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VADOSE ZONE CONTAMINATION
MEASUREMENT AND MODELING

THESIS

Thomas A. Reeder, Major, USMC

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VADOSE ZONE CONTAMINATION MEASUREMENT AND MODELING

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
In Partial Fulfillment of the
Requirements for the Degree of
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Management

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Approved for public release; distribution unlimited

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Thomas A Reeder

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Abstract

This thesis investigated the effects of the slow sorption mechanism on the transport of volatile organic contaminants in the vadose zone. Recent research has shown that slow sorption may have a significant impact on the transport of volatile organic compounds in the subsurface. Specifically, this document examined the effects of slow sorption on the Vapor Extraction System (VES) and the Purge and Trap Measurement System. The VES is a technology that is widely used today by the Department of Defense to remediate contaminated unsaturated zones. The Purge and Trap Measurement System is an analytical technique utilized to determine organic contamination concentration levels in the unsaturated zone. It was found that the slow sorption of organic molecules on soil may profoundly influence the efficiency of VES and purge and trap, as both of these rely on rapid volatilization of organic contaminants in order to successfully function. In addition, this thesis investigated possible alternatives to purge and trap, including the utilization of high energy lasers and optoelectronics. Mathematical simulation and modeling of slow sorption effects during vapor extraction operations was accomplished with the use of the Soil Vapor Extraction (SVE) Computer Model. Model analysis provided valuable information concerning the impact of slow sorption on the effectiveness of vapor extraction remediation.

VADOSE ZONE CONTAMINATION MEASUREMENT AND MODELING

I. Introduction

General Issue

The Department of Defense (DOD) is presently conducting a massive effort to rectify serious, existing environmental hazards located on numerous DOD installations throughout the nation. This effort, known as the Installation Restoration Program (IRP), accounts for millions of dollars of the annual defense budget, and is still in a relatively early stage of development. The ultimate completion of this project will demand numerous, major environmental clean-up programs throughout the United States, and the certain expenditure of billions of dollars.

A major portion of the IRP is concerned with the remediation and treatment of toxic substances and chemicals which were released into the underlying soils of many military installations and bases. This remediation demands a high priority because, left untreated, these toxic substances have the capability to ultimately pollute and contaminate the groundwater and aquifers upon which many of the bases and nearby civilian communities depend for essential water supplies. While much attention has been historically directed at the remediation and treatment of

the groundwater itself, there is another subsurface area of pollution which is rapidly demanding a growing amount of concern. This area, termed the vadose, or unsaturated, zone, consists of that soil which lies between the ground surface and the water table. Increased interest in this area is a result of the realization that untreated contamination in the unsaturated zone has the potential to eventually negate progress gained in the remediation of the groundwater. Untreated toxins left deposited in the vadose zone can continue a steady, downwards migration for years, ultimately re-polluting groundwater which had previously been treated at great expense and difficulty. Unsaturated zone contamination is particularly substantial at those bases possessing unusually deep water tables.

While much practical knowledge has been recently acquired about groundwater remediation, there are still many significant, unanswered questions regarding the less common practice of vadose zone treatment. One specific problem area is the determination of the most suitable method to accurately measure unsaturated zone contaminant concentrations. Additional remediation difficulties are caused by gaps in the understanding of the transport mechanisms of contaminants trapped in this zone and how these mechanisms ultimately affect remediation attempts (1:1886).

Contaminants in the vadose zone can reside in one of five different locations within the soil matrix. The toxic

chemicals may be in a free-liquid phase between soil particles, in a vapor state, dissolved in the soil moisture, adsorbed to the surface of unsaturated zone soil particles, or firmly trapped within the interior of the soil matrix (1:1886). That percentage of the contaminant adsorbed within the soil particles appears to be the most difficult to effectively remediate and accurately measure (1:1886). Unfortunately, at those sites with long term contamination, which includes many DOD facilities, recent evidence indicates that a major portion of the vadose zone contaminant will adsorb to soil particles, confounding measurement and remediation attempts. In fact, the unsaturated zone contamination measurement method of choice for the Environmental Protection Agency, the "purge and trap" method, has been shown in some studies to actually identify less than 11% of the total soil contamination present at sites with long term contamination (2:150).

Current research into vadose zone contaminant transport has identified a complex slow sorption process as one of the mechanisms governing the adsorption of toxic substances to the soil. Contemporary knowledge and understanding of this mechanism reveals that the longer a contaminant remains in the unsaturated zone, the greater the percentage of the toxic substance that will become firmly adsorbed or trapped in the soil matrix (3:682).

This slow sorption mechanism not only frustrates attempts at proper measurement, but has also served to

greatly complicate comprehensive remediation of the vadose zone. Recent studies strongly indicate that a current favored method of unsaturated zone remediation, the Vapor Extraction System (VES), has proved ineffective in removing adsorbed contaminants (1:1886). During VES operations, large volumes of fresh air are forced through the vadose zone with the use of several air injection wells emplaced in the area of contamination. The goal is for fresh air to flow through the spaces of the unsaturated zone, thereby volatilizing the trapped contaminant which is then removed via an extraction port and treated (1:1885). However, there is a rapidly developing opinion among experts that slowly sorbed contaminants are impervious to this method of treatment (1:1886).

This situation is further complicated by the fact that while VES remediation operations are underway, the purge and trap method is commonly utilized to measure the success of the remediation efforts. As previously discussed, the remaining adsorbed pollution, which in the case of long term contamination may account for up to 90% of the total contaminant, will remain undetected by purge and trap measurement, thus giving the false impression of successful remediation of soil which is still seriously contaminated, and still capable of threatening valuable groundwater resources and aquifers (1:1887).

Specific Problem Statement

In order to assist in the effective remediation of the unsaturated zone at IRP sites, this thesis will investigate alternative techniques to determine a more accurate method for vadose zone contamination concentration measurement, and will utilize available modeling techniques to simulate the transport and slow sorption of vadose zone contaminants to provide a more complete understanding of the effects of slow sorption on vapor extraction remediation.

Objectives

1. Determine the mechanisms which impact the transport of organic contaminants which have been residing in the unsaturated zone for extended periods.

2. Determine what modeling techniques are currently available to simulate contaminant transport during soil vapor extraction operations and determine how these models may add to our understanding of the ultimate effects of the sorption mechanism on vapor extraction operations.

3. Determine how the long term physical and chemical processes which have acted upon vadose zone contaminants will affect the accuracy of purge and trap measurements.

4. Investigate alternative measurement procedures for those cases in which the unsaturated zone has been contaminated for an extended period of time.

Scope/Overview

The remainder of this thesis will begin with a

literature search reviewing the slow sorption process in the vadose zone, and its confounding, long-term effects, particularly on the purge and trap measurement system and vapor extraction remediation attempts. Following this, a computer simulation will be conducted using a suitable mathematical model capable of representing organic transport in the unsaturated zone. The goal is for this simulation, performed under conditions similar to those encountered during vapor extraction, and its accompanying sensitivity analysis, to provide a more complete understanding of the effects of slow sorption on vapor extraction remediation efforts. Finally, alternative procedures or enhancement techniques for the purge and trap measurement system will be investigated. The primary tool for this search will be a literature review, however, if possible alternatives are uncovered, which have not yet been explored, an experimental proposal will be drafted.

II. Literature Review

Introduction

The Vapor Extraction System (VES) and the Purge and Trap Measurement Technique share a common, basic principle of operation. Both require the rapid desorption of sorbed volatile organic contaminants in order to successfully function. In the case of the VES, the contaminant is required to rapidly desorb and is then quickly extracted from the vadose zone soils. For the purge and trap technique to successfully operate, sorbed VOCs must quickly volatilize into solution for subsequent quantification. Both of these techniques were based on the assumption that the sorption mechanism which binds the contaminant to the soil particle is equilibrium or "instantaneous" sorption. This equilibrium sorption mechanism allows for both sorption and desorption to occur in a short time span, and was considered the governing mechanism of vadose zone organic contaminant sorption (4:1223). However, as a result of a great deal of recent experimental research and detailed analysis, a slow sorption mechanism associated with organic contaminants in the vadose zone has been discovered and identified (4:1223). This sorption mechanism, which slowly traps the contaminant in the soil micropores over an extended period of time, ultimately frustrates those remediation and measurement techniques relying on the rapid desorption of the toxic substance. Specifically, this slow

sorption mechanism, in cases of long-term contamination, appears to seriously degrade the effectiveness of both the "purge and trap" contaminant measurement procedure and vapor extraction remediation (1:1885-1887). Due to the possible reliance on these two procedures for the eventual remediation and treatment of many Department of Defense sites possessing long-term organic contamination, it is imperative that a careful study of the impact of the slow sorption process be conducted in order to effectively meet the challenges of the future.

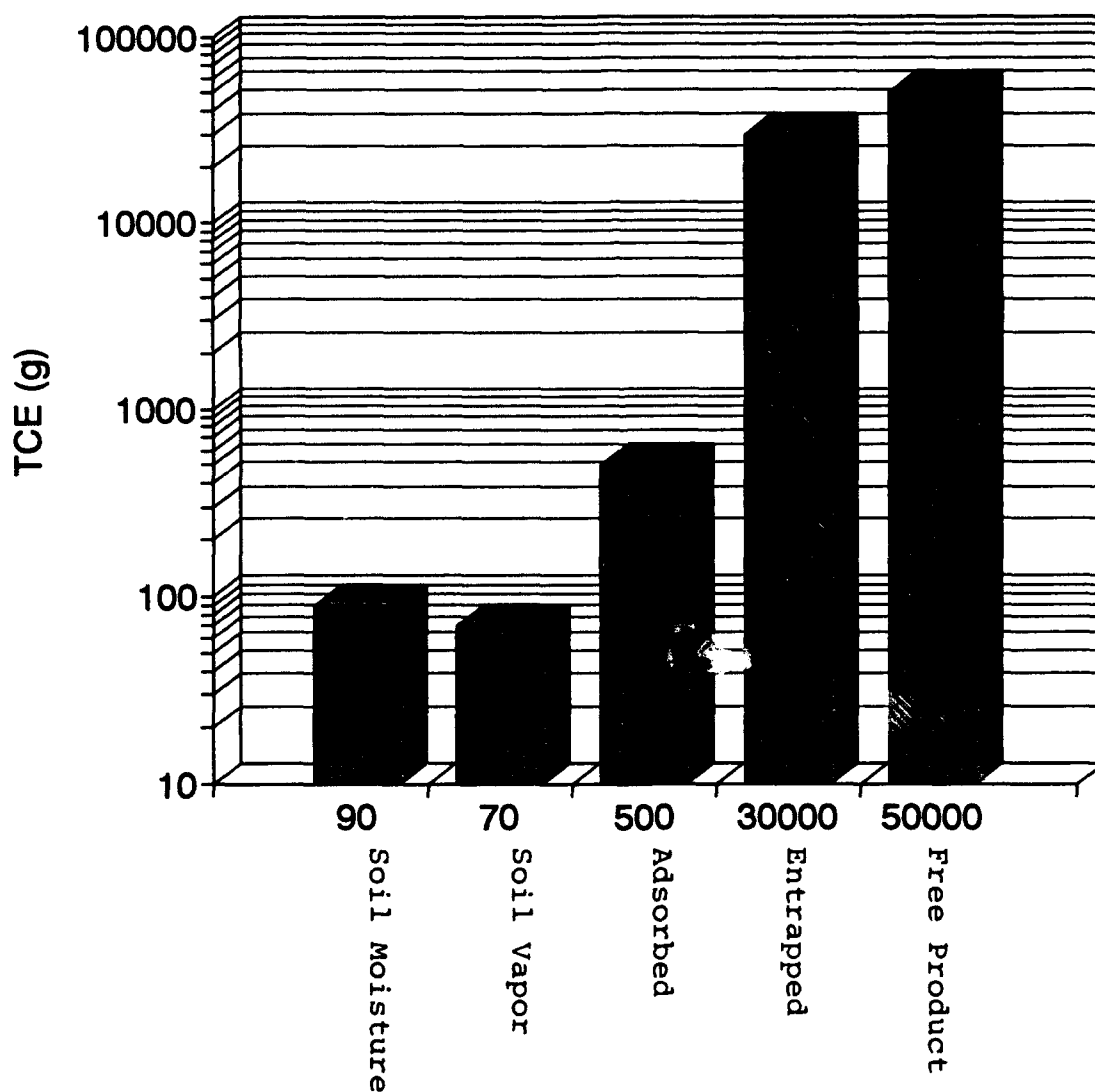
The Soil Matrix

In general, organic contaminants residing in the vadose zone will be encountered in five possible states. It can be found as a free-liquid phase between the soil particles, in a vapor, or gaseous state, dissolved in the soil moisture, adsorbed to the surface of soil particles or other soil organic matter, or trapped and sequestered in the interior of the soil matrix (1:1886) (See figure 1). Contaminants in one of the first three states pose no difficulty to contemporary remediation techniques and are routinely identified, extracted, and treated. It is that percentage of the organic pollutant that is adsorbed or sequestered in the interior of the soil matrix which appears highly resistant to common gaseous diffusion measurement and remediation procedures (1:1886). Recent research indicates that over an extended period of time the

Figure #1

Distribution of 30 L of TCE in One Cubic Meter of Soil

(1:1887)



slow sorption mechanism continuously acts upon organic substances in the vadose zone ultimately binding a greater and greater percentage of the toxic material, making progressively smaller amounts of contaminant accessible for remediation by conventional techniques (1:1886).

The Slow Sorption Mechanism

Past models and understanding of organic contaminants in the vadose zone had been based on a sorption mechanism that was assumed to rapidly achieve equilibrium distribution between sorbed and aqueous forms. The assumption of this single, rapid sorption mechanism was based upon experimentation which only accounted for contaminant residence times of approximately one day, or similarly short periods (4:1223). Currently, however, there is a rapidly growing body of evidence which strongly suggests that there is a second sorption mechanism acting upon organic contaminants in the vadose zone which does not reach equilibrium within the short time periods previously associated with solute transport and degradation (4:1223). Recent studies have repeatedly shown that to reach true equilibrium, organic substances demand "contact times that are significantly longer than is usually allowed in batch and column studies" (5:1237).

In fact, detailed analysis of this situation has revealed what has been described as a "two-box" model of organic adsorption (6:722). This two-box model, based upon

experimental data, shows a rapid uptake at the beginning of the adsorption process (the normal, rapid sorption mechanism), followed by a slower approach to equilibrium conditions (the slow sorption process) (6:722). This evidence strongly suggests that future, more realistic attempts at modeling the transport of organic contaminants in the vadose zone, must comprehensively account for both sorption mechanisms, the rapid mechanism and the slow sorption mechanism, if vadose zone contaminant transport is to be fully understood.

Recent field evidence confirms the existence of this "slow sorption" mechanism. Remediators investigating a polluted site at Picatinny Arsenal in New Jersey suffering from the long-term contamination of trichloroethylene (TCE), an organic pollutant common to many DOD IRP sites, discovered the field TCE distribution between the soil and the soil gas to be from 1 to 3 orders of magnitude greater than the distribution predicted under normal (rapid) equilibrium conditions (3:682). The remediators attributed this inconsistency between observed and predicted results to slow TCE sorption from soil previously exposed to a high level of contamination. They further speculated that "long-term contamination produces a fraction of the sorbed contaminant that is relatively resistant to desorption" (3:682).

In a recent analysis of samples subjected to long-term exposure to the popular organic soil fumigant 1,2-

Dibromoethane (EDB), investigators found an unexpected quantity of residual EDB which was highly resistant to desorption into both air and water (7:1201). Their explanation for this phenomenon was based upon a diffusion model in which the contaminant diffuses over time and becomes entrapped in remote micropores of the soil particle which results in "tenacious binding to soil particles" (7:1207). They concluded that current mathematical fate and transport models for organic contaminants would fail to accurately describe the EDB behavior they had encountered and documented (7:1207).

The persistence displayed by the organic contaminants in the previous two examples has been attributed to a rate-limited sorption process which is estimated to take years to reach equilibrium (8:1108). This complex, "nonequilibrium" behavior results in a fraction of the organic contaminant becoming sequestered in the soil. This fraction is immobile, and resistant to standard extraction and air flow measurement procedures (8:1107). Clearly, the longer the contaminant remains in the soil, the greater the percentage that "tenaciously" binds itself to the soil particles. The implications of this binding process for vapor extraction remediation and purge and trap measurement are clear. Obviously, a large portion of the contaminant trapped in the soil micropores, and resistant to air flow mobilization, will greatly reduce the ultimate effectiveness of these two procedures.

The Purge and Trap Measurement System

The purge and trap contaminant measurement technique is an extremely popular procedure for the determination of the level of organic contamination in the vadose zone and is actually the Environmental Protection Agency's preferred method of contaminant concentration analysis. This purge and trap measurement is based upon the volatilization of trapped contaminants into vapor form for subsequent identification and measurement by a gas chromatograph (1:1886). In order to fully appreciate the deficiencies of the purge and trap system, it is first necessary to understand its basic operating principles.

The most commonly utilized method of purge and trap measurement is normally conducted in the laboratory. In this instance, several grams of the contaminated soil are suspended in distilled water in a glass tube sealed at both ends. This purge tube is surrounded by a glass jacket containing heated water in order to precisely control the temperature of the purging operation. EPA procedures normally call for a controlled temperature of 40° C for the measurement. For the actual purging operation, a gas vapor, often nitrogen, is introduced to the soil sample tube and allowed to "purge" through the suspended sample for 11 minutes, according to EPA specifications. The exiting gas, hopefully the nitrogen plus the volatilized organic contaminant, is captured or "trapped" at the other end of the sample tube. This exit gas is then recovered and

analyzed with a gas chromatograph. The underlying objective of this operation is for the purging gas to cause a representative portion of the organic contaminant present in the soil sample to volatilize for eventual entrapment and gas chromatograph identification and quantification. (2:150)

Another, less common, method of purge and trap measurement is conducted "in situ," or at the actual site of contamination. In this method, stainless steel tubes of a few millimeters in diameter are used as probes and driven into the contaminated soil to a desired depth. Glass sampling bulbs are attached to the probes above ground level to collect the escaping vapors of the vadose zone gasses. A peristaltic pump is utilized to induce gas flow into the collection bulbs. (See figure 2) After a desired time period, the stopcocks on the sampling bulbs are closed and the collected vapors are taken to the laboratory. Once there, the trapped gases, which hopefully contain a representative portion of volatilized organic contaminant, are analyzed with a gas chromatograph. (3:678) Recently, however, investigators have begun to realize that both of these measurement techniques, due to their dependence upon the volatilization of a representative portion of the trapped pollutant, will be frustrated by the slow sorption mechanism previously discussed, which entraps organic material over time and renders it impervious to gaseous diffusion.

Figure #2

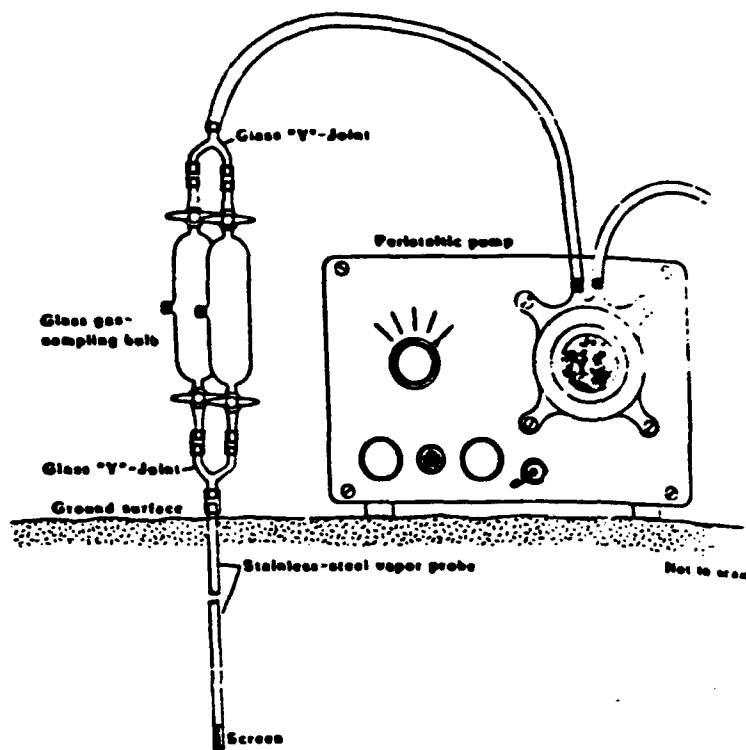


Diagram of "In-Situ" Purge and Trap Operation
(3:678)

Purge and Trap Deficiencies

The purge and trap measurement deficiencies caused by long-term slow sorption of organic contaminants have been clearly documented in many contemporary studies. In fact, the current empirical evidence has prompted some experts to speculate that purge and trap is effective in measuring only .1-10% of the actual contamination present in long-contaminated soils (1:1886).

In a widely-regarded and much analyzed study, purge and trap measurement analysis was conducted on soil samples that had been polluted from 5-15 years with 1,2-Dibromoethane (EDB). Although the analysis was conducted using precise EPA specifications, this method identified less than 10% of the total contaminant present in the soil (2:150). In addition, the investigators found that longer purge times at higher than EPA-specified temperatures did little to improve the quality and precision of the measurement.

In order to verify their conclusions, the investigators experimented by adding fresh EDB to the previously contaminated soil samples. After allowing 3 hours for the fresh EDB to reach equilibrium, enough time for equilibration assuming rapid sorption, the samples were purged. Purging for a period of 100 minutes, almost 10 times the EPA requirement, was required to remove the freshly added, rapidly sorbed, EDB. However, less than 5% of the long-term, slowly sorbed EDB contamination was removed and identified in the same process (7:1204).

Other field studies have also shown a discrepancy between purge and trap measured contaminant concentration and the actual contamination level present in the vadose zone soils. These discrepancies can now be attributed to the slow sorption process associated with long-term organic pollution (3:682). In light of this evidence, the effectiveness of purge and trap measurement has become questionable when this technique is utilized to measure the level of vadose zone contamination at long-polluted sites. Due to the entrapment of slowly sorbed VOCs, the assumption of rapid desorption of sorbed contaminants, required for the purge and trap technique to successfully operate, is not valid. A purge and trap measurement of long contaminated unsaturated zone soils will significantly underestimate the amount of total contaminant present, due to the retention of sorbed contaminants. This will allow sites which are still seriously degraded to appear uncontaminated. Due to this, it would seem imperative that a more effective means of long-term vadose zone contamination measurement be developed.

The Vapor Extraction System

The Vapor Extraction System (VES) is a common, contemporary remediation and treatment procedure based on gaseous diffusion. The VES, which is specifically designed to remove volatile organic compounds from the vadose zone, now comprises 18% of selected remedies at Superfund sites

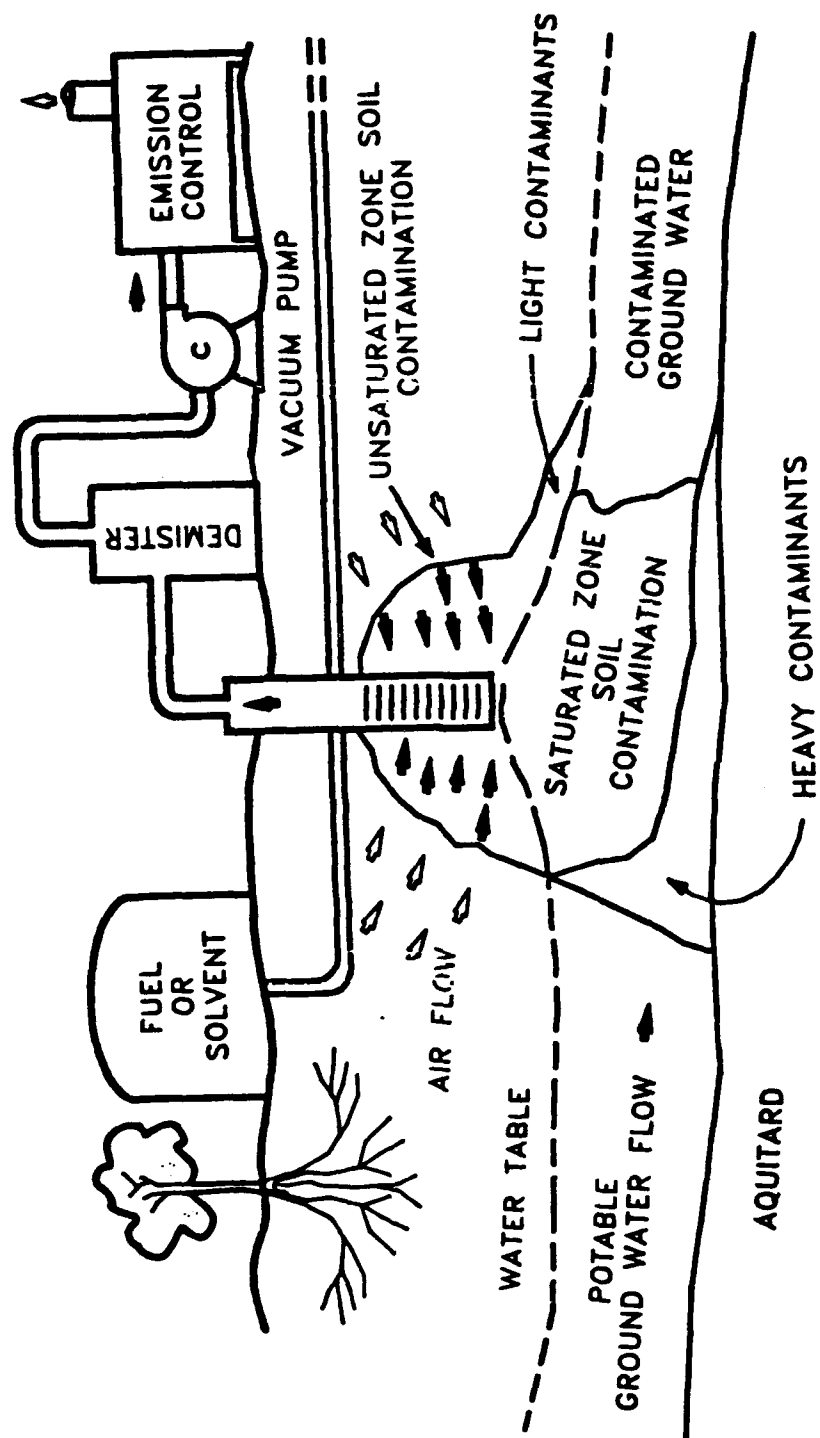
and its popularity continues to grow (1:1885).

The underlying operating principles of in-situ venting operations are fairly simple. Several air injection or extraction wells are located throughout the area of contamination. These air wells are utilized to significantly enhance air flow throughout the vadose zone, thus greatly accelerating the rate of volatilization within this region (9:413). The volatilized contaminant can then be treated on site, or removed to another location for processing. (1:1885) (See figure 3)

Although the actual physical equipment utilized, and the number and types of wells may vary from site to site, depending upon the design strategy selected for the remediation effort, the underlying principles are universal to all vapor extraction operations. The enhanced air flow in the vadose zone is designed to "sweep out the soil gas, disrupting the equilibrium existing between the hydrocarbons that are (1) sorbed on the soil, (2) dissolved in the soil-pore water, (3) present in a separate hydrocarbon phase, and (4) present as vapor" (10:1). However, the eventual and comprehensive success of any VES operation is completely dependent upon the mobilization of the contaminant and its subsequent removal in the air stream (10:3).

The ultimate utilization of vapor extraction is based upon the specific conditions of the contaminated site. Site-specific variables requiring consideration include (1) the size of the spill, (2) the type of the contaminant, and

Figure #3



Typical Vapor Extraction System Operation (10:2)

(3) the geohydrological factors. In most cases vapor extraction remediation is employed in instances of larger and deeper contamination where simple excavation of the contaminated soil is considered too costly or unfeasible. In addition, soil venting can be employed in conjunction with pump and treat groundwater remediation for simultaneous clean-up of the saturated and unsaturated zones (10:3).

In-situ soil venting operations have proven themselves to be a cost-effective remediation technique when dealing with short-term organic contamination in the vadose zone. In particular, this system has demonstrated real value in the rapid clean up of spilled fuels and other volatile organic compounds. However, its inherent weakness is the same deficiency that was previously shown to limit the effectiveness of the purge and trap measurement system. Due to its dependence upon the volatilization and air mobilization of trapped contaminants, the vapor extraction of long-term organic contamination is frustrated by the slow sorption mechanism which traps the pollutant and dramatically increases its resistance to air diffusion.

Vapor Extraction Remediation Deficiencies

Recent analysis and evidence has indicated that the slow sorption mechanism has indeed precipitated difficulties in current vapor extraction remediation operations. There is a rapidly emerging opinion among some experts that in those soils with long-term contamination, a

significant fraction of the organic contaminant is entrapped securely within the soil and consequently rendered inaccessible to both vapor extraction and groundwater pumping (1:1886). This opinion is supported by a growing body of experimental evidence and empirical data.

Recent experiments conducted with long-term, organic-polluted, vadose zone soils in New York found that 48-94% of the sorbed contaminant mass resisted desorption after an initial 168 hours of contact time with a remediating agent. The rate of desorption was found to be dependent upon the residence time of the contaminant. Based upon these results, the investigator concluded that the soils exhibited a "biphasic fast and slow desorption pattern" (11:537). The serious implications of this slow desorption were clear to the authors. It was obvious to them that this mechanism could be a "rate-limiting step" in many of the soil remediation technologies currently in use, including vapor extraction (11:537).

Other evidence strongly supports these conclusions and results. In an experimental setting, investigators found that passing a stream of dry nitrogen gas at the rate of about 30 volumes of gas per volume of soil per minute for 3.5 days through a soil sample long polluted with EDB removed only about 8% of the organic contaminant (7:1203). These results were in direct contrast to previous laboratory experiments in which soils which had only recently been exposed to EDB were successfully "cleansed" within a few

hours via air volatilization of the contaminant (7:1203).

These problems with VES are compounded by the fact that very often purge and trap measurements are utilized in order to verify the effectiveness of vapor extraction remediation attempts. If this does indeed occur, there is the previously mentioned risk that the purge and trap will register an extremely low concentration of remaining contaminant when, in fact, a large amount of the pollutant remains entrapped in the soil micropores (1:1887).

Numerous studies similar to these have documented a very low rate of uptake and adsorption associated with organic contaminants residing in the vadose zone. Due to the fact that, in many instances, the contamination has occurred over a very long period of time, the significance of this process can not be overlooked (5:1247). If successful, comprehensive remediation efforts are to be mounted in the future, a complete understanding of this slow sorption phenomenon must be attained. At present, most current vadose zone transport models fail to fully account for the confounding mechanism of slow sorption and desorption. Therefore, alternative models need to be developed which incorporate this rate-limiting adsorption process and provide a more comprehensive understanding of organic contaminant transport.

Vadose Zone Modeling

Much progress has recently been made in the development

of a suitable model to simulate vadose zone contaminant transport under the influence of slow sorption and desorption. A general consensus has arisen that a satisfactory, comprehensive model must be capable of representing several complex mechanisms. The early, more simple, modeling attempts were designed to solely represent gas phase advective transport based upon the assumption of ideal transport, including instantaneous adsorption and spatially homogeneous media within the vadose zone (12:3189). Previously presented documentation has conclusively demonstrated that instantaneous adsorption is many times not a valid assumption. In addition, the vadose zone is certainly not spatially homogeneous. Many of the conclusions already presented in this document have been based upon the presumed existence of micropores within the soil particles. Therefore, a suitable vadose zone modeling procedure will need to account "for the existence of a two pore domain, macropore (gas-phase) and micropore (liquid phase)" and consider the effects of the rate-limiting adsorption process (12:3189).

Improvements upon the first generation modeling designs were made by B. D. Brown and D. E. Rolston. Their efforts resulted in a gas phase advection model that incorporated the rate-limited adsorption process (12:3189). They recognized the fallacy in the assumption of instantaneous equilibrium and developed a model to quantitatively reflect the "transient-state method" required to "describe the

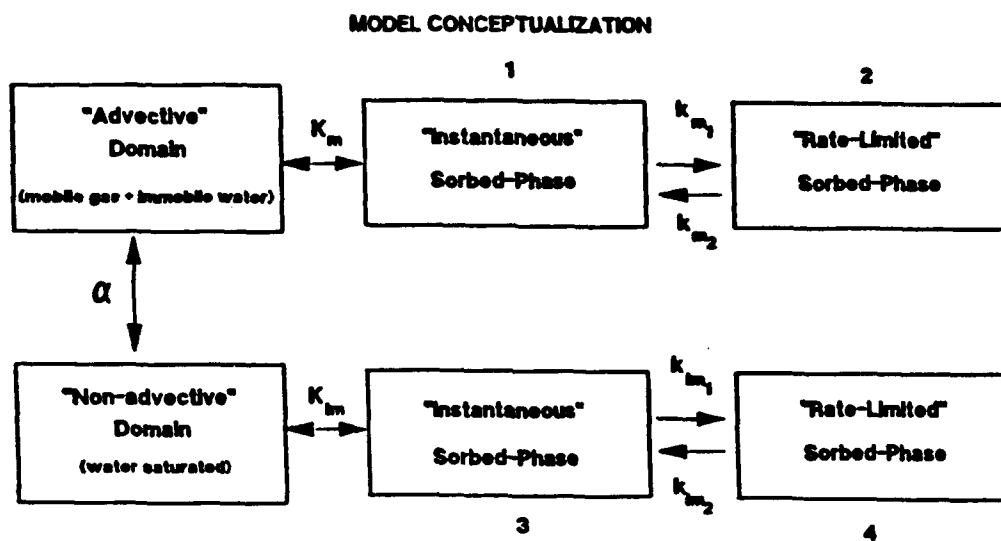
simultaneous mass flow, molecular diffusion, and reversible and irreversible sink processes" that determine contaminant transport (13:69).

Further modeling advancements were made by engineers John S. Gierke, Neil J. Hutzler, and David B. McKenzie. Their contribution consisted of the development of a model capable of simulating both macropore and micropore transport (12:3189). These authors utilized their experimental observations of dilute toluene vapor transport in soil columns to create a model simulation incorporating the effects of "gas diffusion, gas-water equilibrium and mass-transfer, liquid diffusion, and sorption" (14:324).

A vadose zone modeling process which appears to successfully incorporate "rate-limited" sorption was recently presented by researcher Mark Brusseau. Brusseau's model is based upon a conceptual framework which divides the vadose zone into an "advective domain" and "non-advective domain." (See figure 4) The advective domain is characterized by soil macropores and is that area most heavily and directly influenced by vapor-extraction generated air flow. In this domain, sorption to the solid material can be either instantaneous or slow. (12:3190)

Brusseau's model also represents the transport of organic material in the so-called "non-advective" domain. This region is dominated by the micropores and is an environment saturated by water. As previously presented and discussed, this water saturated, micropore domain is highly

Figure #4



Conceptualization of Brusseau's Model

(12:3190)

resistant to the advective gas flow of the vapor extraction process, hence its name-- the "non-advective" domain.

Brusseau's model allows for both instantaneous sorption and slow sorption in this region. In addition, this model describes the transfer of contaminant between the advective and non-advective domain by a first-order rate law.

(12:3190)

Brusseau's model is based upon a number of fundamental assumptions. His assumption that the effects of gas compressibility are negligible and that the effects of slipping, the "Klinkenberg effect," are minimal allows the use of Darcy's equation to represent gas flow. His assumption that molecular diffusion is the predominant diffusion for vadose zone systems allows for the utilization of equations based on Fick's law to simulate diffusive flux within the system. In addition, based upon previous work, Brusseau has assumed the mass transfer between liquid and water to be instantaneous and governed by Henry's law.

(12:3190-3192)

The Brusseau model appears to present a viable means of simulating the effects of slow sorption on vapor extraction operations for the detailed analysis desired in this document. Thus, a version of Brusseau's model was used in the preparation of the analytical portion of this study. More detailed information concerning the Brusseau model, including a discussion of the mathematical equations which are its foundation, will be presented in Chapter 3.

Possible Alternatives to Purge and Trap Measurement

Early in this chapter information was presented which would appear to raise serious questions about the validity of purge and trap measurement of long-contaminated soils. These same questions have prompted a number of individuals to attempt to develop some accurate alternative procedures to the purge and trap technique. In this section, three possible procedures that may eventually enhance the quality of vadose zone measurements will be presented. In addition, a less conventional technique, taken from the field of optical physics, that may be of possible assistance in vadose zone contaminant concentration identification will also be discussed.

Methanol Extraction. Methanol extraction, or hot solvent extraction, as it is sometimes called, is considered by many experts to be the definitive solution to the purge and trap measurement problem. In this procedure, the soil sample is suspended in methanol for a designated period of time, either at room temperature or at a temperature reaching 75° C, if hot solvent extraction is desired. This mixture is then shaken and centrifuged. A gas is then allowed to purge through the resulting supernatant, which is hopefully the methanol with 100% of the organic pollutant drawn from the soil sample and dissolved in the liquid methanol. The exiting gas is then trapped and analyzed with a gas chromatograph for the suspected pollutant, which, in theory, should easily volatilize from the methanol to the

passing gaseous air stream. This system is very similar to the purge and trap technique with the critical addition of the methanol, which draws the organic pollutant from the soil. (2:150) (15:276)

Methanol was considered so effective at removing organic contaminants from the suspended soil samples that this procedure was frequently reported to be completely successful in accurately gauging organic pollution levels in long-contaminated soils. One researcher reported: "The EDB removed by two consecutive extractions with methanol for 24 hours each at 75° C was taken at 100%. Indeed, in most cases, over 95% was removed by the first extraction alone" (2:151). Another experimenter familiar with methanol extraction procedures reported that "one methanol extraction was sufficient for the estimation of the total soil TCE" (15:276). Indeed, confidence in the results of this procedure is so high that the American Petroleum Institute has recently published a new soil analysis method which is based upon the methanol extraction of soil samples. Although the Institute does not claim 100% recovery in every instance, many feel that "this analytical technique will address the concerns" associated with the purge and trap technique (16:420).

However, it does not appear that the questions surrounding vadose zone contaminant concentration measurement will be resolved so easily. Researchers from the Center for Risk Management, Oak Ridge National

Laboratory, recently reported that in studies with spiked soil samples "the addition of methanol yielded only 28-83% of the volatile organic contaminant" (17:421). If methanol recovery was only this effective with recently spiked samples, one must speculate that the recovery in long-contaminated samples would be even lower (17:421). Therefore, it would appear that methanol extraction may fall short of being a panacea to the vadose zone organic measurement question. If so, other methods will need to be developed to solve this important issue.

Pulverization of the Soil Sample. The pulverization of the soil sample is a technique that may have the potential to increase the effectiveness of the purge and trap system. In one laboratory study, pulverization of soil particles in a ball mill increased 15 minute EDB extraction with water from .1% before pulverization to 30% after pulverization of long-contaminated soils. These results led the researcher to conclude that "pulverization prompted release both to the aqueous and gaseous phases" (7:1206). Other studies would seem to support these conclusions. Another investigator, William Ball, found that pulverized samples "obviated the need for long equilibrations" (4:1234). His research with soil samples demonstrated that long-term contamination levels could be reached in the short-term with pulverized soil particles (4:1234). If pulverization did, indeed, decrease the period necessary to achieve equilibrium for the slow sorption mechanism, it would only stand to reason that

the same pulverization might expedite the eventual extraction of the contaminant in question.

Supercritical Fluid Extraction. Supercritical Fluid Extraction is an emerging technology which has generated much recent interest and appears to possess application in the measurement of contaminated soils. Supercritical fluids are substances that manifest themselves as fluids at high temperature and pressure but exhibit the physical characteristics of both a gas and a liquid. Their inherent advantage is that, when in liquid form, these supercritical fluids (SCF) possess unique properties and abilities, such as extremely high dissolving power, and extremely low viscosity (18:806) (19). These low viscosities, coupled with the high solute diffusivities of SCFs, result in superior mass transfer characteristics, as compared to conventional liquid solvents (20:1225). Many organic compounds, such as polychlorinated biphenyls (PCBs) and obsolete explosives, which are normally insoluble in water, will readily dissolve in an SCF (18:807).

In the case of supercritical fluid extraction, the SCF of choice is normally Supercritical Carbon Dioxide (SCCO₂). Two of the advantages of SCCO₂ include its low critical temperature, 304° K, and its moderate critical pressure, 72.8 atm (20:1225). Researchers believe that the extremely low viscosities associated with SCFs make it possible for these substances to penetrate the entirety of the soil matrix and reach the normally inaccessible soil micropores

(19) (20:1225). Once in these interior areas of the soil particle, the high dissolving power of the SCFs permits an easy extraction of any organic pollutants entrapped or sorbed in these remote spaces. In fact, confidence in the abilities of supercritical fluids runs so high that several manufacturers claim that their automated SFE extraction systems are capable of 100% extraction of certain organics in the soil, even in the case of long-term contamination (19) (21). If a supercritical fluid can truly penetrate the recesses of the soil matrix and dissolve those organic contaminants contained within, then, theoretically, SFE should be capable of the accurate measurement of organic contamination in long-contaminated soils.

Microanalysis with Laser Ablation. Much progress has been made in recent years regarding the use of pulsed laser beams for the microanalysis of solid samples. This procedure is dependent upon the ablation, or atomization, of particles on the surface of the solid undergoing analysis. A pulsed, focused laser beam is used to separate a small layer of the material located on the surface of the sample solid. After absorbing the energy of the directed laser, the material located on the surface atomizes into its basic elements. Atomization is normally completed in an air-tight measuring chamber filled with a buffer gas. Once in the buffer gas chamber, the atomized elements can be identified with the use of Optical Emission Spectrometry (OES). OES is a common procedure utilizing a laser fired into the mixture

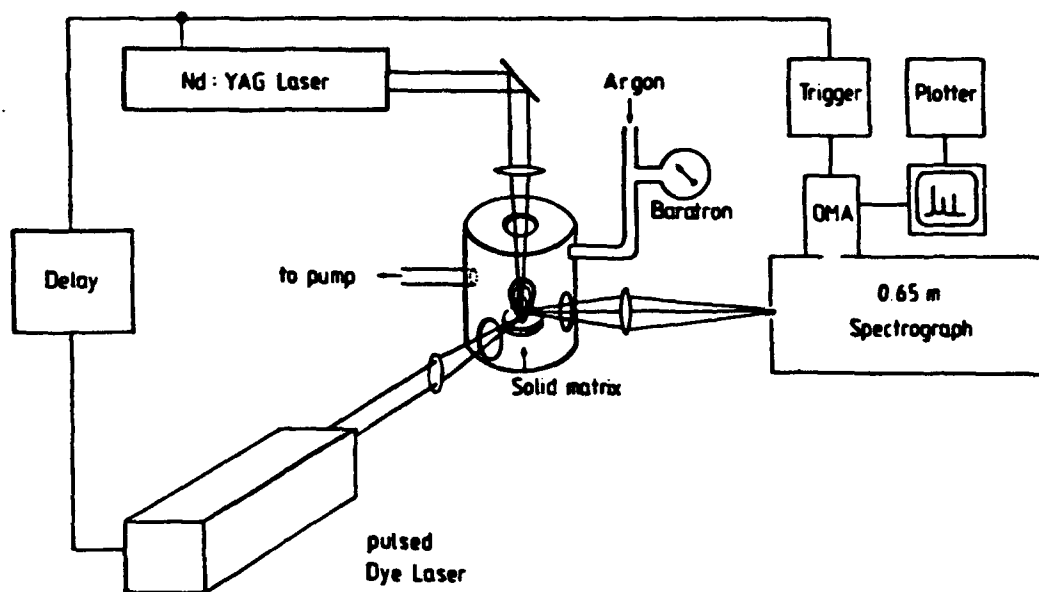
of buffer gas and atomized elements and a spectrograph to positively identify the ablated atoms. The spectrographic laser is tuned to the resonance line of the desired analyte. The spectrograph allows determination of the amount of laser fluorescence absorbed by the ablated atoms. This, in turn, reveals the level of analyte in the buffer gas. (22:229-236)

Although this system is primarily utilized for the microanalysis of the surface of metals, it would seem at least theoretically possible for its application to extend to soil samples. (See figure 5) The appeal of this procedure lies in the fact that the high energy laser atomizes a thin layer of the surface of the sample. This would, of course, include any adsorbed material. In addition, according to Major Glen Perram of the Air Force Institute of Technology, it is at least theoretically possible for the focused laser beam to penetrate the recesses of the soil micropores, ablating the material contained within. Although the contaminant and the soil will be "vaporized" into their elemental atoms, a comparison of the spectrographic analysis of a "clean" soil sample with a contaminated soil sample would reveal the presence and quantity of characteristic atoms contained in the target contaminant, such as chlorine in TCE.

Conclusion

Over the past several years researchers have identified what they feel is a slow, or rate-limited, sorption

Figure #5



Typical Laser Design for the Microanalysis of Solids
(22:227)

mechanism associated with organic contaminants trapped in the vadose zone. This mechanism affects organic transport and, over time, is capable of trapping a large portion of the total bulk of the contaminant within the soil matrix. Once sequestered in the matrix, the entrapped portion of the contaminant becomes highly resistant to gaseous diffusion measurement and remediation.

Two common procedures which rely upon the air mobilization of the contaminant in order to be effective are the purge and trap contaminant concentration measurement system and the vapor extraction remediation procedure. The accuracy of the purge and trap system has been shown in several laboratory and field studies to be seriously degraded by the effects of the slow sorption mechanism. This degradation is so well documented and so severe that many experts now question its usefulness as a measurement tool.

The body of evidence concerning the effects of slow sorption on the vapor extraction system is not as substantial. Although vapor extraction has been shown in laboratory studies to be adversely affected by this rate-limiting mechanism, researchers still disagree about the extent to which this process ultimately frustrates vapor extraction remediation. However, because purge and trap and vapor extraction share the same basic, underlying principles of operation, it would seem reasonable to expect the overall effectiveness of vapor extraction to be substantially

lowered by a transport mechanism which appears to incapacitate the purge and trap system. In light of this, considerable effort has been expended in an attempt to devise a process to model the transport of organics in the vadose zone and to help understand the magnitude of these effects.

It would appear that the basis for a suitable model has already been created. Mark Brusseau, building upon the efforts of previous modelers, has devised a mathematical model to represent organic transport in the unsaturated zone. This model incorporates the complex effects of the heterogeneity of the vadose zone soils, with its macropore and micropore domains, and also accounts for the effects of two sorption processes: the instantaneous sorption mechanism and the slow, or rate-limiting process.

Several alternatives have been presented to deal with the deficiencies of the purge and trap system. Methanol extraction is felt by many to be a solution to the problem. However, recent evidence has come to light which raises questions about the effectiveness of this procedure. Pulverization of the soil samples has shown promise in laboratory studies as a technique to improve the quality of the standard purge and trap procedure. Supercritical fluids appear to possess unique characteristics that might make supercritical fluid extraction a viable alternative to the purge and trap technique.

In addition, a less conventional method of soil

analysis has been proposed: the use of lasers to conduct microanalysis. While this method requires further study to determine if its applicability can be extended to trace organic analysis in soils, it appears, at least theoretically, to possess some capabilities in this area.

III. THE SVE COMPUTER MODEL

Unless otherwise footnoted, the information contained in this section was derived from discussions with LtCol M. N. Goltz, developer of the SVE Computer Model. The four equations presented were taken from the unpublished notes of Goltz and Oxley.

The Soil Vapor Extraction (SVE) Computer Model was developed jointly by LtCol M. N. Goltz, PhD, and Dr. M. Oxley of the Air Force Institute of Technology. The model, which appears capable of simulating the slow sorption mechanism in vapor extraction operations, was utilized extensively to produce the numerous simulations of vapor extraction presented in this document. Drs. Goltz and Oxley based the SVE Computer Model on the model previously published by Mark Brusseau (12), with some modifications. Goltz and Oxley utilized the same basic assumptions and conceptual framework published by Brusseau and previously discussed in Chapter 2 to develop four basic equations representing nonequilibrium transport by gas advection. These four equations simulate equilibrium and "rate-limited" sorption in both the advective and nonadvective domains. However, unlike Brusseau, whose model simulates the one-dimensional transport of contaminant in a column, Goltz and Oxley modified this process to represent the radial transport more representative of actual remediation sites. The governing equations used in the SVE Computer Model are:

(EQN 1)

$$\begin{aligned} &\theta_g [\partial C_g / \partial t] + \theta_{wg} [\partial C_{wg} / \partial t] + \theta_w [\partial C_w / \partial t] + f(\rho) [\partial S_{m1} / \partial t] + f(\rho) [\partial S_{m2} / \partial t] + \\ &(1-f)(\rho) [\partial S_{im1} / \partial t] + (1-f)(\rho) [\partial S_{im2} / \partial t] = \theta_g (\partial / \partial r) (D \partial C_g / \partial r) \\ &\quad - q (\partial C_g / \partial r) + \theta_g [D \partial C_g / r \partial r] \end{aligned}$$

Where, θ_g = Gas Filled Porosity

C_g = Concentration of Solute in Gas Phase [M/L**3]

t = Time [T]

θ_{wg} = Water Filled Porosity of Advective Domain

C_{wg} = Concentration of Solute in Water Located in
Advective Domain, in Equilibrium with Gas
Phase [M/L**3]

θ_w = Water Filled Porosity of Nonadvective Domain

C_w = Concentration of Solute in Water Located in
Nonadvective Domain [M/L**3]

f = Fraction of Sorbent Associated with Advective
Domain

ρ = Soil Bulk Density [M/L**3]

S_{m1} = Concentration of Sorbate in "Instantaneous"
Sorbent Associated with Advective Domain at
Equilibrium,

$$S_{m1} = F_m (K_m) C_{wg} \quad [M/M]$$

F_m = Fraction of Sorbent in the Advective
Domain for which Sorption is Instant

K_a = Equilibrium Distribution Coefficient for
the Advective Domain $[L^3/M]$

S_{a2} = Concentration of Sorbate in "Rate-Limited"
Sorbent Associated with Advective Domain

$$S_{a2} = (1-F_a) (K_a) (C_w) \quad [M/M]$$

S_{ia1} = Concentration of Sorbate in "Instantaneous"
Sorbent Associated with Nonadvective Domain

$$S_{ia1} = F_{ia} (K_{ia}) C_w \quad [M/M]$$

F_{ia} = Fraction of Sorbent in the
Nonadvective Domain for which
Sorption is Instantaneous

K_{ia} = Equilibrium Distribution Coefficient
for the Nonadvective Domain $[L^3/M]$

S_{ia2} = Concentration of Sorbate in "Rate-Limited"
Sorbent Associated with Nonadvective Domain
at Equilibrium,

$$S_{ia2} = (1-F_{ia}) (K_{ia}) (C_w) \quad [M/M]$$

r = radial distance $[L]$

D = Global Dispersion Coefficient

$$D = D_m + D_d \quad [L^2/T]$$

D_m = Mechanical Dispersion Coefficient $[L^2/T]$

D_d = Diffusion Coefficient in Gas Filled Pores
 $[L^2/T]$

q = Darcy Flux $[L/T]$

(Parameter Definitions: 12:3197)

(EQN 2)

$$\theta_w [\partial C_w / \partial t] + (1-f) (\rho) [\partial S_{im1} / \partial t] + (1-f) (\rho) [\partial S_{im2} / \partial t] = (\alpha) [C_g - K_h (C_w)]$$

Where, α = First Order Rate Constant Describing Mass
Transfer Between Advective and Nonadvective
Domains [/T] (12:3197)

K_h = Henry's Constant

(EQN 3)

$$\partial S_{m2} / \partial t = k_{m2} [(1-F_m) K_m C_{wg} - S_{m2}]$$

Where, k_{m2} = First Order Reverse Sorption Rate Constant
for Advective Domain [/T] (12:3197)

(EQN 4)

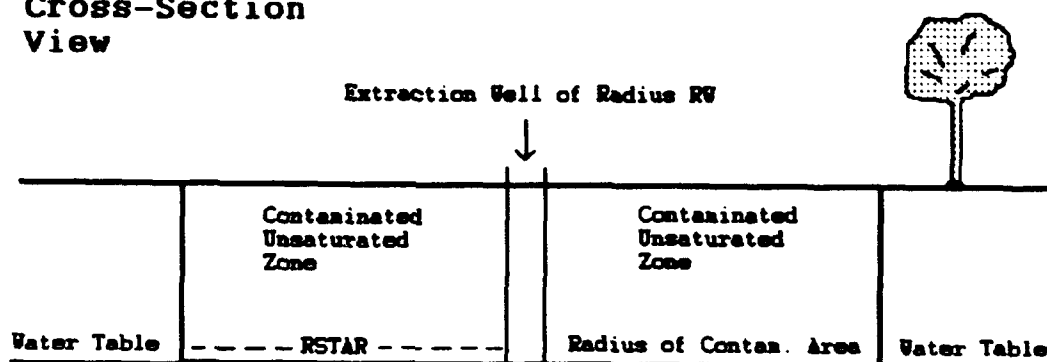
$$\partial S_{im2} / \partial t = k_{im2} [(1-F_{im}) K_{im} C_w - S_{im2}]$$

Where, k_{im2} = First Order Reverse Sorption Rate Constant
for Nonadvective Domain [/T] (12:3197)

These differential equations are the basis of both the Brusseau model (in one-dimension) and the Goltz and Oxley SVE Computer Model. In the SVE Model these equations are utilized to calculate the breakthrough curve at a vacuum extraction well located in the unsaturated zone at the center of a circular, contaminated area (23) (see Figure #6). In order to solve these equations, Goltz and Oxley converted these four partial differential equations in real

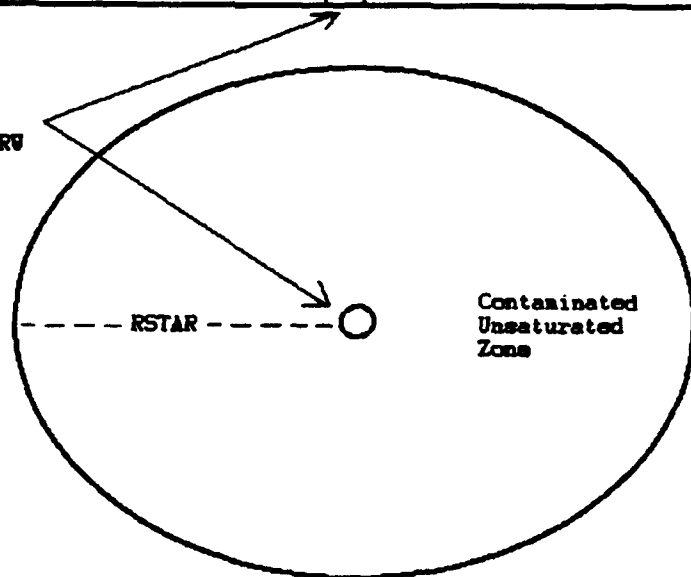
Figure #6

Cross-Section
View



Extraction
Well
of Radius R_W

Top
View



SVE Model Extraction Well Schematic

time to ordinary differential equations in Laplace time. Following this conversion, the resulting ordinary differential equations are solved analytically in Laplace time and then these solutions are numerically inverted from Laplace time to real time through the use of the Stehfest Algorithm. The SVE Model is capable of allowing sorption/desorption to be controlled by either the local equilibrium assumption or by a first order rate limitation. Model output consists of relative contaminant concentration at the extraction well versus real time.

Conclusion

The SVE Computer Model may be used to simulate the effects of slow sorption on vapor extraction operations. Based on the Brusseau model, the Goltz and Oxley model should, in theory, provide outputs capable of more fully illustrating the possible effects of "rate-limited" sorption on contemporary vapor extraction remediation attempts. The SVE Model is, in fact, a slight improvement of Brusseau's work in that it allows for the simulations to occur in more realistic, multi-dimensional, radial space. In the next chapter, a sensitivity analysis of the SVE Computer Model will be presented. This analysis should provide further information, both about the capabilities of the model, and the effects of slow sorption on vapor extraction operations.

IV. SVE MODEL ANALYSIS

INTRODUCTION

The analysis of the SVE Computer Model simulations was performed utilizing the parameters associated with two contaminants of concern in hazardous waste site remediation. The contaminants chosen for this analysis were trichloroethylene (TCE) and benzene. These particular chemicals were chosen for several reasons. First, both are commonly found at Department of Defense IRP sites and have been associated with unsaturated zone contamination. In addition, both of these chemicals of concern possess Henry's Constants which indicate a high degree of volatility, making both of them ideal candidates for remediation by vapor extraction processes. Finally, both TCE and benzene also have relatively high numerical "KD" values, or sorption coefficients. These high KD values indicate that both contaminants will significantly sorb onto soil material, therefore making both highly susceptible to the effects of slow sorption. This susceptibility will allow us to utilize the SVE computer model simulations to analyze the effects of the slow sorption process.

The overall framework of the analysis plan is fairly simple. Following the selection of default input parameters, a sensitivity analysis of the SVE Computer Model will be accomplished for each chemical of concern. Model output will consist of relative concentration of contaminant

at an extraction well vs time (in days). This output will be represented graphically to aid interpretation. Of particular interest, we will look for "tailing," early breakthrough, and other effects of the slow sorption process. Tailing is perhaps one of the more obvious characteristics of the slow sorption mechanism present in the output curves. This phenomenon often follows a rapid breakthrough and corresponding drop in relative contaminant concentration. Tailing occurs when the remediation effort seems to "bottom out" and contaminant concentration, or relative concentration in this case, begins to fall very little over a long period of time, in contrast to the initial, rapid drop in relative concentration. This "tailing" is due to contaminant molecules being retained in the soil particles by the slow sorption mechanism, and only slowly desorbing during remediation efforts. Slow sorption tailing can frustrate and greatly extend attempts at comprehensive remediation of organic contaminants.

Input parameters can be divided into three broad categories. Plant parameters are those parameters associated with the physical characteristics of the actual vapor extraction process, such as well diameter, pumping rate, etc... These values were chosen based upon typical values of contemporary vapor extraction operations. Chemical parameters are those values specifically associated with the chemical of concern, such as Henry's Constant. The values for these parameters were extracted from The Handbook

of Chemical Properties Estimation Methods (24). The third category consists of site specific characteristics. These are parameters which are dependent upon the actual remediation site conditions. Some of these parameters were varied over a wide range during the modeling iterations so that the slow sorption effects could be identified and analyzed.

TCE Modeling

Input Parameters. Input parameters are displayed in Table #1, with their corresponding units. In addition, both the nomenclature for Equations 1-4 and their corresponding SVE Model names are presented. Pumping rate, aquifer thickness, well radius, contaminated area radius, and the time parameters are all considered Plant Parameters and have been assigned reasonable values. The following variables have been denoted as site specific characteristics: gas-filled porosity (PORGAS), water-filled porosity of nonadvective domain (PORW), water-filled porosity of advective domain (PORWG), soil bulk density (RHO), the first order rate constant describing mass transfer between the advective and non-advective domains (ALFA), the fraction of sorbent associated with the advective domain (EF), the fraction of sorbent in both domains for which sorption is instantaneous (FM) (FIM), and the first order desorption rate constant (K2). Due to the fact that some of these variables are not easily measurable,

Table #1

INPUT VARIABLES

QW=Pumping Rate=1000 [m**3/day]
 B=Aquifer Thickness=20 [m]
 D=Dispersion Coefficient=5 [m**2/day]
 Θ_g = PORGAS=Gas-Filled Porosity=.15
 Θ_w = PORW=Water Filled Porosity of Nonadvective Domain=0-.2
 Θ_{wg} = PORWG=Water Filled Porosity of Advective Domain=0-.15
 ρ = RHO=Soil Bulk Density=1.76 [gm/cm**3]
 K_h = KH=Henry's Constant=.42 [dimensionless]
 RW=Well Radius=.01 [m]
 RSTAR=Radius of Contaminated Area=40 [m]
 TINIT=Starting Time=0 [days]
 DELTT=Time Step=100 [days]
 TFIN=Final Time=2000 [days]
 K_m = KM=Equil Dist Coef for Adv Domain=1.6 [cm**3/gm]
 K_{im} = KIM=Equil Dist Coef for NonAdv Domain=1.6 [cm**3/gm]
 α = Alpha=First Order Rate Constnt Describing Mass
 Transfer Between Adv and NonAdv Domains=100-.01 [/h]
 f = EF=Fraction of Sorbent Assoc with Adv Domain=.9999-.1
 F_m = FM=Frac of Sorbent in the Adv Domain for which Sorption
 is Instantaneous=.9999-.1
 F_{im} = FIM=Frac of Sorbent in the NonAdv Domain for which
 Sorption is Instantaneous=.9999-.1
 k_2 = K2=First Order Desorption Rate Constant=10-.001 [/h]

and yet, directly impact the importance of the slow sorption process, their values were varied over several orders of magnitude in an attempt to illustrate the effects of the slow sorption mechanism. The range of values used for these parameters is presented in Table #1.

The chemical specific parameters for TCE are Henry's Constant, K_H , and the two equilibrium distribution coefficients, K_M and K_{IM} . The dimensionless Henry's Constant used was obtained from The Handbook of Chemical Properties Estimation Methods (24). Each chemical's K_D was assumed to be a reasonable representation of the corresponding values of K_M and K_{IM} . The value of K_D was derived from the following equation:

$$K_D = K_{OC} \times F_{OC} \quad (24)$$

Where K_{OC} is the organic carbon adsorption coefficient. In the case of TCE the value of K_{OC} of 160 [cm^3/gm] was found in The Handbook of Chemical Properties Estimation Methods (24:4-23). F_{OC} represents the fraction of the organic content of the soil and was assigned a reasonable value of .01. Therefore, in the specific case of TCE,

$$K_M = K_{IM} = K_D = 160 \times (.01) = 1.6 [\text{cm}^3/\text{gm}]$$

No Sorption Model. The input parameters for the no sorption model are displayed in Table #2, with the subsequent output, in graphical form, shown in Figure #7. To eliminate sorption a low equilibrium distribution coefficient was used for both the advective and non-advective domains ($K_M=.001/K_{IM}=.0001 [\text{cm}^3/\text{gm}]$). In

TABLE #2

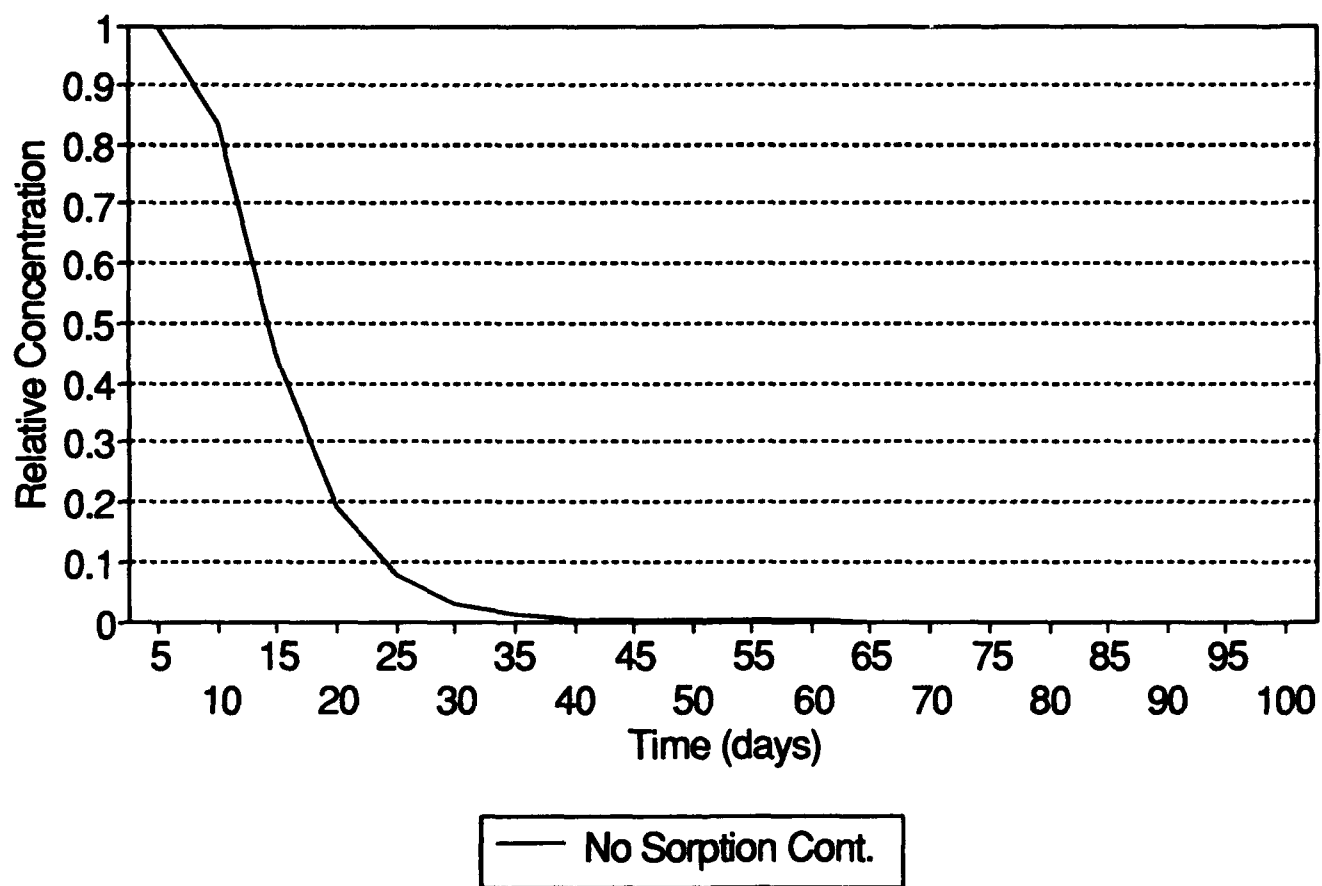
INPUT VARIABLES

QW=Pumping Rate=1000 [m**3/day]
 B=Aquifer Thickness=20 [m]
 D=Dispersion Coefficient=5 [m**2/day]
 PORGAS=Gas-Filled Porosity=.15
 PORW=Water Filled Porosity of Nonadvective Domain=0
 PORWG=Water Filled Porosity of Advective Domain=0
 RHO=Soil Bulk Density=1.76 [gm/cm**3]
 KH=Henry's Constant=.42 [dimensionless]
 RW=Well Radius=.01 [m]
 RSTAR=Radius of Contaminated Area=40 [m]
 TINIT=Starting Time=0 [days]
 DELTT=Time Step=5 [days]
 TFIN=Final Time=100 [days]
 KM=Equil Dist Coef for Adv Domain=.001 [cm**3/gm]
 KIM=Equil Dist Coef for NonAdv Domain=.0001 [cm**3/gm]
 Alpha=First Order Rate Constsnt Describing Mass Transfer
 Between Adv and NonAdv Domains=100 [/h]
 EF=Fraction of Sorbent Assoc with Adv Domain=.9999
 FM=Frac of Sorbent in the Adv Domain for which Sorption
 is Instantaneous=.9999
 FIM=Frac of Sorbent in the NonAdv Domain for which
 Sorption is Instantaneous=.9999
 K2=First Order Desorption Rate Constant=10 [/h]

Figure #7

Contaminant Conc at Well

No Sorption Case

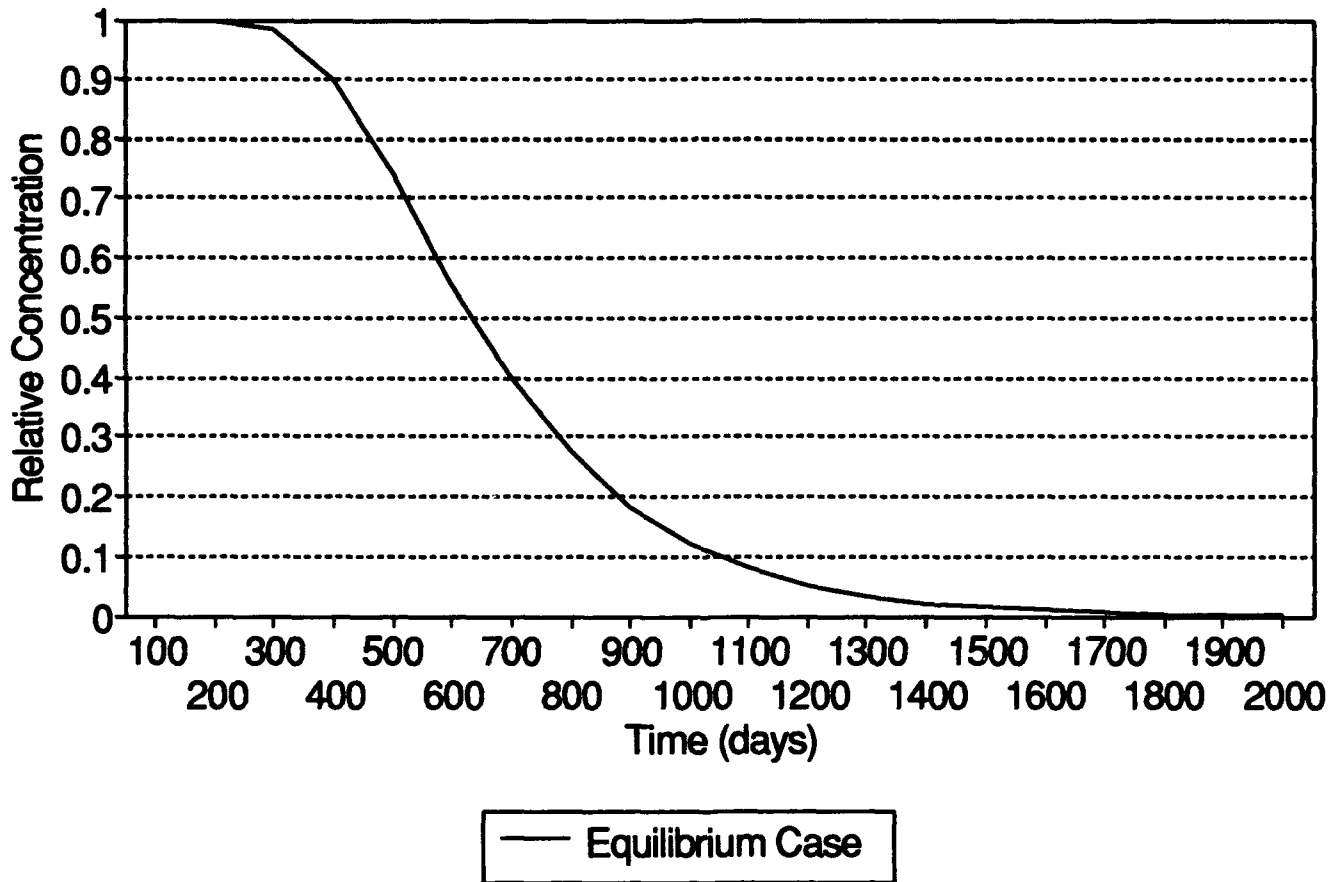


addition the no sorption simulation has been conducted with extremely high values for Alpha, K2, EF, FM, and FIM. This simulates a non-adsorbing contaminant, located almost entirely within the advective domain. Figure #7, the output, reflects this graphically. The breakthrough is immediate and symmetric. By 45 days the residual contamination level appears negligible.

TCE Simulations. For the first TCE simulation, TCE-specific values for KH, KM, and KIM were used (see Table #1). In this simulation, as in the no sorption simulation, the slow sorption-governing variables, Alpha, K2, EF, FM, and FIM were assigned extremely high values to minimize the effects of this mechanism. The model was run to simulate 2000 days, with output values calculated at 100 day increments. The graphical output is displayed in Figure #8. The retardation of TCE transport due to sorption is obvious from a comparison of this output curve with that of Figure #7. The TCE simulation shows a much slower remediation. The initial breakthrough appears to occur at approximately 350 days followed by a descent in the relative concentration values. At the 1000 day point approximately 15% of the original contaminant concentration remains and the curve smoothly drops to negligible values for relative concentration with no apparent slow sorption "tailing" after 2000 days of vapor extraction remediation.

Figure #8

TCE Concentration at Well Equilibrium Case



Retardation Factor. Since equilibrium was assumed in the first two simulations (the no sorption simulation and the TCE equilibrium simulation) these simulations can be utilized to calculate the retardation factor for TCE.

The mathematical determination of the Retardation Factor is easily accomplished. Brusseau (12) showed that,

$$(EQN 5) \quad RF = 1 + ((PORW+PORWG)/(PORGAS \times KH)) + (RHO/(PORGAS \times KH)) \times KP$$

Where,

$$KP = EF(KM) + (1 - EF)KIM$$

Therefore, from Table #3,

$$RF = 1 + 0/ (.15 (.42)) + (1.76/ (.15 (.42))) \times [.9999(1.6) + [(1-.9999)(1.6)]] = 45.7$$

Retardation factor can be approximated by comparing the no sorption output with the TCE equilibrium output. The time required for the relative concentration to drop to .5 will be the point of comparison in this analysis. If accurate, the time required in the TCE simulation should be 45.7 times as long as the number of days required in the no sorption output for the same reduction in the relative concentration.

From the no sorption output (see Figure #7), it is seen that,

$$\text{No sorption (.5 relative concentration)} = 13.6 \text{ days}$$

Using the same process on the TCE output,

$$\text{TCE (.5 relative concentration)} = 637 \text{ days}$$

Therefore,

$\text{TCE (.5) / No sorption (.5) = Retardation Factor}$

$637/13.6 = 46.8 \quad (\text{Retardation Factor})$

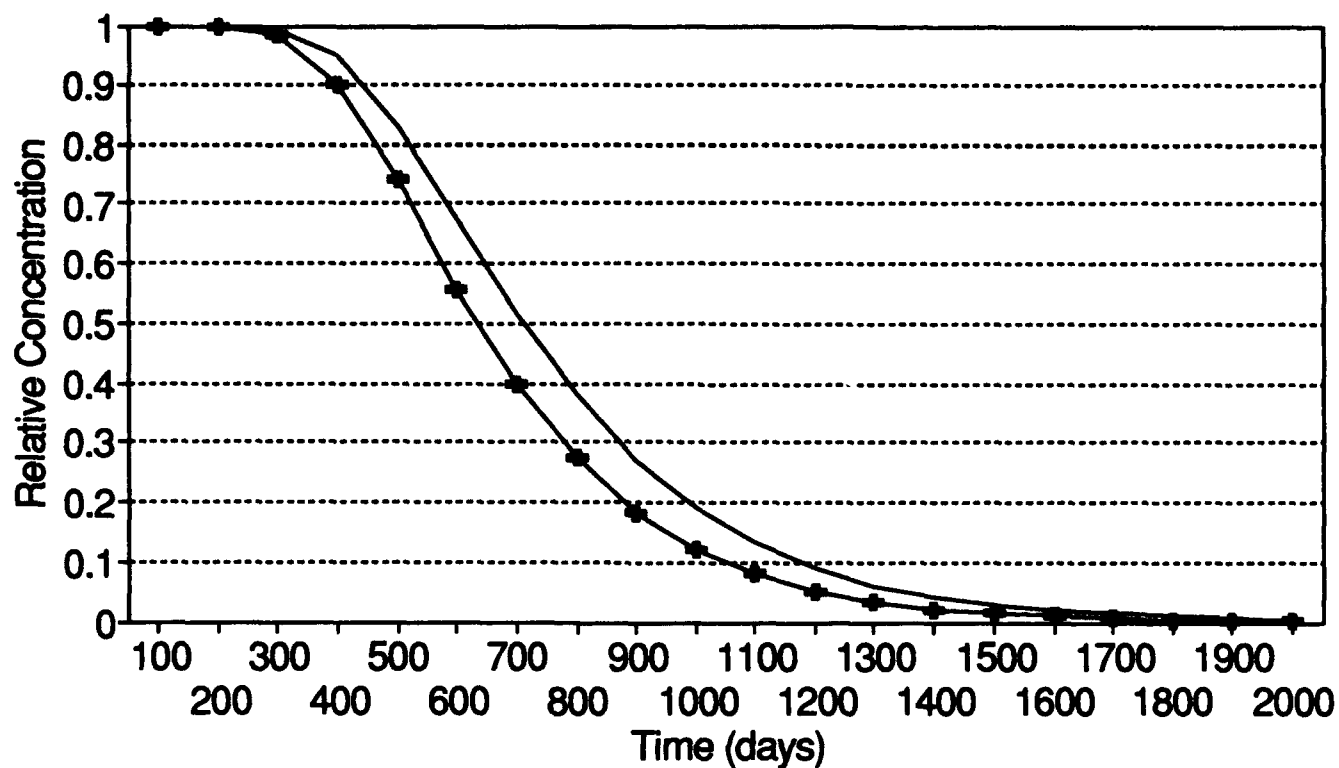
The close agreement between the two retardation factors gives confidence in the capabilities of the SVE Computer Model.

It was desired in the next iteration to examine the effects of water-filled porosity in both the advective and non-advective domains. To accomplish this, all input values remain unchanged, except for PORW and PORWG, which were assigned reasonable values of .2 and .15, respectively. The resulting model output is displayed in Figure #9, with the equilibrium output for comparison. A comparison of the two curves reveals the effects of the added water. The water in the soil voids has served to apparently retard contaminant movement and slowed the remediation process. Examine the relative concentration line of ".8" on both of the outputs in question. The equilibrium curve (with no water-filled porosity) appears to cross that line at 450 days. In the simulation with the water-filled porosity this does not occur until approximately day 525, evidence of the slowing of the contaminant transport. This effect is repeated for the remainder of the curve. An examination of equation (5) reveals that this slowing is expected. From equation (5) it is seen that non-zero values for "PORW" and "PORWG" serve to increase the value of the retardation factor thus slowing contaminant transport. At this point, it would again be

Figure #9

TCE Concentration at Well

PW=.2/PWG=.15 & Equil Case



— PW=.2/PWG=.15 Case ♦ Equilibrium Case

useful to compare the retardation factor calculated from equation (5) with the retardation factor determined from comparing the breakthrough curve simulations.

By utilizing equation (5),

$$RF = 1 + (.35/ (.15 (.42))) + (1.76/ (.15 (.42))) \times \\ [.9999(1.6) + [(1-.9999)(1.6)]] = 51.3$$

Comparing the two output curves:

No sorption (.5) = 13.6 days

PW/PWG (.5) = 707 days

$707 / 13.6 = 52$ (Retardation Factor)

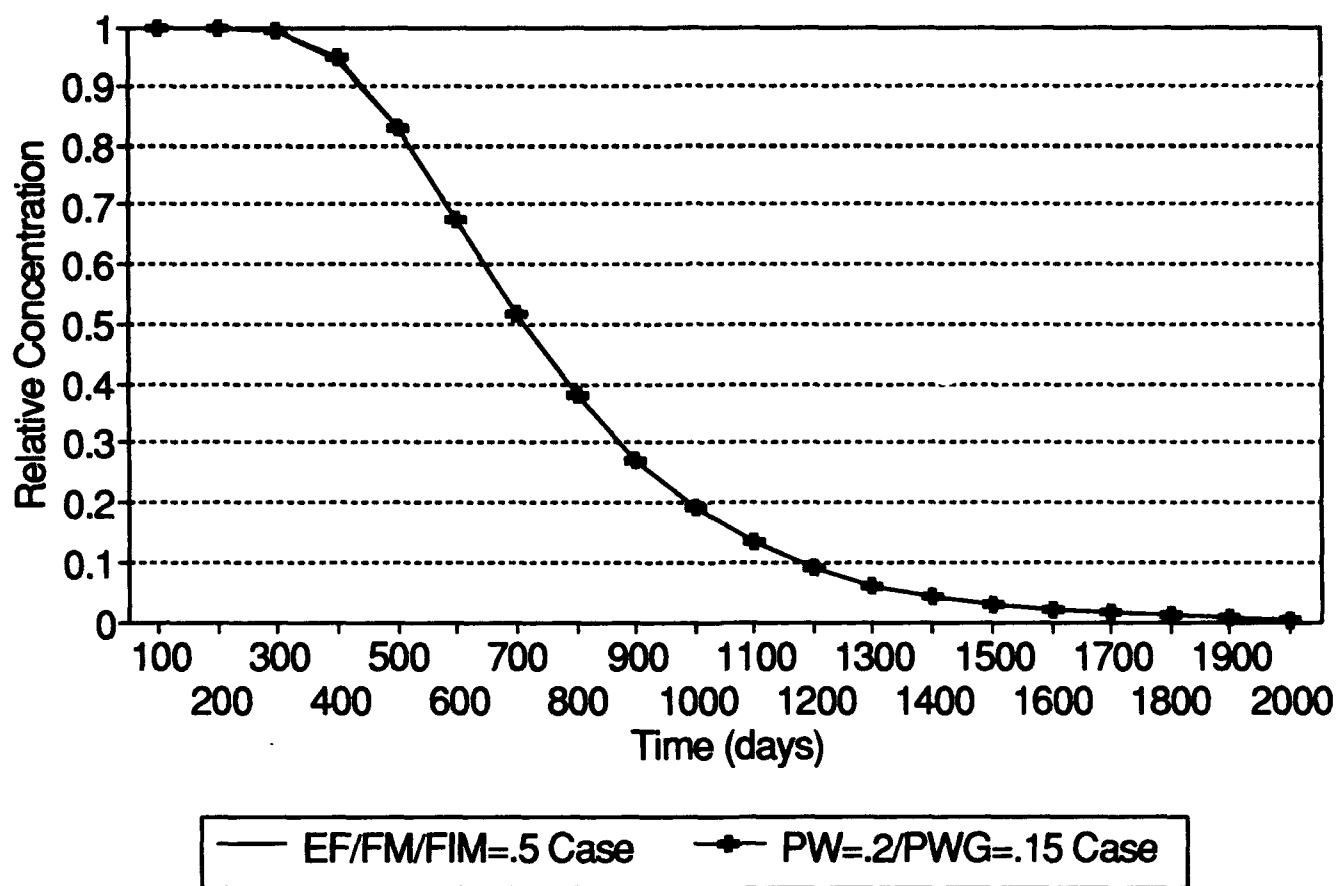
Once again, the close agreement between the two determinations gives confidence in the credibility of the SVE model.

The next simulation was conducted in order to see the effects of slow sorption. Parameters EF, FM, and FIM, were reduced from .9999 to .5. With this change, half of the contaminant is initially assumed to be sorbed to sites in the non-advective domain, and half of the sites in both the advective and nonadvective domains are assumed to be "slow sorption sites". However, the graphic representation of the output, displayed in Figure #10, appears identical to the previous output, which is also displayed and which possessed the high values for EF, FM, and FIM. The reason for this may be determined by reexamining the input parameters. Note that the values for both Alpha and K2 are still relatively high. The high Alpha allows for an almost instantaneous exchange between the two domains, and the high K2 causes

Figure #10

TCE Concentration at Well

EF/FM/FIM=.5 & PW/PWG Cases



rapid desorption, thus negating the effects of the slow sorption process. This is what is reflected in Figure #10.

In order to more clearly view the effects of slow sorption, it will be necessary to lower the values of Alpha and K2. This has been done for the next simulation. Both Alpha and K2 have been reduced to .01 [/h], and the other values remain unchanged from the previous simulation. The output curve resulting from these input values is shown in Figure #11. The effects of slow sorption are clearly seen when compared with the previous output, also displayed. The initial breakthrough is immediate and steep, as the TCE in the advective domain moves quickly to the well. By day 1000, however, the curve flattens out as the slow sorption mechanism begins to govern the removal of the remaining contaminant. At day 2000 the "tailing" is obvious as relative concentration stubbornly remains at approximately .05.

Is it possible to increase the effects of slow sorption? It would appear that the easiest way to accomplish this goal would be to lower the values of EF, FM, and FIM. This would, in effect, place more of the original TCE in the non-advective domain, and increase that percentage of the contaminant which is controlled by the slow sorption process. This is what has been done to the input values for the next simulation. All values remain unchanged from the previous iteration except that EF, FM, and FIM have been lowered to .1. The output, Figure #12,

Figure #11

TCE Concentration at Well

$AK_2=.01$ & $EF/FM/FIM=.5$ Cases

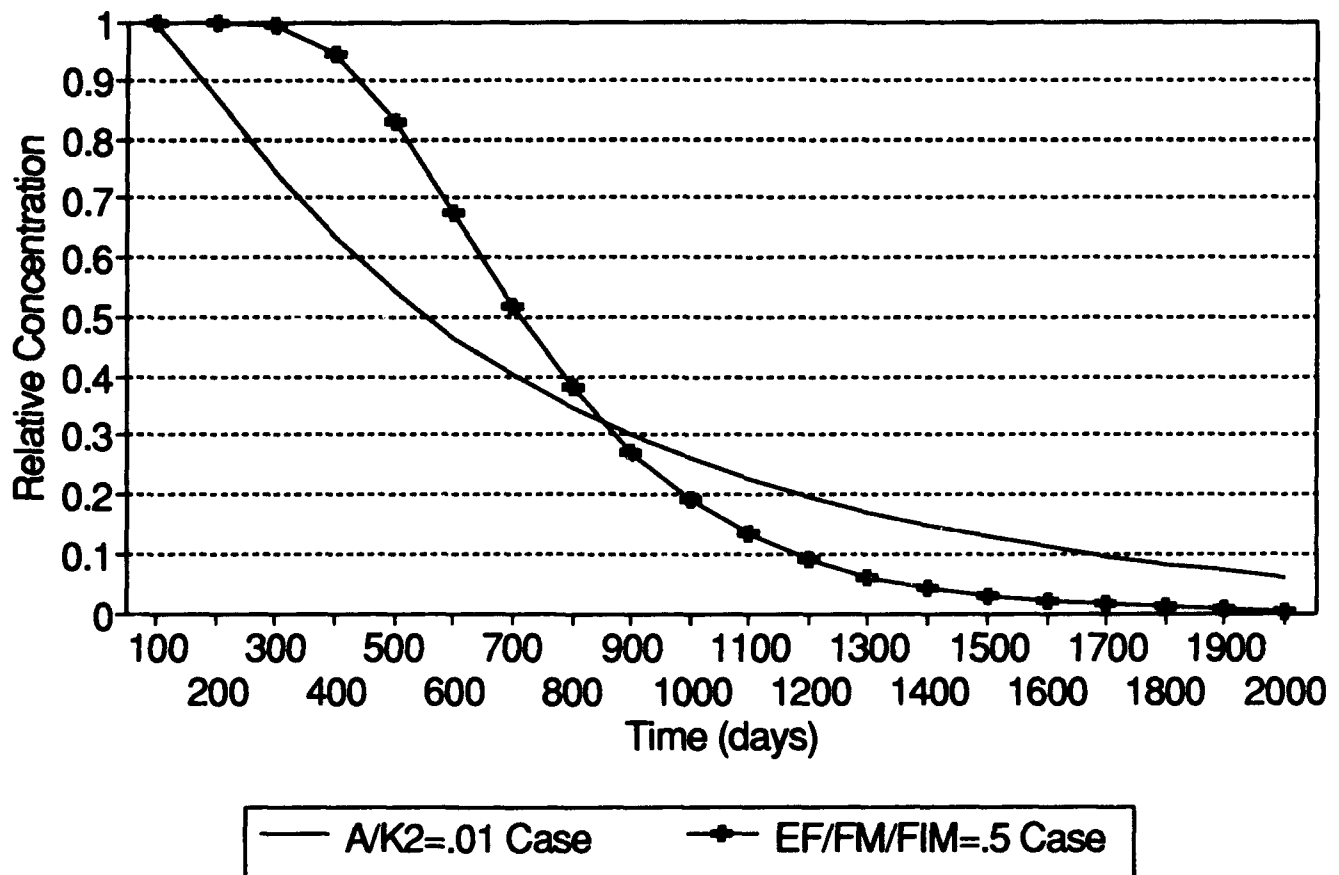
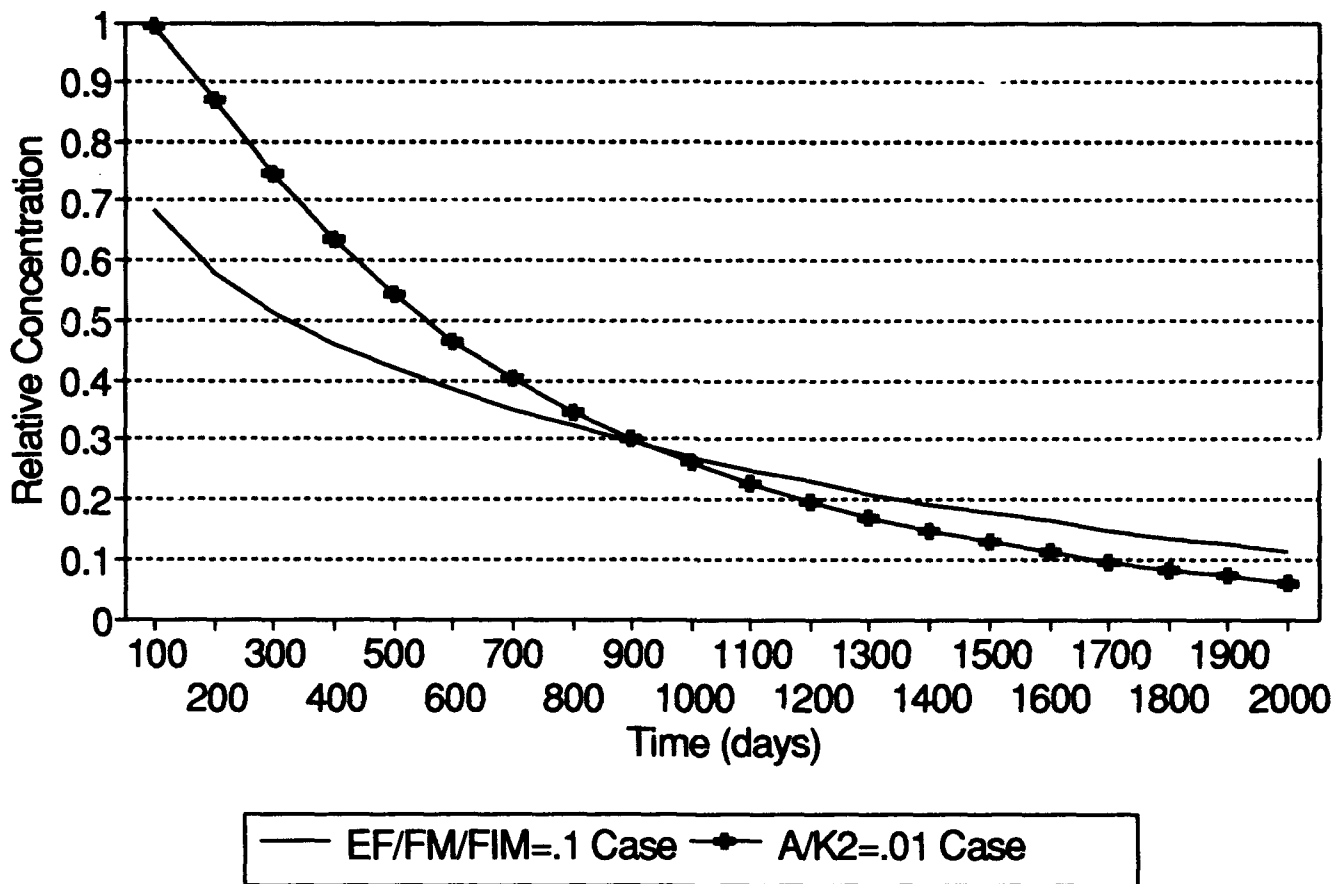


Figure #12

TCE Concentration at Well

EF/FM/FIM=.1 & A/K2=.01 Cases



shows the effects of increased slow sorption, as the curve clearly exhibits more extensive tailing. This tailing is still severe at the end point of the simulation, where, after 2000 days of simulated remediation, the relative concentration has dropped to only .11 and the slow sorption mechanism tenaciously retains the TCE in the soil.

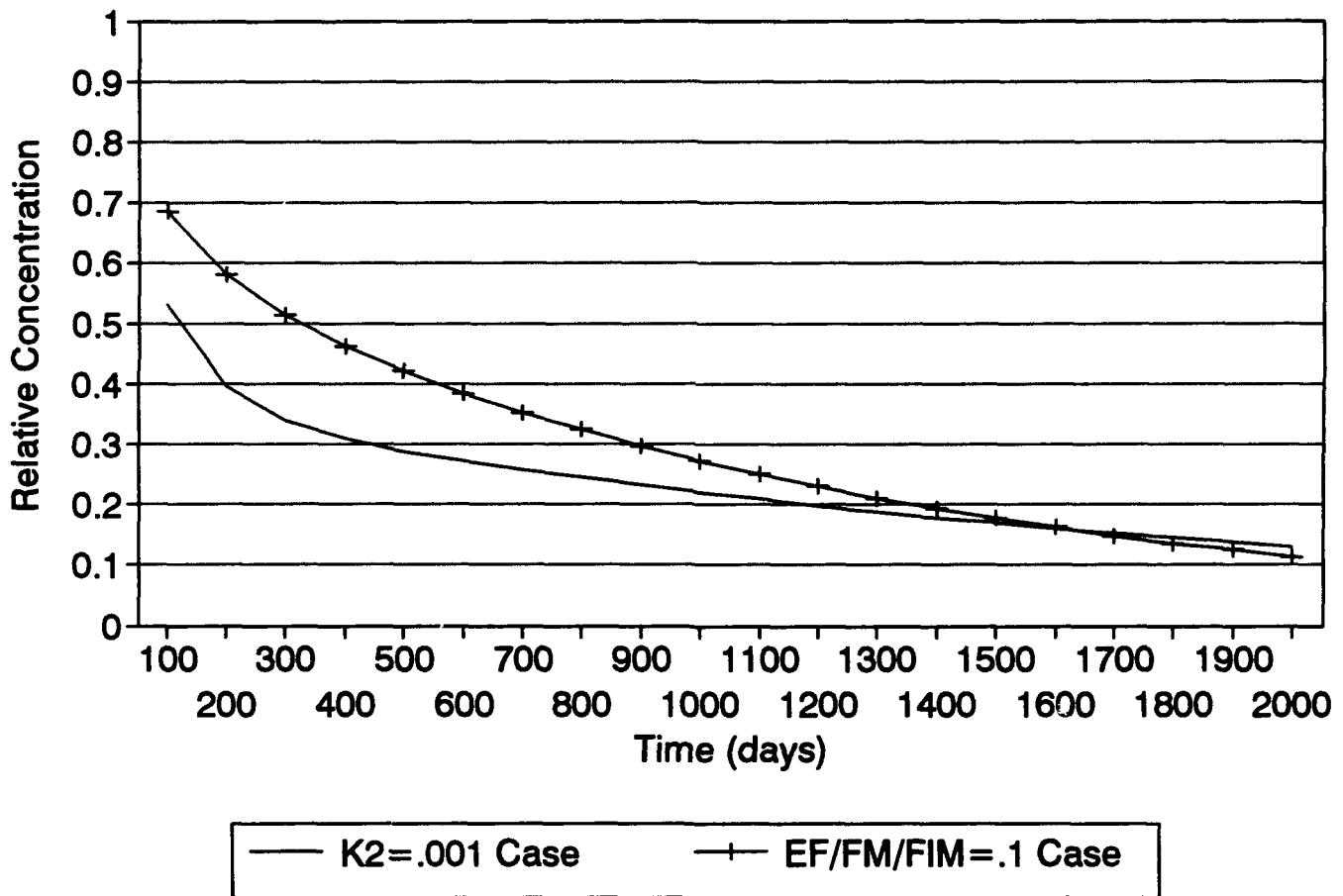
One final TCE simulation was conducted to further examine the impact of slow sorption on soil vapor extraction. Since contaminant desorption is one of the major controlling mechanisms of the remediation process, it stands to reason that lowering K_2 , the desorption rate constant, to an extreme value should serve to increase the effects of the slow sorption process. All parameter values remain unchanged for this simulation, except for K_2 which has been lowered to .001. The output produced is displayed in Figure #13 and, as expected, the graphic representation of the slow sorption effects are even more pronounced. The breakthrough is earlier, and the tailing is more pronounced. After 2000 days, approximately 5.5 years of continuous simulated remediation, the relative concentration remains at approximately .13.

It would appear, at least in the case of TCE, that the SVE Model has performed almost exactly as one would expect, based on current laboratory and field studies, and appears to successfully incorporate the effects of the slow sorption mechanism in its simulations. In addition the model has demonstrated the manner in which the slow sorption mechanism

Figure #13

TCE Concentration at Well

$K_2 = .001$ & $EF/FM/FIM = .1$ Cases



may impact TCE vapor extraction remediation efforts. Of particular interest are the tailing effects, indicating a sorbed contaminant that will not be easily remediated or removed by vapor extraction techniques.

Quantification of Tailing

For this document, it was desired to attempt to quantify the extent of tailing apparent in the individual TCE output graphs. It was felt that this measurement might provide an indication of the degree of slow sorption reflected in the output. Obviously, the more tailing displayed, the greater the effects of slow sorption in that simulation. In order to accomplish this, a rudimentary "tailing measurement" was developed for employment in the preceding graphical outputs. Each TCE output curve was traced from its origin to the point of ".5 relative concentration." This trace was then inverted and inserted into the output graph, beginning at the reference point of ".5 relative concentration." (see Figure #14) The difference between the trace curve, from the point .5 and beyond, and the actual model output curve was determined to be a measure of the lack of symmetry or "skewness" of the output curve. This skewness, in turn, is felt to be a measure of the degree of "tailing" present in the output. The difference between the two curves was quantified in terms of area, or cm^2 . Employing this system, the results displayed in Table #3 were derived.

Figure #14

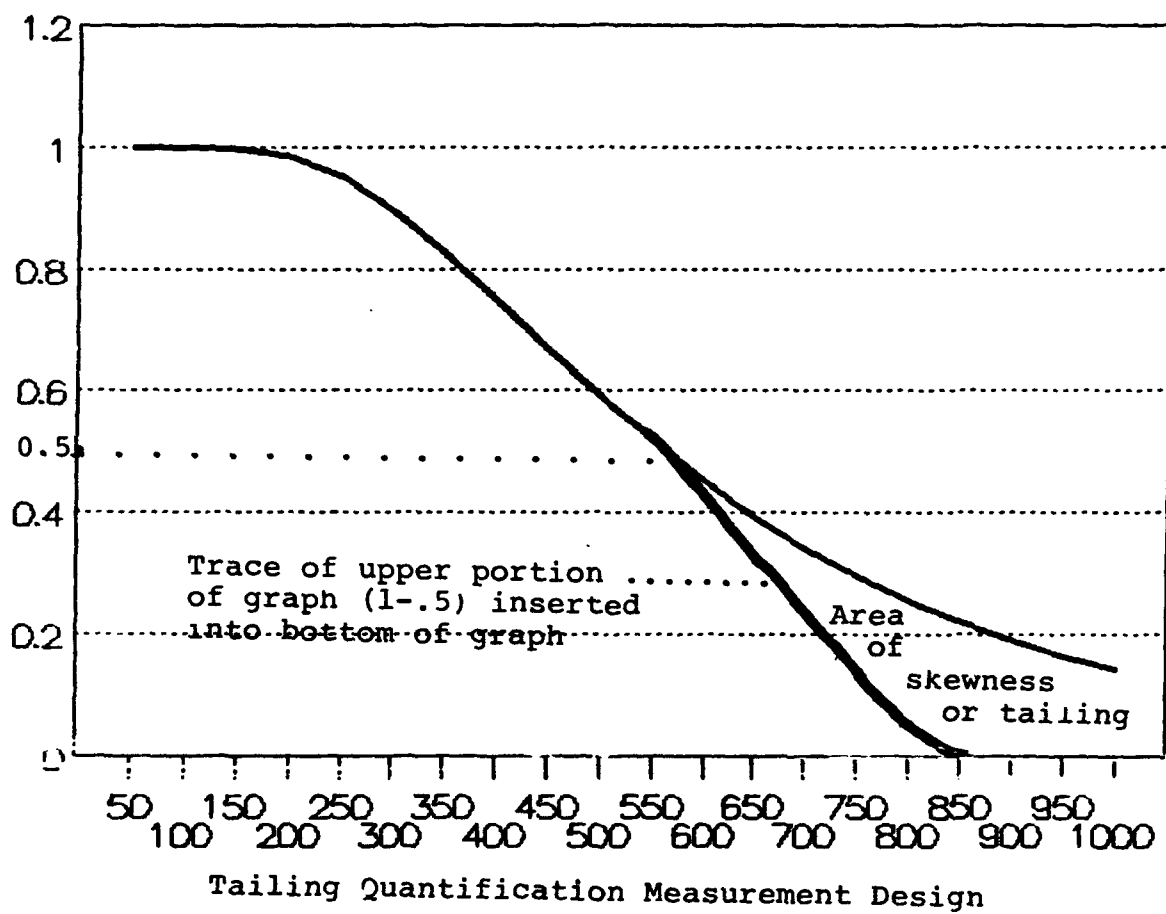


Table #3

<u>Figure #</u>	<u>Key Variable</u>	<u>Tailing Measurement</u>
7	TCE Equilibrium	17.5
8	PW=.2/PWG=.15	26.25
9	EF/FM/FIM=.5	26.25
10	A/K2=.01	85
11	EF/FM/FIM=.1	150
12	K2=.001	177.5

These quantification measurements support the conclusions derived from a study of the graphical outputs. The addition of water in the void spaces appears to retard the contaminant transport to the degree that some minor increase in tailing is generated. No significant increase in tailing is apparent until the Alfa and K2 values are reduced to relatively "slow" values. Of particular interest is the fact that a reduction in EF/FM/FIM from .5-.1 almost doubled the amount of tailing present in the output graphs. This is indicative of the real "danger" of the slow sorption mechanism. In theory, the longer the organic contaminant remains in the unsaturated zone soils the greater the percentage that is controlled by slow sorption and entrapped in the nonadvective domain. This correlates to lower values for EF/FM/FIM in the input values of this computer model. It is clear from Table #3 that long-term contamination, coupled with "low" Alfa and K2 values, could easily lead to a remediation situation which is hampered by severe slow sorption tailing.

Benzene Modeling

The entire modeling process just presented for TCE was conducted a second time with benzene as the contaminant of concern. The input values and ranges for the benzene simulations are displayed in Table #4. Of particular interest in this table are the chemical specific values of KH and KM/KIM. The SVE Computer Model used these benzene

TABLE #4

INPUT VARIABLES

QW=Pumping Rate=1000 [m**3/day]
 B=Aquifer Thickness=20 [m]
 D=Dispersion Coefficient=5 [m**2/day]
 PORGAS=Gas-Filled Porosity=.15
 PORW=Water Filled Porosity of Nonadvective Domain=0-.2
 PORWG=Water Filled Porosity of Advective Domain=0-.15
 RHO=Soil Bulk Density=1.76 [gm/cm**3]
 KH=Henry's Constant=.24 [dimensionless]
 RW=Well Radius=.01 [m]
 RSTAR=Radius of Contaminated Area=40 [m]
 TINIT=Starting Time=0 [days]
 DELTT=Time Step=100 [days]
 TFIN=Final Time=2000 [days]
 KM=Equil Dist Coef for Adv Domain=.83 [cm**3/gm]
 KIM=Equil Dist Coef for NonAdv Domain=.83 [cm**3/gm]
 Alpha=First Order Rate Constants Describing Mass Transfer
 Between Adv and NonAdv Domains=100-.01 [/h]
 EF=Fraction of Sorbent Assoc with Adv Domain=.9999-.1
 FM=Fract of Sorbent in the Adv Domain for which Sorption
 is Instantaneous=.9999-.1
 FIM=Fract of Sorbent in the NonAdv Domain for which
 Sorption is Instantaneous=.9999-.1
 K2=First Order Desorption Rate Constant=10-.001 [/h]

default parameters for the same specific simulations as TCE in order to see if the same patterns of contaminant transport would appear for a different organic contaminant.

Figure #15 displays the original TCE equilibrium output with the benzene equilibrium curve. A comparison of the output curves reveals that the benzene equilibrium output displays an earlier initial breakthrough and an earlier drop to "0" relative concentration. This is probably attributable to the fact that benzene possesses a substantially lower KM and KIM (.83 [cm**3/gm], almost 50% lower) than TCE. These lower values translate to a lower retardation factor and less sorption affecting the benzene during remediation attempts, thus the quicker breakthrough and extraction. This "quicker" curve, as compared with the TCE outputs, is a characteristic of most of the benzene outputs throughout the entire modeling process.

Outputs for the next several iterations of the benzene modeling process are displayed in Figure #16. As with the TCE simulations, the introduction of water in the void spaces served to slow contaminant transport. As was also noted earlier, the slow sorption mechanism, with its tailing effect, did not become noticeable until the ALFA and K2 values were reduced.

When the input values for EF, FM and FIM were lowered to .1 the resulting output (Figure #17) was produced for benzene. This output curve is displayed with the TCE output

Figure #15

Contaminant Conc at Well

BZ Equil & TCE Equil Cases

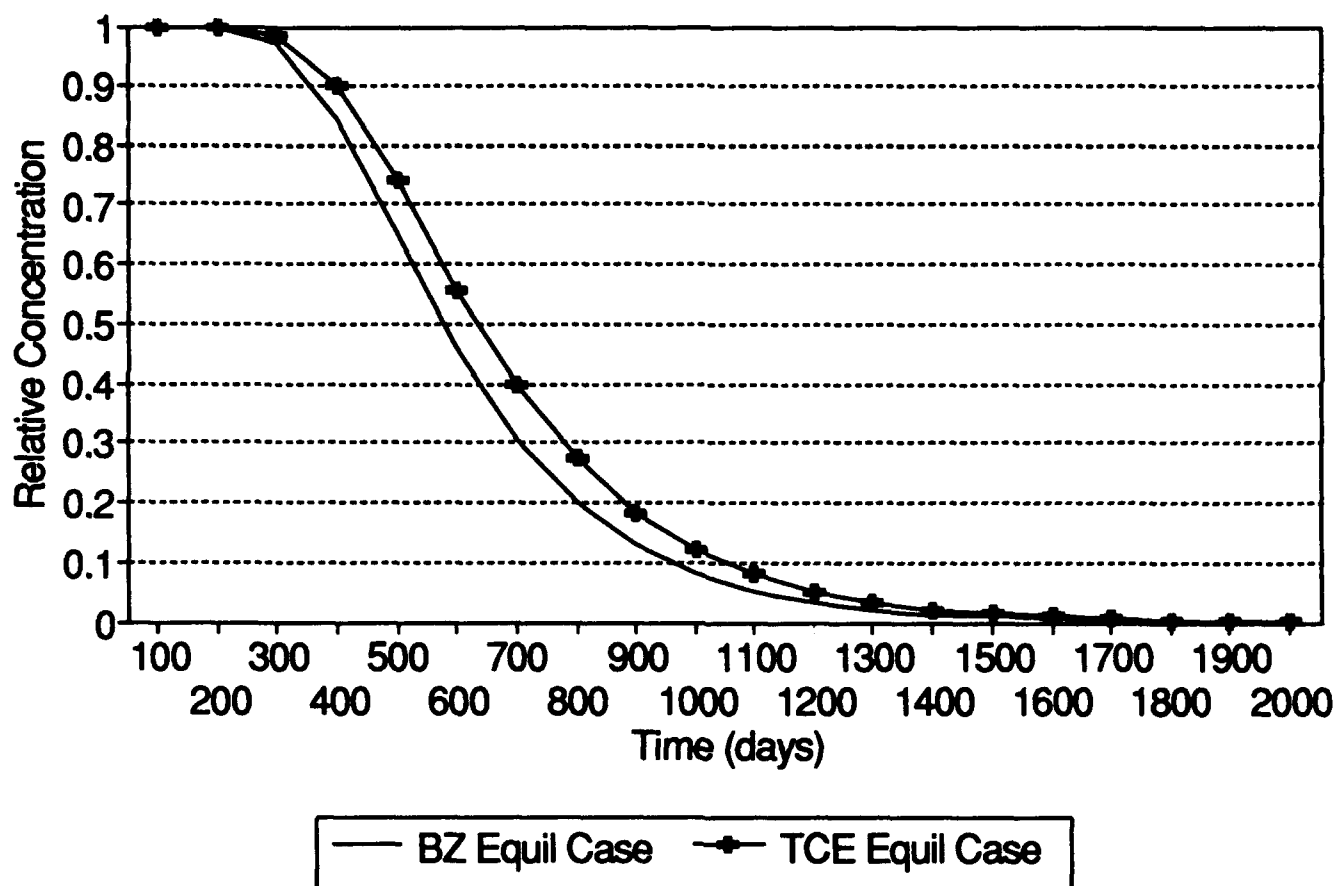
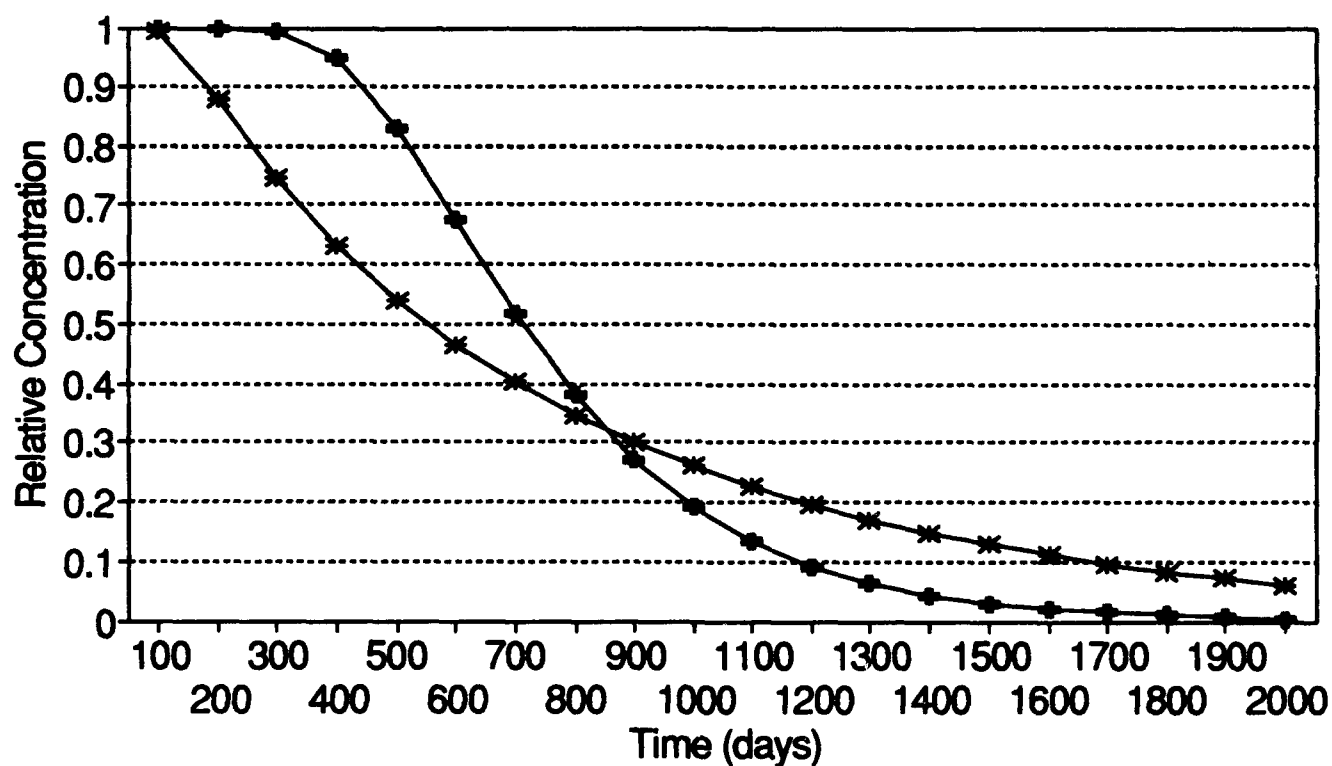


Figure #16

BZ Concentration at Well

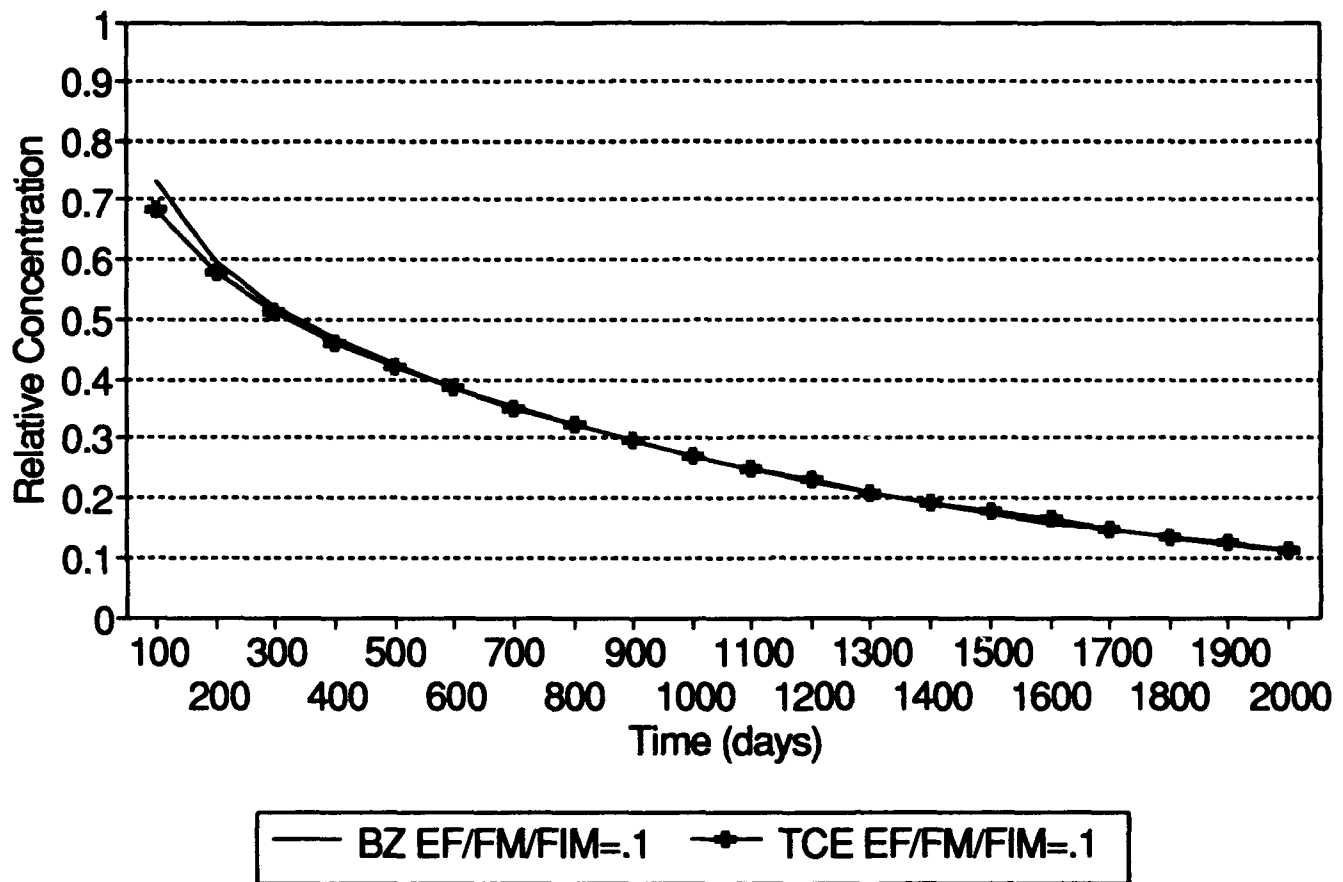
PW/PWG & EF=.5 & AK2=.01 Cases



— PW=.2/PWG=.15 Cas —◆— EF/FM/FIM=.5 Case —*— AK2=.01 Case

Figure #17

Contaminant Conc at Well BZ & TCE EF/FM/FIM=.1 Cases



resulting from identical default parameters. It is interesting to note in this graph that although TCE and benzene possess substantially different equilibrium distribution coefficients, K_M/K_{IM} , the slow sorption mechanism at this point has appeared to minimize this difference, obvious in earlier outputs, to produce the same output graphs with severe tailing for both of these contaminants.

One final iteration was performed in this benzene modeling process. In an effort to examine just how extensive the tailing effect of the slow sorption mechanism really was, the worst case simulation, $K_2 = .001$, was programmed to run for 4000 days. The result is displayed in Figure #18. The output graph reveals that the slow sorption bonding is so tenacious that, in the case of benzene, after 4000 days of simulated vapor extraction remediation, almost 11 years, approximately 1/2 of 1% of the original level of contaminant remains in the soil.

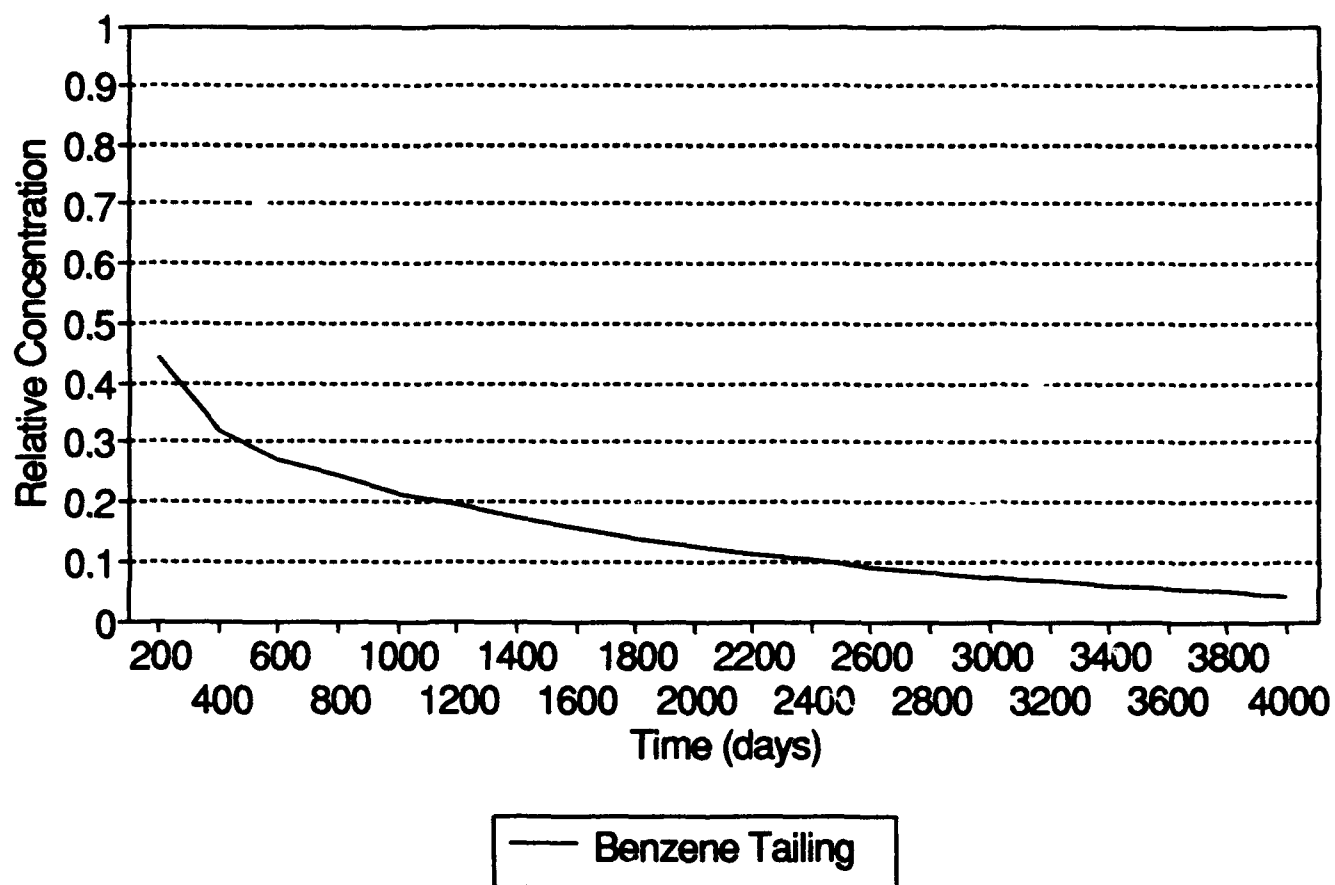
Worst Case Scenario

For the purpose of examining the role played by the chemical specific values of the Henry's Constant and sorption coefficient, K_D , one final simulation was conducted in this SVE Model analysis. In this final iteration, a "hypothetical" contaminant was devised with an extremely low Henry's Constant (.1), making this substance less volatile, and a "high" sorption coefficient ($2.5 \text{ [cm}^3/\text{gm}]$), making

Figure #18

Benzene Conc at Well

Benzene Tailing Case



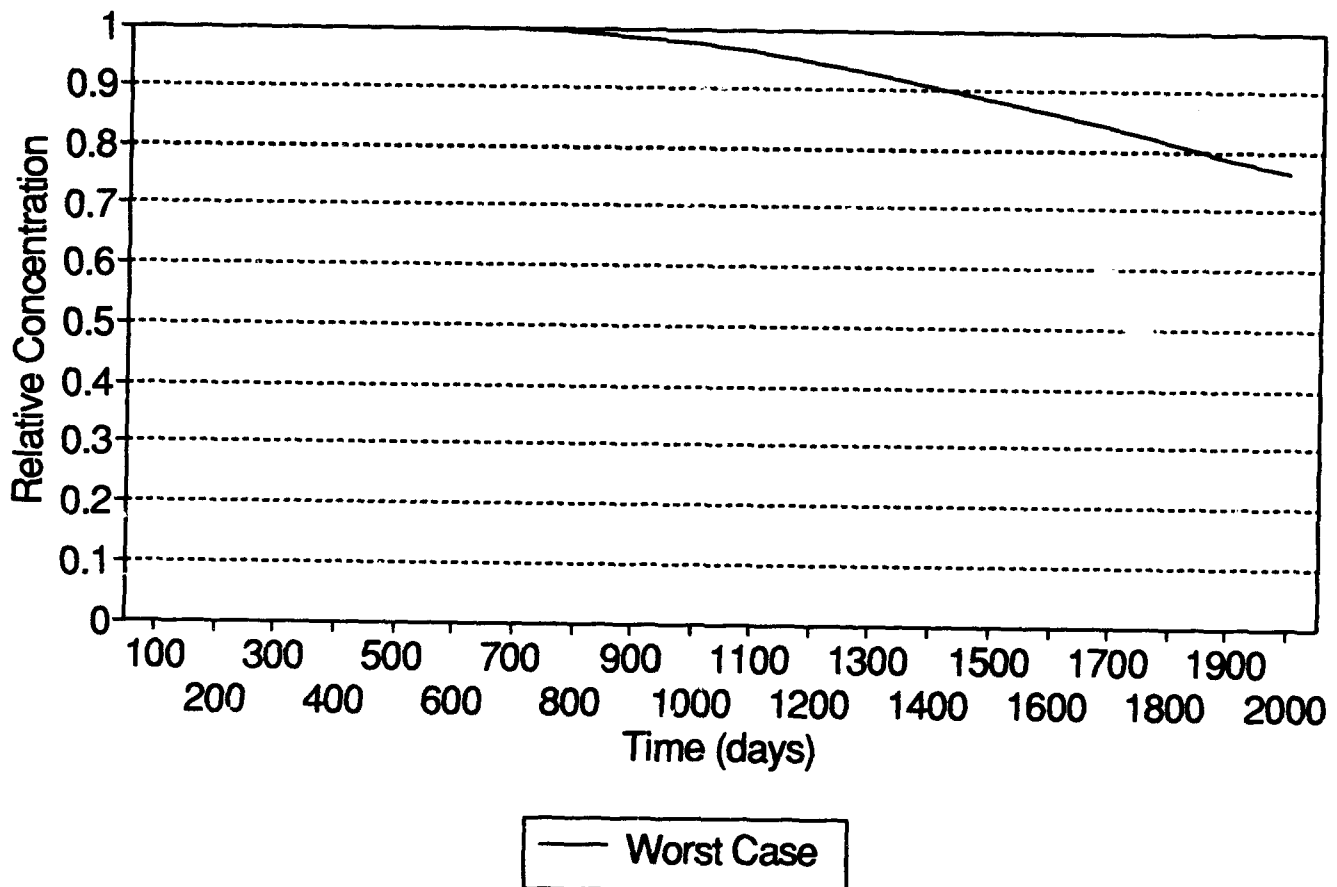
it extremely susceptible to slow sorption. Both of these factors should serve to make this hypothetical organic substance resistant to vapor extraction remediation. To ensure that the slow sorption effects would be visible in the output, Alpha and K2 were assigned the relatively low value of .01 [/h]. Finally, for this simulation, EF, FM, and FIM were assigned a "moderate" value of .5. The combined effect of the low Henry's Constant coupled with the high sorption coefficient is immediately obvious in the output, Figure #19. The bulk of the hypothetical organic substance remains in the soil following 2000 days of simulated vapor extraction. In fact, at the 2000 day point, 5.5 years of simulated remediation, relative concentration remains stubbornly at almost .75. This would appear to be clear evidence of the critical importance and impact of both KH and KD in vapor extraction remediation operations.

CONCLUSIONS

The outputs provided by the model in these simulations appeared to qualitatively be in accord with the data previously gained through laboratory studies and practical experience. The model, if indeed accurate, provided further insight into the slow sorption mechanism and its effects on organic vapor extraction remediation attempts. The model clearly demonstrated the importance of the variables Alpha and K2, the first order rate constant describing mass transfer between advective and non-advective domains and the

Figure #19

Concentration at Well Worst Case Scenario



first order desorption rate constant. High values of these parameters allowed for equilibrium sorption. Scenarios in which half of the overall contaminant was trapped in the nonadvective domain were rapidly remediated so long as Alpha and K2 values were high. High, or "fast," values for Alpha and K2, approximately 10 [1/h] and higher, allow the contaminant molecules to rapidly transfer from the nonadvective to advective domain for vapor extraction and permit rapid desorption from the soil particles. The combination of these two factors appears, in the preceding simulations, to minimize slow sorption effects and permit almost equilibrium sorption/desorption. However, the model also revealed that the effects of the slow sorption mechanism must not be misunderstood or disregarded. The SVE Model clearly demonstrated that under certain circumstances even moderate amounts of contaminant trapped in the nonadvective domain (amounts which have been documented in field studies cited at the beginning of this thesis) may demand years of continuous vapor extraction remediation in order to accomplish complete removal. Finally, the model demonstrates the critical impact of the chemical properties of the actual contaminants. It was clearly shown that values such as Henry's Constants and Sorption Coefficients play a crucial role in determining the applicability of vapor extraction. From this rudimentary, basic analysis, the SVE Computer Model appears to be a viable vapor extraction modeling tool, worthy of more detailed follow-on

study and consideration. Its incorporation of the slow sorption mechanism makes it a useful tool to help understand the effects of this mechanism on vadose zone remediation efforts.

V. ALTERNATIVES TO THE PURGE AND TRAP TECHNIQUE

Introduction

In Chapter 2 several alternatives to the purge and trap measurement technique were presented and briefly discussed. The purpose of this chapter to examine those alternatives which appear to possess the greatest potential and warrant further attention. It is desired that this discussion will provide the reader with a clearer understanding of both the current status of the measurement of volatile organic compounds (VOCs) in long contaminated vadose zone soils and also the directions researchers may take in the future in order to provide a comprehensive solution to the measurement problem. The alternatives that will be examined in detail are: (1) Methanol Extraction- the current state-of-the-art purge and trap modification. (2) Supercritical Fluid Extraction- An emerging technology with an inherent deficiency for the measurement of VOCs, and (3) A less conventional technique utilizing laser optics and developed during the research for this thesis.

Methanol Extraction

In Chapter 2 of this document, there was a brief discussion of the methanol extraction technique, primarily a modification of the standard purge and trap procedure in which a methanol slurry is utilized to enhance the extraction of sorbed organics (2:150) (15:276). The

American Petroleum Institute (API), one of the pioneers in this technology, recently produced a technical publication describing this method and outlining its advantages. One inherent advantage of methanol as an extraction medium is the fact that the methanol breaks down the soil sample exposing more of the pore spaces for subsequent extraction (16:420). Roger Class, one of the developers of the methanol extraction technique at API, explains that the term "methanol extraction" really encompasses a number of different methodologies. According to Mr Class, API has developed three basic procedures employing methanol and its derivatives as an extraction agent: one for "gas range organics," another for "diesel range organics," and still a third procedure for the recovery of petroleum hydrocarbons (25). Each of these methods possesses a unique set of procedures and requirements, dependent upon the specific contaminant of concern. For instance, in the case of contamination by diesel range pollutants, API suggests the utilization of a methyl chloride agent, vice the standard methanol. Mr Class further explains that the increased recovery of sorbed organic contaminants from soil samples was basically a secondary effect and not the primary reason for API's developmental work with methanol extraction. Their primary aim was to reduce the loss of organic contaminant molecules from the soil sample through volatilization/evaporation during handling at the laboratory, prior to measurement and quantification. To

this end, the addition of methanol to a soil sample, if accomplished at the field site immediately after removal, is, they feel, a successful solution to this volatilization/evaporation problem. However, Class agrees with the many other researchers who concede that no methodology currently exists that can extract 100% of sorbed volatile organic contaminants from a soil sample. He feels that the methanol extracts more of the sorbed organics than the standard purge and trap technique, but that sorption binding will certainly retain some of the contaminant within the soil matrix (25). In fact, a validation study is currently underway at API to determine the percentage of sorbed contaminants that can be consistently removed by methanol extraction. Class agrees with a number of other researchers when he states that purge and trap with methanol extraction is the best soil analysis tool currently available to investigators, and is certainly the best method for determining "the total number of petroleum hydrocarbons in the ground" (25).

Conclusion. Purge and trap with methanol extraction does not appear to be the ultimate solution to the sorbed organic contaminant measurement problem. Although it has shown itself in studies to be a significant improvement over the standard purge and trap technique (2:150), no one claims that it approaches 100% of sorbed organic contaminant extraction. However, there is what appears to be a growing consensus among researchers that purge and trap modified

with methanol extraction is the best analytical tool for the measurement of volatile organics in soils currently available to investigators. Perhaps this is what is most important. With no complete solution yet developed, remediators should utilize the most reliable tool available, and, in this case, it appears to be the methanol extraction technique.

In addition, previously in Chapter 2, it was noted that soil pulverization has shown in laboratory tests that it might enhance the extraction capability of the standard purge and trap procedure (4:1234). In an effort to maximize sorbed volatile organic removal from soil samples, it might behoove researchers to experiment with methanol extraction enhanced with soil pulverization. The combination of these two procedures may very well increase the overall recovery of the sorbed contaminants.

Supercritical Fluid Extraction

In the Literature Review, the emerging field of Supercritical Fluid Extraction (SFE) was briefly introduced. The Supercritical Fluids (SCFs) with their low viscosities and high dissolving power appeared to have real potential as a viable alternative to purge and trap measurement. However, further investigation revealed that current SFE technology possesses an inherent flaw for the comprehensive measurement of volatile organic compounds.

Two manufacturers which are at the forefront of SFE

technology development are the Suprex Corporation of Pittsburgh, PA, and Isco Inc., of Lincoln, NE. These two firms market what are currently considered state-of-the-art automated SFE laboratory analysis systems, the AutoPrep 44 and the SFX 3560, respectively (26:776). However, discussions with representatives from these two firms quickly reveal the shortcomings of the SFE process in terms of the extraction and measurement of volatile organic compounds (VOCs), such as TCE and benzene. It would appear that, for measurement purposes, the volatile organics are too soluble in the SCFs and can not, as of now, be completely separated from the supercritical fluid after extraction from the soil particle. As Lori Dolata of Suprex explains, after the supercritical carbon dioxide (SCCO₂) has been purged through the soil sample in liquid form and the targeted organic pollutant has been extracted from the soil, the contaminant must then be separated from the supercritical fluid for precise measurement. Normally this is accomplished by passing the SCF, still in liquid state, through some form of chemical trap, such as liquid methanol, designed to remove the organic. Following this, the SCCO₂ is released from the trap in gaseous form, leaving behind the contaminant in the chemical trap, ready for follow-on measurement and quantification. However, in the case of VOCs, the highly volatile nature of these compounds frustrates this trap system, and some portion of the contaminant resists separation and remains dissolved in the

SCCO₂, subsequently escaping in vapor form. (19) (21)

Suprex has attacked this problem in their AutoPrep 44 with the utilization of cryogenic technology that can cool their liquid trap down to -60° C in an attempt to retrieve as much of the volatile contaminant from the SCF as possible.

However, Ms Dolata admits that the current system does not accomplish 100% removal of all the VOC from the supercritical fluid, and states that research is still being conducted into a method to "optimize" VOC recovery in their SFE system. Dr. Joe Tehrani, the SFX 3560 product manager for Isco, admits that their system currently does not possess a cryogenic trap for volatiles, and that because of this the SFX 3560 "can not presently replace the purge and trap system for volatile organic compounds" (19). However, Dr Tehrani added that he is currently developing an automated cryogenic system that will utilize a super cold bubble of chilled methanol and, he believes, will eventually render their system more effective for the measurement and analysis of VOCs (19). According to Lori Dolata, no SFE system has yet been developed that is 100% effective when targeted against soil samples contaminated with volatile organics. However, both she and Dr Tehrani agree that these systems are completely and comprehensively effective in the extraction and measurement of less difficult semi-volatile organics, such as naphthalene. (19) (21)

Conclusion. It would appear that, at present, supercritical fluid extraction is not the ultimate solution

to the problem of the complete extraction and measurement of volatile organic contaminants in soil samples suffering from long-term contamination. Like many others, researchers at the Center for Risk Management at the Oak Ridge National Laboratory believe that SFE possesses potential application in this field and deserves further attention, but they also believe that the system to extract and recover 100% of the VOCs from soil samples has yet to be fully developed (27). Perhaps this is because the answer to this dilemma lies outside the sphere of conventional chemical measurement and analysis techniques. The next section of this document will propose a possible solution, derived from the field of laser physics.

THE LASER ALTERNATIVE

Unless otherwise footnoted, the information presented in the following section was derived from discussions with Major Glen Perram of the Air Force Institute of Technology.

In Chapter 2 the discussion of the use of lasers in soil sample analysis centered around the technique of laser ablation, or "vaporization," of a portion of the sample undergoing analysis. During research, however, it was discovered that vaporization of the soil sample would also destroy the molecular structure of the VOCs making accurate measurement and quantification most difficult. What is presented in the following section is a similar laser analysis technique, basically a derivative of the "ablation

method," utilizing the same energy transference capabilities of laser light and the use of optical spectroscopy for contaminant measurement.

Introduction. During the course of the research and analysis of the purge and trap measurement system and its possible alternatives, it became apparent that high-energy laser beams and the field of optoelectronics may possess some potential application in solving this measurement problem. This realization was initially based upon a thorough understanding of the soil, the organic contaminant, and their chemical interaction. The slow sorption effect is a consequence of the hydrophobic partitioning of the organic contaminant. This partitioning causes the pollutant to retreat from the moisture present in the soil pore spaces and partition into the organic material adhering to the soil particles. This strong mutual attraction, between the two organics, almost resembles a chemical bond, either an instantaneous "equilibrium bond" or the stronger "rate limiting bond", or attraction, which occurs over a longer period of time. In addition, both of these attraction mechanisms can take place on either the surface of the soil particle, or deep within the soil micropores, as the contaminant continues to recede over a long period of time and retreat from the moisture of the soil void spaces. However, it must be noted that this "sorbent" partitioning which adheres the contaminant to the soil is much weaker than the internal molecular bond of the organic compound.

This realization has led researchers to construct several different techniques in an attempt to break the "weak" sorbent bond and volatilize the contaminant from the soil for measurement. Many of these attempts have been based upon the idea of using heat as the energy source (2:150-151). The underlying concept of this technique is that if enough energy can be transferred to the soil sample through the increase in temperature, the sorbent bond will eventually break and the contaminant will volatilize into a solution for subsequent measuring. However this method, although sound in theory, has encountered practical difficulties. Results indicate that by the time enough energy has been transferred to the soil, via the slow heating process, to break the sorbent bond, the organic pollutant has absorbed so much heat energy that it volatilizes, as desired, but then rapidly decomposes before it can be measured (2:150-151).

However, laser light possesses physical characteristics that would seem to make it ideal for overcoming the difficulties just described. A concentrated high-energy laser beam is capable of transferring a large amount of energy to a soil sample in a period of nanoseconds, almost instantaneously. In addition, through the use of optical spectroscopy, it is possible to measure the desorbing contaminant in the span of microseconds. This means that the entire process, from the energization of the soil, to volatilization, to the measurement of the contaminant, could

be completed in less than one second. The extremely "fast" nature of this process would seem to ensure that the contaminant could be measured prior to any decomposition. In addition, the almost instantaneous energization of the soil should, theoretically, allow for a clear break of the weak sorbent bond and contaminant volatilization prior to the incidental transfer of enough energy to the actual contaminant molecule to precipitate subsequent decomposition. Unlike the heating of a soil sample in a furnace, the utilization of precision lasers allows an experimenter to precisely control the amount of energy that is ultimately transferred to the sample undergoing analysis. With this in mind, it should be hypothetically possible to eventually calibrate a laser source to contain enough energy to break the sorbent bonds of a soil sample and effect contaminant volatilization, without releasing the energy required to generate molecular decomposition. Finally, it has been shown through experimental research, that it is possible to "vaporize" a solid sample with a pulsed laser source leaving entirely intact the molecules of a specific compound contained within the sample. This is done by varying the wavelength of the laser light utilized to a value which is "friendly" or resistant to the destruction of the specific substance desired to remain intact. Armed with this knowledge, any diagnostic tool utilizing lasers and designed to conduct soil contamination analysis, should possess a pulsed source using light of a wavelength which

has been found to be resistant to the destruction of the contaminant in question.

One final advantage gained through the utilization of lasers as an energy source will be discussed. One inherent weakness of the purge and trap and methanol extraction techniques previously discussed in this document is that neither of the extraction mediums, nitrogen or methanol, are able to adequately penetrate the interior of the soil matrix to volatilize and remove the bulk of the long-term contamination. This deficiency may be overcome through the use of laser light as an extraction medium. The high energy contained in the impacting laser beam will be distributed to the whole of the target soil particle, thereby breaking all sorbent bonds and releasing the bulk of the contaminant for follow-on optical measurement.

The Alternative. Based upon the preceding discussion, the following laser measurement tool has been designed for use in the analysis of vadose zone soils possessing long-term volatile organic contamination. In the simplest terms, the arrangement operates in the following manner. A thin layer of substrate, or soil to be analyzed, is spread and held in place by a reflective filter. The soil is then illuminated by a high-energy pulsed laser. This is the beam which transfers energy to the soil and breaks the organic attraction. Experimentation will be required to determine the amount of energy necessary to sufficiently ensure the destruction of all the hydrophobic partitioning and to also

calculate the optimal wavelength for this pulsed laser light. As mentioned earlier in this section, this wavelength will be chosen so the molecules of the contaminant undergoing extraction are not destroyed. In theory, this energization of the soil sample should break the "rate-limited" organic attraction, or "bonds" and subsequently volatilize and release the contaminant from the soil matrix.

Immediately following the illumination of the sample by the pulsed laser and during the subsequent contaminant release, the soil will again be illuminated, this time by a light source designed to conduct optical spectroscopy measurement. This light might also originate from a laser source, either in the visible light or infrared spectrum. The wavelength of this light will also be predetermined, based upon the light cross-absorption spectrum of the contaminant undergoing analysis. All chemical compounds have an associated light cross-absorption spectrum which indicates the specific wavelength of light most completely absorbed by that molecular structure. This principle, and the resulting light absorption, are the foundation of optical spectroscopy. Therefore, in this case, the analyzed soil will be illuminated with a light beam of a wavelength that will be absorbed by the suspected contaminant during the desorption. A measurement of the amount of light absorbed by the volatilizing contaminant, coupled with a working knowledge of Beer's Law, allow for the calculation

of the amount and concentration of the contaminant originally in the soil. However, care must be taken at this point of the process to ensure that the spectroscopic measurements include only the light absorbed by the desired organic pollutant and not the light absorption of other substances with similar cross-absorption spectrums incidentally vaporized by the soil energization process. However, this confounding effect can be hopefully avoided if the contaminant in question possesses a unique cross-absorption spectrum, not shared with any of the other substances present in the soil sample.

Conclusion. The laser analysis process just described currently exists in theory only. It has yet to undergo any practical experimentation or study. However, the theory it was derived from is sound, and based upon the results of previous experimentation and proven principles. All of this seems to indicate that this laser soil analysis process, if properly constructed, would possess a strong chance of successful operation. It has already been pointed out how the utilization of lasers can overcome many of the obstacles associated with current, conventional unsaturated zone analysis techniques and provide what might be a truly comprehensive measurement method of the "slowly-sorbed" organic compounds in long-term contaminated soils. This fact, coupled with the knowledge that the laser analysis technique is founded upon sound scientific theory, would appear to warrant further investigation of this method.

VI. Conclusions and Recommendations

Purge and Trap Alternatives

Conclusions. The recently identified slow sorption mechanism appears to have a clear, detrimental impact on the standard EPA-approved "purge and trap" measurement of vadose zone soils suffering from long term contamination by volatile organic compounds (VOCs). This conclusion is supported both theoretically, by a scientific understanding of the mechanism and effects of slow sorption, and by experimental data derived from actual vadose zone soils. Over a period of time, slow sorption appears to entrap VOCs in the interior of the soil matrix, rendering these compounds impervious to the air mobilization and volatilization by the bubbling gases of the purge and trap technique. This deficiency is critical due to the fact that it causes purge and trap measurement to significantly, in some cases, underestimate the total contamination present in soils suffering from long term contamination. In these cases, soils, when checked with the purge and trap system, may appear "clean" or successfully remediated, when, in fact, these soils are still suffering from a serious level of contamination that may reemerge from the soil matrices in the years to come.

In an attempt to find a suitable alternative to the purge and trap system a number of alternatives and modifications have been developed or proposed. Of these

modifications, the utilization of methanol extraction to enhance the standard purge and trap technique appears to provide the most accurate measurement means available at this moment. The use of a methanol slurry as an extraction agent has been shown in laboratory studies to enhance the ability of purge and trap to extract slowly sorbed contaminants within the interior of the soil matrix. However, other researchers have shown that this method, even with the improvements generated by the addition of the methanol, is still not comprehensive and can underestimate total contamination, in some cases, by as much as 60%. Even with this deficiency, however, the purge and trap technique with methanol extraction appears to provide the most reliable measurement of contaminants in soils suffering from long term contamination by VOCs.

A number of emerging technologies may eventually be capable of solving this vadose zone soil contamination measurement problem. Supercritical Fluid Extraction (SFE) is one of the technologies which possesses potential application in this area and has generated recent interest. Supercritical Fluids (SCF) possess the ability to penetrate the micropores and interior of the soil matrix, due to their extremely low viscosities, and also have high dissolving powers and can consequently extract the sorbed contaminants present in these spaces. However, the high dissolving powers of SCFs appear to be also their shortcoming in regards to the measurement of VOCs. Although it is

generally accepted that SFE can successfully remove 100% of semi-volatile contaminants for subsequent measurement, there are, at present, difficulties in separating all of the dissolved VOCs from the SCF following extraction from the soil sample. This shortcoming renders SCF currently unable to accomplish the comprehensive measurement of VOCs in long contaminated soils. However, developments are ongoing that may eventually overcome this obstacle.

Another alternative to the purge and trap technique which has been developed for this thesis is based upon the utilization of electro-optics, specifically lasers. Theoretically, it appears that the use of high energy pulsed lasers and measurement by optical spectroscopy may circumvent many of the deficiencies and shortcomings which currently degrade purge and trap and its present derivations. This laser alternative has been reviewed and appears fully capable, in theory, of performing the comprehensive measurement of long contaminated soils.

Recommendations. Based upon the information previously presented in this thesis, the following recommendations are submitted concerning the purge and trap measurement technique and its alternatives.

1. That remediators and investigators at DOD IRP sites suffering from long term contamination by volatile organic compounds be made aware of the possible limitations of the purge and trap measurement technique. At present, the purge and trap technique remains the EPA method-of-choice for the

measurement of organic contamination in unsaturated zone soils. Data and studies presented in this thesis have shown that the purge and trap method can, in some cases, significantly underestimate the total amount of pollution present in soils suffering from long term contamination. This underestimation can lead to still polluted soils appearing to be successfully remediated. In light of this, it seems only reasonable that remediators and investigators at DOD sites be made aware of the shortcomings of the purge and trap method and its inherent limitations.

2. That purge and trap measurement at DOD IRP sites be enhanced with the addition of methanol extraction. Although the purge and trap technique appears to be far from comprehensive, the addition of a methanol slurry as an extraction medium has been shown to significantly increase the effectiveness of this method. In light of the fact that no more effective alternative is currently available, it is recommended that the Department of Defense utilize the most effective means presently accepted- purge and trap with methanol extraction. In addition, pulverization of the soil sample has displayed some potential to further increase the extraction capabilities of purge and trap measurement. With this in mind, it would seem beneficial to conduct further research into the extraction capabilities of purge and trap with soil pulverization and methanol extraction, versus the abilities of purge and trap with methanol extraction and no soil pulverization.

3. That attention be directed at the emerging technologies that may eventually replace purge and trap measurement. A number of researchers are currently attempting to determine an ultimate solution to this measurement problem. In this search, a number of modifications and technological advancements have been proposed. It seems probable that until a comprehensive solution is finally reached a number of possible alternatives will continue to appear in the near future. The Department of Defense should remain cognizant of this research to eventually replace the purge and trap technique by a truly effective method.

4. That further research and study be directed, if possible, at the use of lasers for soil sample analysis. This thesis has proposed a method of soil contamination measurement utilizing high energy lasers which appears theoretically capable of successfully measuring total VOC contamination in soils suffering from long term pollution. It seems reasonable, if the necessary resources are available, to conduct further research to determine if this laser measurement tool is indeed technically and practically feasible.

Slow Sorption Effects on the Vapor Extraction System

Conclusions. The identified slow sorption or "rate-limited" sorption of organic contaminants also appears to have a detrimental impact on vapor extraction system (VES)

remediation operations in the vadose zone. The same entrapment of contaminant molecules in the soil matrix which frustrates purge and trap measurement also frustrates the air mobilization and volatilization required for successful vapor extraction remediation. This slow sorption binding can, under some circumstances, be so tenacious that complete remediation may demand years of continuous vapor extraction.

In an effort to more fully comprehend and illustrate the effects of slow sorption on vapor extraction operations researchers have designed a number of mathematical models in an attempt to simulate the slow sorption mechanism. One of these models, developed by researcher Mark Brusseau, appears to viably incorporate slow sorption in its simulations of contaminant transport by gas advection. This "Brusseau" model, with some modifications, formed the basis of the SVE Computer Model, developed by M. N. Goltz and M. Oxley, researchers from the Air Force Institute of Technology. The SVE Computer Model, which also incorporates slow sorption in its simulations, outputs computer generated breakthrough curves at a vacuum extraction well in the unsaturated zone.

A basic sensitivity analysis was conducted with the SVE Model in order to test its responses against experimentally derived data and to better illustrate the varying effects of slow sorption on vapor extraction operations. This sensitivity analysis appeared to support the credibility and validity of model's outputs. In addition, if indeed accurate, the model provided useful information about slow

sorption and its relation to vapor extraction remediation. The model demonstrated that under certain parametric conditions, chemicals such as TCE and benzene could be effected by slow sorption to the degree that their comprehensive remediation by vapor extraction, if possible, may require years of concentrated effort. In general, the SVE Model appeared to confirm that sites with relatively low rates of transfer between the nonadvective and advective domain coupled with "slow" desorption rates could lead to "slow sorption tailing" and difficult vapor extraction remediation for substances possessing moderate sorption coefficients and long residence time in the soil. The model seemed to confirm the hypothesis that sites suffering from long term contamination were the most highly susceptible to slow sorption, and are therefore, the most challenging vapor extraction remediation projects.

Recommendations. Based upon the information previously presented in this thesis, the following recommendations are submitted.

1. That the Department of Defense make its remediators fully aware of the difficulties that may be present when attempting to remediate sites suffering from long term contamination. A great deal of data has been presented in this document, some experimentally derived, some provided by model simulation, which appears to indicate that the slow sorption of organics may degrade the capabilities of vapor extraction remediation of the unsaturated zone. In some

worst case scenarios, contaminant "tailing," precipitated by slow sorption, may demand many years of concentrated effort to achieve complete remediation. In addition, this data has indicated what could be a proportional relationship between the length of time an organic has remained in the unsaturated zone, and the percentage of that contaminant which has become slowly sorbed or entrapped in soil micropores. In light of this, it seems reasonable that the DOD personnel involved in unsaturated zone remediation be made aware of these possible limitations of the vapor extraction system.

2. That follow-on analysis be conducted of the SVE Computer Model. In the analysis conducted within this thesis, the SVE Model appeared to competently incorporate the slow sorption mechanism in its simulations of vapor extraction operations. If proven to be credible, this package could possibly assist DOD personnel contemplating vadose zone remediation. In light of this, it is recommended that the slow sorption mechanism be incorporated into a numerical model for use in simulating the conditions of actual DOD remediation sites.

Possible Areas for Further Research

- 1) The effects of soil pulverization on purge and trap measurement enhanced with methanol extraction.
- 2) Alternative technologies for soil sample analysis.
- 3) The utilization of lasers for soil sample analysis.

4) Incorporate slow sorption into a numerical model to simulate actual DOD remediation sites.

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Vita

Thomas Reeder was born in Cincinnati, Ohio. He graduated from the Virginia Military Institute in 1978 and is currently a Major in the United States Marine Corps.

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