.

Another problem, which particularly applies to the application of biological cleanup methodologies, is the general consensus that biological methods intrinsically require very long cleanup times, which when compared to excavation is true. However, excavation is not always an option, particularly when whole buildings have to be demolished. The only alternative in those instances would be the application of measures of abatement. In most instances, however, it will then be possible to apply in situ methodologies for restoration, which eventually will make pollution control measures superfluous. In addition, when large scale aquifer restoration methods have to be carried out at high costs, the additional costs for applying an in situ methodology like bioventing, are relatively insignificant when compared to the results achieved.

Another advantage of an in situ technique such as bioventing is, that it can also be considered in terms of the goal of prevention. For, when soil cleanup has been achieved as a result of the application of bioventing, the system, when left intact can always be reactivated at relatively low costs, whenever an accidental spill reoccurs in the underground. It has the additional advantage, that the extra costs to remove the system can be avoided.

To date, the technique of venting to remove petroleum vapors from the vadose zone, has been well documented (2). The use of bioventing to enhance volatilization and to stimulate biodegradation in the vadose zone, was first reported in 1986 (1, 4). An investigation into the possibilities for bioventing was prompted by the results of lysimeter studies on microbially mediated gasoline removal from sand. In the absence of bioventing, almost 100 percent removal was achieved in a period of 7 to 8 years (6).

Laboratory studies carried out with sand columns which had been saturated with gasoline or diesel oil, showed for gasoline, that 99 percent could be vented off in a period of 6 weeks, by passing water vapor saturated air through these sand columns with a venting ratio, d , of 30. The venting ratio, d , equals air flow per m^3 soil per day, divided by the air filled porosity of the soil (pore volumes exchanged per day). Such high ratios are unlikely to be achieved in the field and the contribution of biodegradation to the removal of petroleum components at lower venting ratios, say 6, is therefore also important (7). On the basis of carbon dioxide production measured in the gas phase, the vented columns containing diesel oil ($d = 6$) showed a hydrocarbon biodegradation rate of approximately 100 grams per m^3 soil per day which is equivalent to 60 mg/kg/day if soil bulk density equals 1.67 g/cm^3 .

A feasibility study carried out to evaluate the possibilities for venting under field conditions, showed that for hydraulic conductivities in soil equal to or greater than 10^{-5} m/sec , venting can be used either to remove volatile hydrocarbons from subsurface soil strata or to stimulate biodegradation of the less volatile petroleum components (8, 12).

A large scale field experiment was subsequently carried out to validate the feasibility study (8, 9). The results of these studies are summarized in Tables 1, 2, and 3, and show that gasoline is largely removed by venting and to a lesser degree by bioventing. In contrast, for diesel oil, the contribution of enhanced volatilization is negligible and enhanced biodegradation appears to be the main attenuation mechanism. Table 2 also shows, that the benzene, toluene, xylene (BTX) trio is removed preferentially, and, except for the xylenes, to almost background levels. The xylenes appear both more difficult to biodegrade and to evaporate and either need more time or, supplementary treatment measures. This will be discussed later in more detail.

As a follow up, a contaminated location at a retail gasoline station was selected to demonstrate the bioventing approach in a real spill situation. This demonstration Project, supported by the Department for the Environment (Grant no. MJZ 20D 8037) has been reported before (10). Therefore only a cursory description of the project will be given in this paper. The results, and the scope as well as the limitations of the bioventing technique, however, will be discussed in more detail.

INSTALLATION OF AN IN SITU AND ON SITE CLEANUP SYSTEM

The installation of an in situ and on site cleanup system for the selected site (Figure 1), required the necessary preparations, which are summarized as follows:

Design Parameters

Soil structure and composition

Data on soil structure and composition are required for the design of a remedial system both for soil and ground water. Hydraulic conductivities for soil were calculated from grain size distribution curves and also determined in the laboratory. An average, calculated hydraulic conductivity of $1.0\text{E-}04 \text{ m/s}$ was selected on the basis of these two sets of data. Hydrogeological parameters were required for the installation of two pumping wells, to contain, pump and treat the polluted ground water.

Degree and extent of contamination

The degree and extent of contamination was determined very accurately, based on an extensive soil and ground water sampling procedure (Figure 1, Figure 2 and Tables 4, 5, and 6).

Hydraulic conductivity for soil

Hydraulic conductivity data for soil were collected to carry out calculations on ground water transport and ground water withdrawal. In addition this data is used to get an insight into soil air permeability.

Soil air permeability

Soil air permeability was derived from the hydraulic conductivities and the parameter used for the air filled porosity was adjusted for soil moisture content. On the basis of hydraulic conductivities, a value of $8.7\text{E-}04$ m/s, was calculated for soil air permeability.

Model Calculations

Air transport calculations

Air transport calculations were carried out to determine the spacing of the air wells. Air transport was calculated, using the Hydrology Contaminant Transport Model (12). Air permeability for moist soil was calculated with the help of the Karman-Kozeny equation. Based on these calculations, a distance of three meters was selected between the air wells, resulting in a calculated air flux of $68\text{ m}^3/\text{day}$, at a negative pressure of -0.05 bar.

Vapor transport calculations

Vapor transport calculations were carried out to get an insight into the time required to remove the bulk of volatile contaminants, particularly the BTX components, from soil (Figure 3).

Calculations of pumping rates for ground water

Pumping rates for the cleanup of contaminated ground water were calculated with the computer program called SLAEM, Single Layer Analytic Element Model (5). The model was verified with measured data on ground water and surface water levels. For the numerical calculations, a K_d of $250\text{ m}^2/\text{day}$ was assumed and a net rainwater infiltration rate of 0.15 m/year . A pumping rate of 5 m^3 per hour was shown to produce a radius of influence sufficiently large, to contain and to treat the contaminant plume.

Evaluation of biodegradation rates

On the basis of an air flux of 68 m^3 per day per air well, a minimum venting ratio of 6 can be calculated. This will sustain a biodegradation rate of 100 g per m^3 per day, which in view of rates determined before in the field (9), is more than adequate.

System Design

The complete remedial system was composed of the following parts:

Pumping wells

Because the aquifer appeared to be contaminated up to 10 meters below ground surface, two pumping wells had to be installed, one with a filter at 4 m below ground surface and one with a filter at 11 m below ground surface (Figure 4).

Pumping air wells

A total of 24 pumping air wells were installed as part of the soil bioventing system (Figure 4). Each individual air well is connected to the main pipeline which is connected to the blower. As the ground surface has an impermeable pavement, access of air is obtained via two horizontal drains installed below the pavement (Figure 5).

Impermeable Pavement

An impermeable pavement is an integral part of this venting system for several reasons. The venting system has to be protected from any form of adverse effect or damage, caused, for instance, by heavy trucks. In addition, because the retail gasoline station has an on-going business during the period of remediation, migration of fresh spilled products into the treated zone had to be excluded.

Air and ground water cleanup system

The cleanup system for air and ground water is shown in Figure 6. The ground water, which is mainly contaminated with volatile petroleum components, is cleaned up in a stripping tower. An oil water separator was installed, because boring B2 (Table 4, Figure 1) had indicated the presence of free product floating on the ground water table. As the soil had been shown to contain a considerable amount of iron, which as a result of aeration will produce iron hydroxide, a sand filter was installed after the cascade aerator.

Biofilter

A biofilter which was installed to remove gaseous petroleum components from air extracted from the soil, was also used for the cleanup of air from the stripping tower. The biofilter contained 60 percent heather, 40 percent peat, and 0.1 percent activated sludge taken from a biotreater used for the cleanup of ground water contaminated with petroleum. The total volume amounted to 18 m³ (called Biomix).

Monitoring and control

Progress of the cleanup process is monitored via vented air samples by determining the concentration of carbon dioxide and total hydrocarbons. Ground water cleanup is monitored from ground water samples obtained from observation wells. Soil samples will be taken in the final stages of the cleanup process.

RESULTS

Venting

To avoid the possibility of overloading the biofilter, only air extracted from the soil was passed over the biofilter when the in situ cleanup operation was started. When after several weeks of operation air sampling showed that the biofilter was working effectively, the pumping wells for ground water were also activated. Air produced by the air stripper was then fed into the biofilter too. At the start of the operation, the air flux amounted to approximately 20 m³/h. After two weeks it increased to 32 m³/h. The average over a period of 12 months amounted to around 36 m³/h. Air transport calculations predicted a value of 68 m³/d per air well (24 air wells were installed). The removal of petroleum vapors from soil by venting, is shown in Table 7. Over a total period of 13 months, approximately 770 kg of petroleum vapors were extracted from the subsurface. These results confirm results obtained before(7), which showed that components like benzene can be removed quickly and effectively. After 3 months, the benzene concentration had been reduced to 4 percent of its starting value. For toluene and the xylenes, the figures are 9 percent and 24 percent respectively.

Bioventing

The removal of petroleum from soil as a result of bioventing is shown in Figure 7. The data was obtained by dividing the weight of the CO₂ produced by the weight of [CH₂] oxidized, i.e. 44/14 or 3.14. In a period of roughly one year, approximately 430 kg of petroleum components were removed as a result of bioventing. The data represented in Figure 7 indicates that CO₂ production rates are presently falling off. This, however, may at least in part be the result of a seasonal temperature fluctuation. This is underlined by the CO₂ data represented in Figure 8, which clearly shows a steady increase in ppm produced throughout the season and a decrease in September. It is noteworthy that the first and the last CO₂ value determined around the same time differ significantly, which may be caused by the presence and absence respectively of toxic petroleum components, like BTX.

Biofilter performance

Unfortunately, it is not possible to produce actual data on biofilter performance. The reason is, that local environmental authorities, as yet, do not impose strict quantitative restrictions on the amount of petroleum vapors which can be vented off onto the atmosphere. All that is presently being required is, that the vented air is odorless. To get an insight into the biofilter performance, air samples were taken before entering and after passing the filter with Drager tubes. These tubes are designed, however, to determine BTX compounds singly and not in combination. The results, therefore, are only indicative, but do show that BTX compounds, after three weeks of operation can not longer be detected. Assuming a 50 percent removal rate during the first three weeks and a 100 percent removal for the remaining period (see Table 7), an average removal rate of 0.120 kg/m³/day can be calculated.

Ground water cleanup

Tables 8 and 9 show the hydrocarbon levels analyzed in the two influents discharged into the cleanup system. The data show, that ground water extracted from the deep pumping well is only marginally polluted. Ground water pumped from the shallow well is, in contrast to the deep well, considerably polluted.

Approximately three months after the start of the demonstration project, hydrocarbon levels start to rise significantly. It appeared to be caused by free product entering the pumping well. Two months later, concentrations start to fall again, particularly those for benzene, toluene, and the xylenes. Hydrocarbon concentrations in the effluent were determined to comply with requirements for discharge. Maximum allowable levels for petroleum and BTX compounds, prior to discharge into the sewer are 10 mg/l and 100 ug/l respectively. Analysis show that these targets are being met by the ground water cleanup system.

DISCUSSION

If soil has a hydraulic conductivity equal to or greater than 10^{-5} m/s, the technique of venting is very useful for the removal of volatiles from soil (8, 12). To date, the application of venting to remove volatile hydrocarbons from soil has been well documented (2). In the field experiment (7), BTX components were reduced in a period of 50 weeks to between 1 and 10 percent (Table 2) of the starting value (uncorrected for biodegradation). Calculations show, however, that higher removal efficiencies can be obtained by venting over extended periods of time. The technique of venting, therefore, is an effective method for the removal of volatiles from soil. Enhanced biodegradation as a concomitant result of bioventing will mop up the less volatile components.

For diesel oil, the situation is different. The field experiment mentioned before, showed that the volatilization of diesel oil is insignificant. Enhanced biodegradation as a result of bioventing is for diesel oil the most important process for the removal of the petroleum components. The question, however, is: will biodegradation as a result of bioventing achieve complete cleanup of the soil? Because the more water soluble components of petroleum products are removed more quickly as a result of leaching and subsequent biodegradation, the viscosity of the residual fraction increases. This will progressively slow down the biodegradation of the residual petroleum components. This could explain an observation reported before, that the relative concentration of polycyclic aromatics (PCAs) in diesel oil during bioremediation, increases. Except for the naphthalenes which sublime easily (naphthalene > methyl-naphthalene > dimethyl-naphthalene), the relative concentrations of compounds like fluoranthene, increases significantly with time (see Table 10).

Complete biodegradation of diesel oil in soil may therefore require considerable longer cleanup times than anticipated on the basis of the initial removal rates. In the Netherlands, a standard soil with respect to organics, is assumed to have an organic matter content of 10 percent and the reference values (R) are based on this assumption. If the organic matter content is smaller than or equal to 2 percent, the value of 2 percent is maintained. This reduces the value of R five times. For petroleum, $R = 50$ mg/kg. If the organic matter content is 2 percent, the value of R is obtained by dividing the standard value of R by 10 and multiply it by 2, which reduces R to 10 mg/kg. The average residual diesel oil concentration which we determined in the field experiment at a sampling depth of 1.25 to 1.5 m below ground surface was 23,087 mg/kg at t_0 .

On the basis of the percentage composition of PCAs, for this particular diesel oil, (Table 10), this results in the following concentrations:

<u>COMPONENT</u>	<u>RESIDUAL CONCENTRATION</u> (mg/kg at t ₀)	<u>R(OM=2%)</u> (mg/kg)
PETROLEUM	20,387	10
NAPHTHALENE	18.8	0.002
ANTHRACENE/PHENANTHRENE	42.8	0.020
FLUORANTHENE	5.1	0.020
PYRENE	10.0	0.020

This data, when compared to the final levels to be achieved as listed in the second column shows, that a considerable reduction is to be achieved, which in view of the observed initial enrichment, won't be easy to accomplish. A true limitation for bioventing with respect to the removal of diesel oil from soil may be caused by the fact, that soil polluted by liquid petroleum products contains free products in places which are inaccessible to micro-organisms. This is probably one reason for the observation, that hydrocarbon concentrations in landfarming operations usually appear to remain unchanged at the level of one gram per kg, which according to the Dutch Act on Soil Protection and Soil Remediation, is 100 times larger than the cleanup values to be achieved. The decrease in the rate of biodegradation due to the increase in viscosity may be acceptable, because it only prolongs the period required for remediation. However, inaccessibility, if true, would make it eventually impossible for an in situ technique to achieve the levels required.

Fortunately, at this point, the microbe itself may solve the problem for us. Due to microbial action, the solubility of hydrocarbons can increase significantly (up to a 100,000 times) for example (3). The solution to the problem therefore may be to exploit this phenomenon by intermittent flushing of the soil. This idea is supported by an observation made by Verstraete et al. (1975), that gasoil entrapped in soil columns could be leached out (up to 15 times), by percolating water enriched in minerals through these columns.

The in situ flushing may have the same effect as tilling in landfarming operations, namely to expose inaccessible residues to microbial action, in part as a result of microbial solubilizing factors. Experiments carried out in our laboratory (to be reported) show, that intermittent flushing of vented columns, reduces residual petroleum concentrations much faster and much more efficiently than bioventing alone .

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**Table 1. Mass balance for the removal of gasoline from soil by bioventing
(van Eyk and Vreeken, 1988)**

Applied	125 kg
Mobile gasoline lost via drains	2 kg
Removed by venting *	72 kg
Lost by uncontrolled evaporation **	6.8 kg
Dissolved products lost via drains	7.5 kg
Residual gasoline	4.5 kg
Removed by biodegradation (as determined from CaCO ₃ leaching)	27 kg
119.8/125 x 100X = 96% can be accounted for	119.8 kg

* Preliminary results determined by gas chromatographic analysis

** Lost to the air during application and during the periods of time when the sealing of the field had to be removed

Table 2. Effect of venting on the percentage contribution of BTX components to gasoline in soil samples after a venting period of 12 months

sample depth m	petrol ppm	gasoline components ² in ppm			
		benzene	toluene	xylene	
.50 - .75	25	< 0.50 .20	< 0.10 1.8	<0.10 2.2	found calcd ¹
.75 - 1.00	31	< 0.50 .20	< 0.10 2.3	<0.10 2.7	found calcd
1.00 - 1.25	402	< 0.50 3.0	< 0.50 29.3	3.6 35	found calcd

¹ Calculated on the basis that the total hydrocarbon content of the soil sample represents genuine petrol

²The gasoline used for this particular experiment, contained 0.75% benzene, 7.3% toluene, and 8.7% xylenes

Table 3. Mass balance for the removal of diesel oil from soil by bioventing (van Eyk and Vreeken, 1989b)

RESIDUAL DIESEL OIL AFTER 50 WEEKS	84 kg
REMOVED BY BIODEGRADATION	32 kg
TOTAL ACCOUNTED FOR	116 kg
APPLIED	125 kg
UNACCOUNTED FOR	9 kg (7%)
BIODEGRADATION RATE: 8 MG/KG/DAY	

Table 4. Results of borings B1 to B4 with respect to mineral oil and BTX in mg/kg.

Component	B1 0.0-3.0	B2 0.0-3.0	B3 0.0-3.0	B4 1.0-3.0
Benzene	< .5	130	39	5.4
Toluene	< .5	860	250	130
Ethylbenzene	< .5	280	96	60
Xylenes	< .5	2100	740	430
CH-total	< 50	6900	2300	1300
Mineral oil	< 100	15000	1300	320

Table 5. Analysis results of handborings carried out under the garage floor in mg/kg.

Component	Boring number and depth below ground surface		
	No. 11 1.0-1.5	No. 12 1.5-2.0	No. 13 1.0-1.3
Benzene	0.15	3.7	28
Toluene	0.56	5.6	270
Ethyl- benzene	0.09	1.1	81
Xylenes	0.75	4.9	460
Mineral oil	<20	<20	850

Table 6. Results of BTEX analyses for groundwater samples.

Component µg/l	Monitoring well		Groundwater sample probe number and depth below GS			
	no 11 ^a	no 36 ^b	GW2 9.0	GW3 9.5	GW4 7.5	GW5 9.5
Benzene	40000	280	3.2	< 0.2	< 0.2	< 0.2
Toluene	85000	1400	1.7	< 0.5	< 0.5	< 0.5
Ethylbenzene	8400	150	< 0.5	< 0.5	< 0.5	< 0.5
Xylenes	58000	980	0.8	< 0.5	< 0.5	< 0.5
CH-total	200000	3300	< 20	< 20	< 20	< 20
a - filter at 1.60 - 4.10 - GS b - filter at 9.10 - 11.10 - GS						

Table 7. Hydrocarbons removed by venting

WEEK	FLUX m ³ /hr	AIR CONCENTRATION in mg/L				TOTAL HC REMOVED IN KG
		BENZENE	TOLUENE	XYLENE	TOTAL HC	
0	19.2	2.37	4.71	1.84	33.28	117
1	24.8	0.44	1.64	1.23	9.32	190
2	32.0	0.16	1.00	0.87	5.11	227
3	35.0	0.12	0.64	0.50	3.88	253
7	29.8	0.09	0.37	0.52	3.00	331
14	33.0	0.10	0.41	0.45	2.90	436
30	30.2	0.034	0.21	0.41	1.60	573
38	47.7	0.0423	0.169	0.296	1.69	677
43	39.0	0.016	0.103	0.22	1.14	718
48	41.5	0.006	0.054	0.196	0.987	75
56	39.8	0.007	0.008	0.075	0.354	77

Table 8. Deep ground water cleanup. Influent concentrations in mg/l filter at 11 m - GS

DATE	MINERAL OIL	BENZENE	TOLUENE	XYLENE
10/12/90	53	<0.2	<0.5	<0.5
11/13/90	<50	<0.2	<0.5	<0.5
12/11/90	<50	<0.2	<0.5	<0.5
1/14/91	97	<0.2	<0.5	<0.5
3/5/91	<50	<0.2	<0.5	<0.5
4/3/91	<100	<0.2	<0.5	<0.5
5/2/91	<100	<0.2	<0.5	<0.5

Table 9. Shallow ground water cleanup. Influent concentrations in mg/l Filter at 4 m BGS

	Volatile Aromatics	Benzene	Toluene	Ethyl-benzene	Xylene	Mineral oil	Chemical Oxygen Demand
B-value	30	1	15	20	20	200	
Disposal Norm	100					10000	
10/12/90	5900	1600	2100		2100	6900	
11/13/90	22000	2600	7800		11000	91000	
12/10/90	16000	1400	5300	1250	8000	72000	116
1/14/91	3800	510	1200	300	1750	88000	
3/5/91	2000	200	570	63	1150	9100	60
4/4/91	3200	300	970	150	1760	2800	46
5/1/91	--	--	--	--	--	--	41
5/30/91	--	--	--	--	--	--	31
6/27/91	348	40	110	9	189	--	31
7/22/91	125	16	20	--	87	--	35
8/2/91	300	32	98	18	143	--	31
8/6/91	300	33	99	21	141	150	20
9/6/91	--	--	--	--	--	--	29
9/11/91	270	16	60	20	54	210	--
9/17/91	120	14	34	7	38	--	--

- Background values

Table 10. Removal of PCAs from soil after a bioventing period of 18 months (van Eyk and Vreeken, 1989b)

SAMPLING DEPTH AT 1.25- 1.50 M-GS			
COMPONENT	CONCENTRATION (MG/KG)		DIESELOIL %
NAPHTHALENE	<0.1*	(8.8)**	0.092
METHYL-NAPHTHALENE	29	(83)	0.87
DI-METHYL-NAPHTHALENE	67	(162)	1.7
ANTHRACENE/PHENANTHRENE	35	(20)	0.21
FLUORANTHENE	11	(2.4)	0.025
PYRENE	9	(4.7)	0.049
TOTAL PCAs			3.5

* Determined

** Calculated on the basis of total oil after a bioventing period of 18 months. (9535 mg/kg_{ds}, which amounts to approximately 46% of the concentration at t.

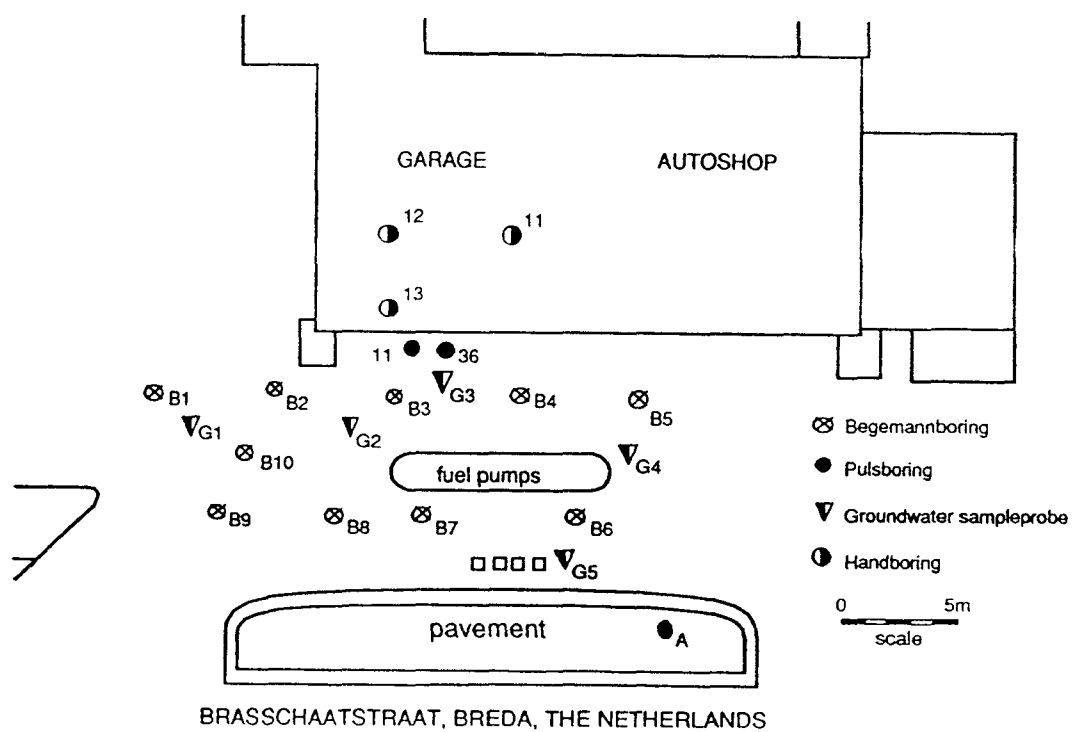


Figure 1. Planview of retail gasoline station, showing the locations for soil and ground water sampling.

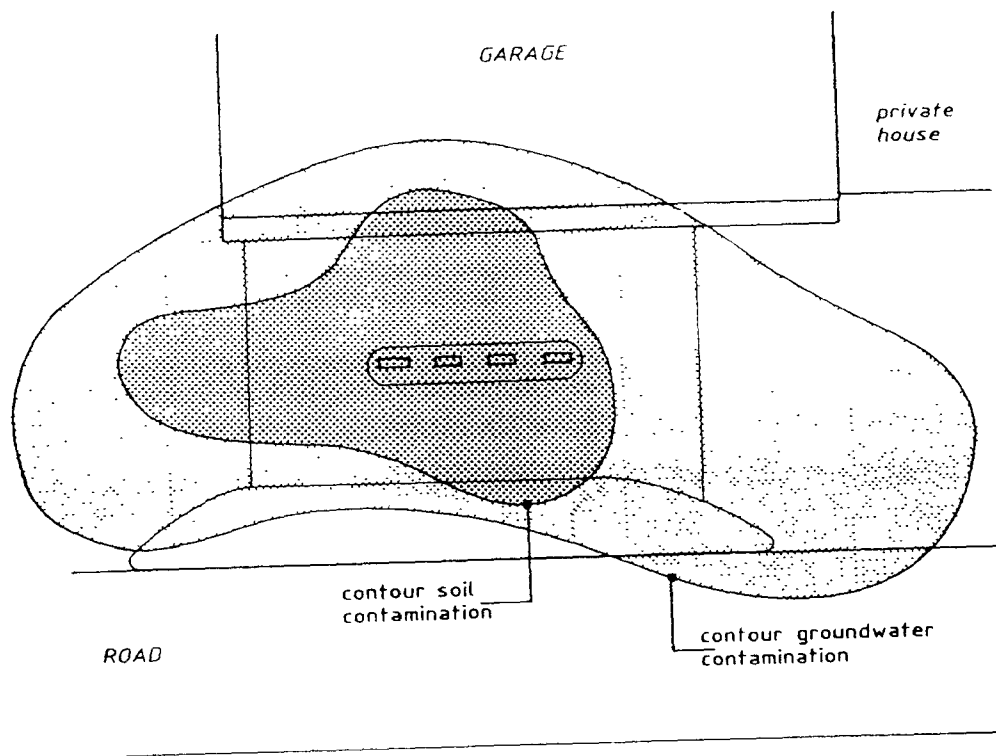


Figure 2. Contours for soil and ground water contamination.

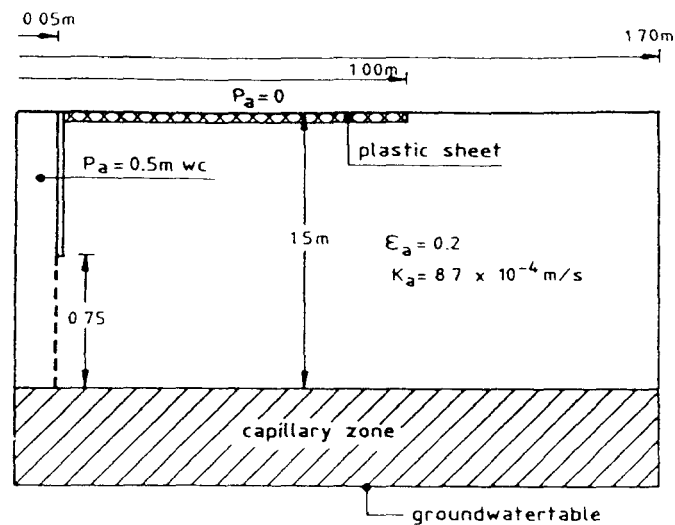


Figure 3. Computational scheme to calculate air transport in soil.

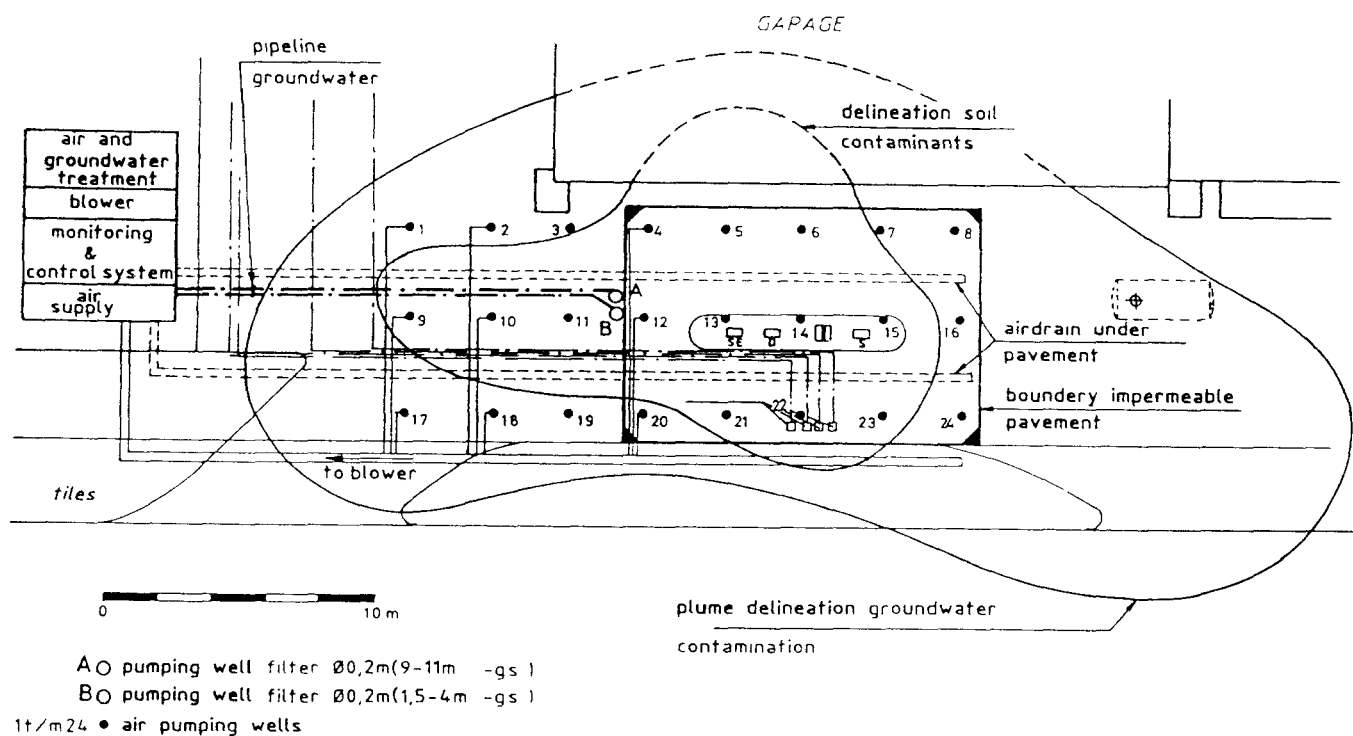


Figure 4. Plan view of retail gasoline station outlining the installation of the venting system, pumping wells, cleanup and monitoring system.

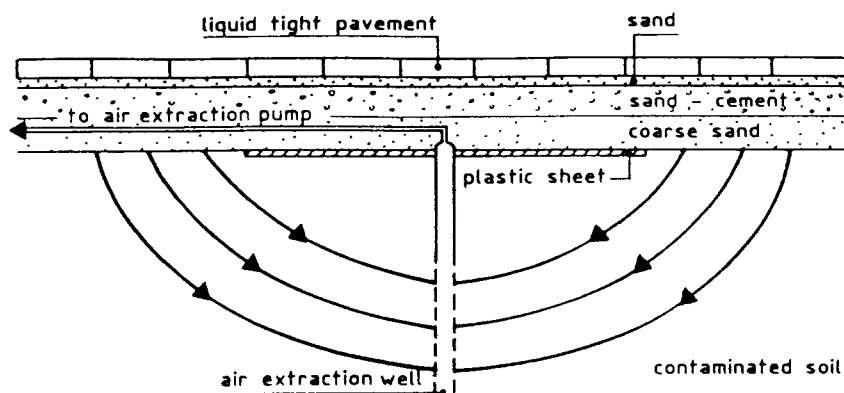


Figure 5. Outlining of the design of air extraction wells under the liquid tight pavement.

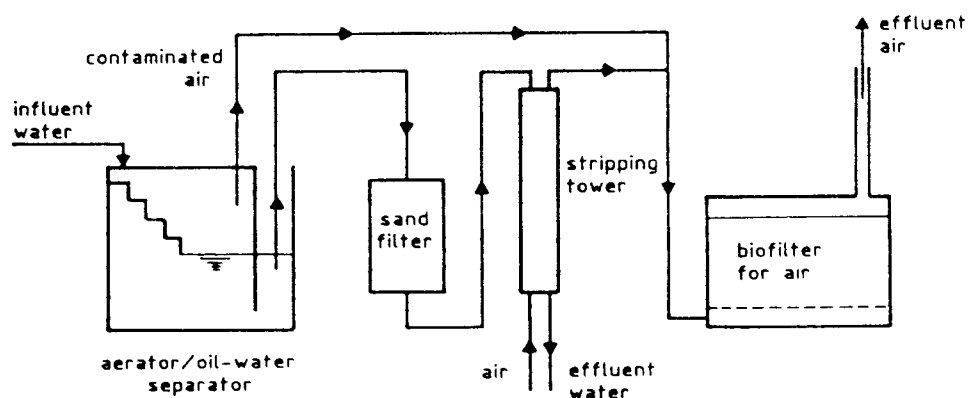


Figure 6. Schematic overview of the system for treatment of polluted air and ground water.

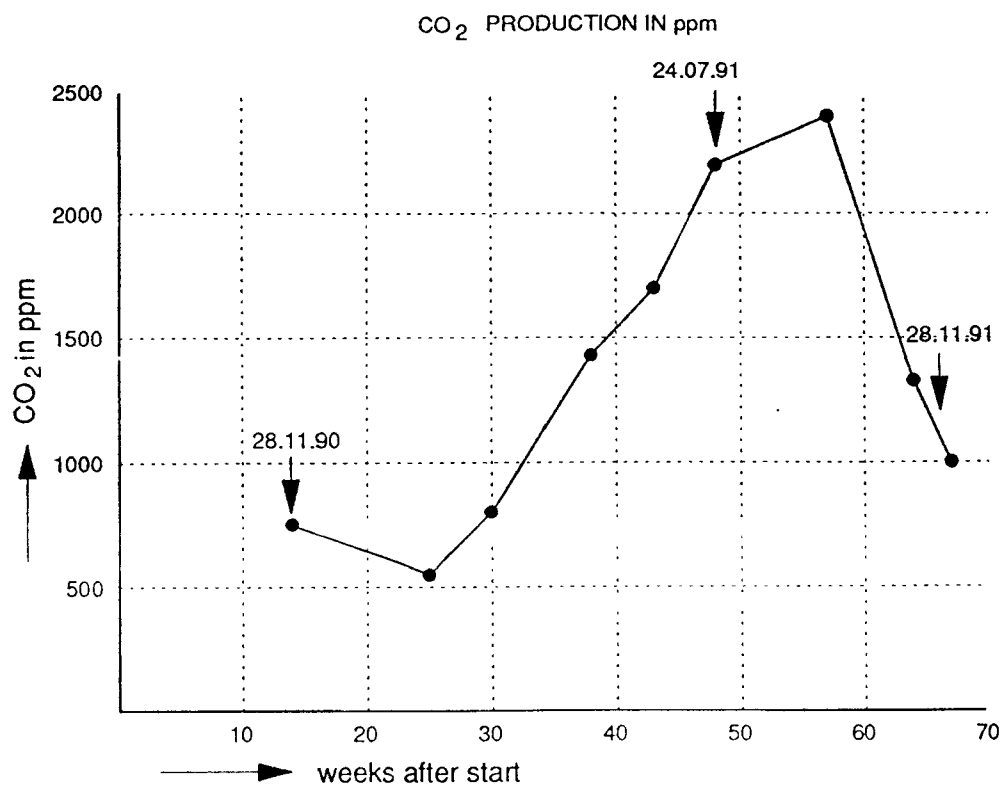


Figure 7.

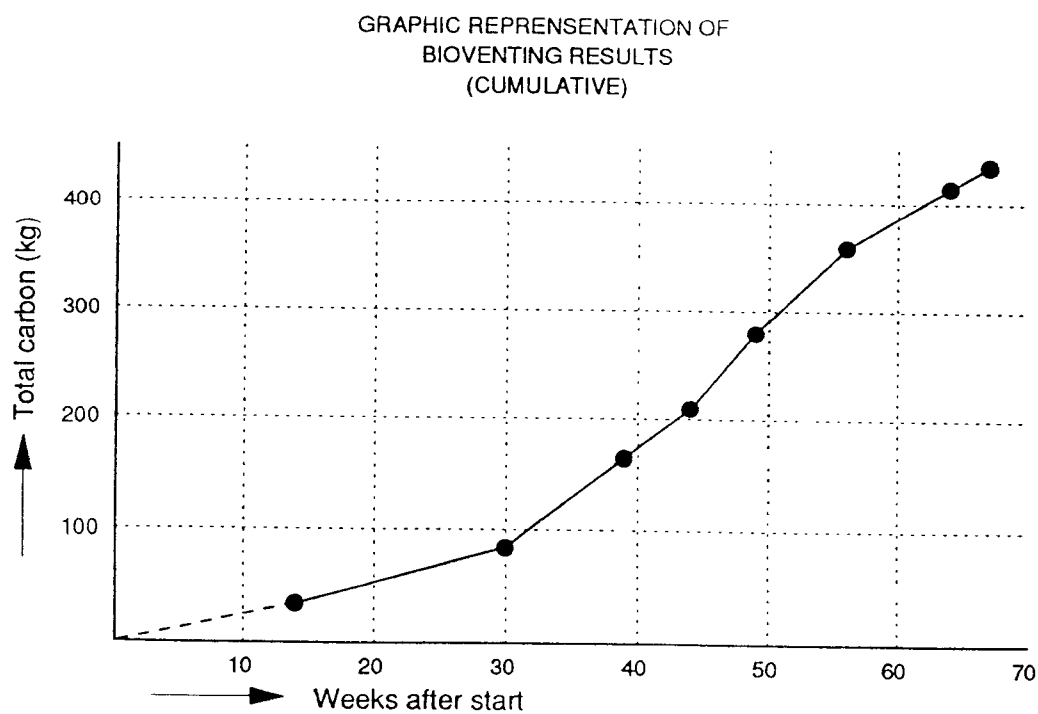


Figure 8.