ANL/EAD/TM-97

Twin Cities Army Ammunition Plant Soil Vapor Extraction System: A Post-Audit Modeling Study

Environmental Assessment Division
Argonne National Laboratory

Operated by The University of Chicago,
under Contract W-31-109-Eng-38, for the

United States Department of Energy

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October 2000

Work sponsored by U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

CONTENTS

CONTENTS (Cont.)

TABLES

TABLES (Cont.)

FIGURES

FIGURES (Cont.)

FIGURES (Cont.)

NOTATION

ACRONYMS AND ABBREVIATIONS

AEC	U.S. Army Environmental Center
EPA	U.S. Environmental Protection Agency
IRA	interim remedial action
MISER	Michigan Soil Vapor Extraction Remediation model
NAPL	nonaqueous phase liquid
PCB	polychlorinated biphenyl
SVE	soil vapor extraction
SVOC	semivolatile organic compound
T12DCE	trans-1,2-dichloroethene
TCAAP	Twin Cities Army Ammunition Plant
TCA	1,1,1-trichloroethane
TCE	trichloroethene
VOC	volatile organic compound

UNITS OF MEASURE

cfm	cubic foot (feet) per minute	lb	pound(s)
cm^3	cubic centimeters(s)	m	meter(s)
d	day(s)	m^2	square meter(s)
°F	degree(s) Fahrenheit	m^3	cubic meter(s)
ft	foot (feet)	min	minute(s)
ft^3	cubic foot (feet)	mol	mole(s)
g	gram(s)	Pa	Pascal(s)
hp	horsepower	ppm	part(s) per million
in.	inch(es)	s	second(s)
K	Kelvin	µg	microgram(s)
kg	kilogram(s)	yr	year(s)

TWIN CITIES ARMY AMMUNITION PLANT
SOIL VAPOR EXTRACTION SYSTEM:
A POST-AUDIT MODELING STUDY

by

G.P. Williams, D. Tomasko, and Z. Jiang

SUMMARY

The goals of this study were to (1) evaluate an existing multiphase, multicomponent transport code, T2VOC, to determine if it is applicable for modeling the long-term operation of soil vapor extraction (SVE) systems and (2) model an existing SVE system located at the Twin Cities Army Ammunition Plant (TCAAP) to make recommendations for its future operation. In particular, three questions were addressed. Should system operation be modified? Should deep vents be installed? Should the system continue to operate? Another objective of this study was to develop a method of analysis that would enable the results and numerical techniques developed for this site to be applied to similar sites to promote cost-effective, dependable restoration strategies.

A large number of Army sites have subsurface contamination problems that stem from the disposal of volatile organic compounds (VOCs). At some sites, this VOC contamination is located in the unsaturated soil (vadose zone) above the water table. SVE has often proven to be a cost-effective method for remediating the unsaturated zone, because it leaves soil in place during the cleanup process. SVE systems work by forcing air through the subsurface, volatilizing the VOCs, and then transporting the VOCs to a collection system for surface treatment. Empirical models of single-phase gas flow are usually the basis for the field design and implementation of SVE systems. Complex multiphase computer codes are not typically used, because numerically implementing the processes required to model SVE processes can be difficult. Because of these computer limitations, the prediction of cleanup times is often highly uncertain.

SVE has proven to be effective in reducing concentrations of VOCs and certain semivolatile organic compounds (SVOCs) found in petroleum products that are contaminating the vadose zone. The initial rates at which SVE extracts these contaminants are generally very fast, provided that the permeability of the soil is high and its clay content is low. With time, the rate of removal rapidly decreases, but it rarely goes to zero. Instead, the extraction rate approaches an asymptotic, small value (i.e., the mass removal rate “tails”). Additional pumping under these conditions does not reduce the mass extraction rate further.

The tailing effect observed in field SVE systems has been extensively studied by the scientific community. Some researchers believe that the effect is caused by complex chemical and physical processes (e.g., nonequilibrium partitioning of the gas phase). Others feel that the tailing is produced by the potentially complex geology of the field sites. An example of such complex geology is layered systems, which are composed of alternating layers of clay and more permeable material; another example is small pockets of nonaqueous phase liquids (NAPLs), which are trapped at residual saturations. Whatever the cause of tailing is, numerical modeling of the entire cleanup process from beginning to end is difficult and, in many cases, impossible because of limitations in today's computers. Because of these limitations, the basis for designing SVE systems is generally empirical correlations or engineering judgment. The design is thus subject to inefficiency and uncertainty. In addition, SVE systems are frequently operated during the asymptotic period on the basis of the belief that continued extraction is removing residual VOCs from the soil matrix.

This study demonstrates that the tailing behavior seen at TCAAP is being produced when volatile contaminant vapors are extracted from VOC-contaminated groundwater in the saturated (phreatic) zone. This process has not been discussed in the literature and has been omitted from most modeling and design studies because it was thought that the vertical zone of influence created by the extraction wells would not reach the water table.

This study used the computer model T2VOC to evaluate the SVE system at Site D at TCAAP. The SVE system was designed to remove trichloroethylene (TCE) and other VOCs of concern. T2VOC is a numerical simulator that can compute three-phase, three-component, nonisothermal, heterogeneous flow and transport in three dimensions. The code was developed by Lawrence Berkeley Laboratory and was designed to model near-surface remediation processes such as steam-sweeping and SVE.

Site D at TCAAP was used from approximately 1952 to 1968, and possibly as late as 1973, for the disposal and/or burning of wastes (including oil, solvents, rags, maizo, neutralized cyanide, mercurous nitrate, powder water, and scrap propellant powder) in five disposal pits. Soil borings revealed the presence of VOC contamination (TCE, 1,1,1-trichloroethene [TCA], and trans-1,2-dichloroethene [T12DCE] in the Arsenal Sand Formation beneath the site. In the vicinity of the disposal pits, the soil was stained, and residues extended from 4.5 ft to a maximum of 39 ft (1.4 to 11.9 m) below the ground surface. Additional VOC contamination was found in an extensive groundwater plume. A clay cap was installed to limit infiltration of precipitation and prevent additional impacts on the underlying groundwater.

An SVE system with 39 extraction wells was installed at the site; it began operation in 1986. This system, which was empirically designed, did not account for the improved efficiency that had been created by the clay cap. Approximately 100,000 lb (45,350 kg) of VOCs was removed from the site. The peak mass extraction rate was 1,300 lb (590 kg) of VOC per day, which occurred on the third day of operations. By 1998, the mass removal rate approached a nearly asymptotic value of about 2 lb (0.9 kg) per day, nearly three orders of magnitude less than the initial value.

In this study, the extraction of TCE from the Arsenal Sand Formation was investigated by using a number of geometries designed to simulate the effects of (1) a homogeneous clean sand; (2) alternating layers of clayey-sand and sand; and (3) randomly generated, blocky heterogeneities with a volume of approximately 27 ft^3 (0.8 m^3). The area modeled was 1/13 of the actual size of the SVE system and included three extraction vents. This simplification was justified because there was a twofold symmetry in the locations of the 39 existing extraction wells. Initial conditions for T2VOC were developed to simulate field conditions in the zone of contamination. In addition, a number of calculations were performed to simulate an initially clean unsaturated zone and contamination in the underlying groundwater.

This study looked at various material parameters, material distributions, and operational configurations for the SVE systems by using sets of simulations. Within a simulation set, individual computer runs were designed to evaluate the model's sensitivity to the various parameters under study. The results of each set of simulations were compared with the measured data to determine if the mechanism evaluated might be a cause of the tailing or if it should be neglected. The simulation sets were designed to isolate a single mechanism and evaluate whether it could be causing the tailing behavior. In addition, a number of simulation sets that combined various possible mechanisms were used to match the full history of the field data.

Many of the geometries simulated with T2VOC resulted in mass removal curves that approximated the shape of the observed extraction curve for limited periods of time (either early or late). However, the simulations that exhibited long tails did not duplicate the initial rapid drop in extraction rates that was observed, and the simulations that matched the early behavior of the system did not match its long-term behavior. In order to make the simulations match the measured results (very high initial extraction rates, followed by a rapid dropoff in removal, followed by a long asymptotic tail of low but measurable mass removal), contaminated groundwater had to be incorporated into the model. Only when this condition was added could the full extraction curve derived from field measurements be replicated.

The simulations showed that the amount of time it takes for SVE systems to remove VOCs from the subsurface is exponential in nature. Removal of the first 90% of the mass takes less time than removal of the next 9%. The simulations thus suggest that the percentage change from the initial extraction rate can indicate the percentage of mass removed from the subsurface. The simulations showed that when the extraction rate drops below 2 to 5% of the initial rate, approximately 90% of the initial mass has been removed. Continued operation of the system removes the mass only very slowly.

In the spring of 1997, additional field work was performed at TCAAP. This field work included VOC sampling and installation of a deep-well extraction system. The results of this additional field work showed that only very low concentrations of TCE occurred near the water table (5 to 50 μg/kg), the permeability of the porous medium was 1.7×10^{-12} m^2, and the highest concentration of VOCs in the effluent occurred in wells that were screened immediately above the water table. The field work results provided independent validation of the numerical results obtained in this study: (1) residual TCE contamination in deep soils is very small (i.e., most of the initial VOC contamination has been removed by the SVE system), (2) permeabilities used in T2VOC are consistent with measured field values, and (3) contaminated groundwater contributes VOC vapors to the extraction system and creates the asymptotic tail currently seen.

This study was successful in demonstrating these general conclusions:

- Advanced multiphase, multicomponent computer codes such as T2VOC can be used for engineering evaluations of field-scale SVE systems.

- Local equilibrium models are capable of duplicating observed field behavior.

- Contaminated groundwater beneath SVE systems can have significant impacts on long-term tailing behavior. (This finding has not been previously reported in the literature.)

The study also provided answers to specific questions about future operations of the TCAAP SVE system:

- Deep contamination does not exist at TCAAP, so deep vents are not needed. (This finding is supported by recent field data.)

- The most likely cause of long-term tailing behavior at TCAAP is contaminated groundwater beneath the site.

- The TCAAP SVE system achieved its stated objective of source control.

The study was successful in developing some general guidelines for operation of other SVE systems. These include the following:

- Contaminated groundwater is a potential source of long-term tailing behavior. (This finding should be considered when designing field sampling programs.)

- The percentage change in the extraction rate could indicate the VOC mass remaining in the subsurface.

- Operation of SVE systems becomes increasingly inefficient over the long term.

- SVE operations should be reviewed when extraction rates drop to about 5 or 10% of the initial rates.

None of these operational guidelines are absolute. Their best use is to help decide when it would be reasonable to reevaluate SVE system operations. The study also provides important insights into physical processes that might be affecting long-term SVE system behavior.

In summary, this study successfully demonstrated that contaminated groundwater beneath a VOC-contaminated site can produce the asymptotic tailing behavior observed in SVE extraction systems. It was not necessary to introduce fine-scale residual pockets of contamination, complex multilayered systems, or nonequilibrium effects in order to replicate the observed field performance.

1 INTRODUCTION

A large number of Army sites have subsurface contamination problems that stem from the disposal of volatile organic compounds (VOCs). At some sites, this VOC contamination is located in the unsaturated soil (vadose zone) above the water table. Soil vapor extraction (SVE) has often proven to be a cost-effective method for remediating the unsaturated zone, because it leaves soil in place during the cleanup process. SVE systems work by forcing air through the subsurface, volatilizing any VOCs, and then transporting them to a collection system for surface treatment (Figure 1).

Empirical models of single-phase gas flow are usually the basis for the field design and implementation of SVE systems. Complex multiphase computer codes are not typically used because numerically implementing the processes required to model the SVE process can be difficult. Because of these computer limitations, the prediction of cleanup times is often highly uncertain.

This study investigated currently existing scientific research codes to determine if any are applicable for conducting engineering evaluations of the long-term operation of SVE systems. In addition, this study evaluated the utility of one such code by using the historical data generated by two SVE systems (one at Site D and one at Site G) at Twin Cities Army Ammunition Plant (TCAAP). The study then attempted to provide guidance regarding the future operation of these systems.

Results from long-term SVE system operation have shown that vapor concentrations extracted from the system exhibit a tailing behavior that was not predicted by the empirical models used to design the system. In other words, after a long time, the measured concentration of the contaminant is greater than any predicted values. Tailing is the continued existence of a measurable contaminant flux over long time periods. These fluxes appear to approach some nonzero value in an asymptotic way. In addition to exhibiting tailing behavior, the SVE system exhibits contaminant extraction rates that decrease significantly with time. For example, within 3 years, the rate for

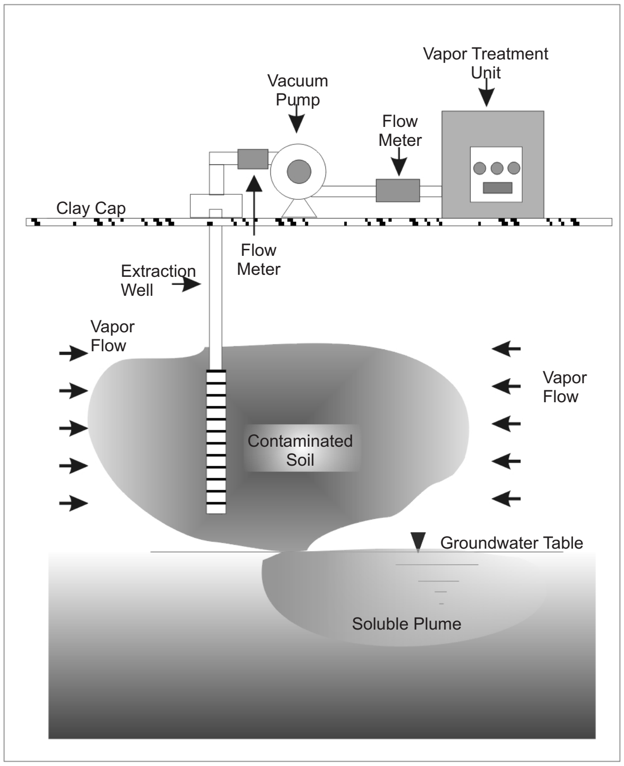

FIGURE 1 Diagram of Typical SVE System That Uses a Clay Cap to Enhance the Air Flow Regime

one TCAAP SVE system dropped to only 5% of the initial extraction rate. For both TCAAP SVE systems, even after long periods of operation, measurable fluxes of contaminants are still being removed from the subsurface. This behavior has been observed at many SVE installations.

In the initial design calculations for the TCAAP SVE systems, it was estimated that cleanup would be complete in approximately two to three years (Weston 1985). However, the systems have now been in nearly continuous operation for 14 years. Although extracted contaminant fluxes have decreased significantly over this period, they are still measurable and significant. The SVE systems have removed five times more mass from the subsurface than was initially estimated to be in place. There is a debate about why these SVE systems are still removing measurable amounts of VOCs and what these fluxes mean for future operations.

This study used site-specific data to develop a multiphase, multicomponent, three-dimensional model of the vadose zone that covers the main physical and chemical processes required to model SVE systems. As a part of this study, a currently available research code was evaluated to determine if it could be used to effectively model field SVE systems. Once a model that reasonably matched field data was developed, it was used to assess the possible processes that could produce long-term tailing behavior as well as to evaluate future operations of the TCAAP SVE systems. The results of this modeling study were analyzed to develop general guidelines for long-term SVE operation at other sites.

The data used in this study came from the operation of two SVE systems installed at TCAAP. The U.S. Army Environmental Center (AEC) has been conducting characterization and cleanup activities at TCAAP to address contaminated soils, sediment, and groundwater. Parts of these cleanup efforts include the use of two SVE systems to reduce contaminant migration to groundwater. These systems have been in operation since 1986. Daily volumes of extracted VOCs have decreased significantly over this time period (by approximately two orders of magnitude).

1.1 CURRENT RESEARCH

1.1.1 Studies on Tailing Behavior

The scientific community is studying the tailing effect observed in field SVE systems. Some researchers feel that this effect is caused by complex chemical and physical processes not considered in currently available models. Other researchers feel that this tailing effect might be a result of the complex geology of actual field sites and that, even though current models have sufficiently complex physical and chemical data to simulate the processes, and even though the code might include all the necessary processes, current computers and numerical solvers are not generally able to solve grids at sufficient resolution to duplicate observations of complex field situations.

A number of recent publications have examined secondary and tertiary processes that might cause the observed long-term tailing effect. Some researchers have focused on chemical or physical processes that might result in long-term tailing behavior. Fischer et al. (1996) studied a laboratory-scale SVE system composed of various VOCs, water, and clean quartz sand. Under these conditions, the contaminants did not sorb onto the solid materials. The authors attributed the tailing behavior in this experiment solely to diffusion in the interparticle water and suggested that this behavior could be modeled with a first-order kinetics approach. Poulsen et al. (1996) investigated the nonaqueous phase liquid-air mass transfer rate, well vacuum, and inhomogeneities in the soil. The authors concluded that contaminant removal fluxes depended more on well vacuum and soil permeability than on the liquid-air mass transfer rate. Conant et al. (1996) examined vapor transport at the Bordan field site to quantify the effects of seasonal temperature variations. In addition to temperature variations, these authors found that organic carbon content and soil moisture significantly affected vapor transport and thus the contaminant extraction flux. These processes could all contribute to long-term tailing behavior, but none of these reports addressed the long term specifically.

Researchers have also studied the impact of geologic complexity on the long-term operation of SVE systems. Kaleris and Croise (1998) developed an analytic solution for an SVE system in layered soils. They identified a number of different flow regimes, one of which relied on gaseous diffusion as the mechanism by which contaminant fluxes moved from a tight clay layer into a more permeable layer, where the contaminants could be advectively transported to the extraction well. This approach showed promise in matching experimental data and suggested a mechanism for long-term tailing behavior observed at field sites.

Garg and Rixey (1998) studied the dissolution of a number of nonaqueous phase liquids (NAPLs) from small pockets trapped at residual saturation values. The experiments were configured so that contaminant fluxes were limited by mass transfer rates. These experiments showed that mass transfer rates can affect underground vapor transport.

All of these studies successfully demonstrated that under short-term field or laboratory conditions, tailing behavior could be successfully modeled by using various secondary and tertiary chemical physical phenomena not typically considered when designing an SVE system. However, there was some question as to whether these long-term tailing results could be duplicated with existing numerical models without incorporating such complex phenomena. One goal of this study was to determine whether the tailing effects observed in the field could be duplicated with local equilibrium chemical models and rate-limited transfer rather than with a model that requires chemical nonequilibrium kinetics.

1.1.2 Computer Code and Models

In recent years, a number of researchers have developed codes to model SVE systems. These models vary in their levels of complexity and in the processes they simulate (Abriola et al. 1997). The simplest models are analytical solutions of gas flow alone and do not include VOC or transport calculations. They are used to help design SVE systems and determine well spacing and required flow rates. Because the models do not include the transport or partitioning of VOCs, they do not predict long-term removal rates of VOCs and are generally used for developing and screening a field design (Abriola et al. 1997). Some examples of these models are those by Massmann (1989); Johnson et al. (1990); McWhorter (1990); Cho and DiGiulio (1992); Massmann and Madden (1994); Beckett and Huntley (1994); and Baehr et al. (1995). Numerical implementations of gas-phase advection have also been developed (Croise and Kaleris 1992; Edwards and Jones 1994) and are used for similar applications (Abriola et al. 1997).

Another group of models assumes a steady-state gas flow but includes advective contaminant transport and VOC partitioning. These models are limited by the assumptions made about gas flow in the system and by the details of the partitioning models used (Abriola et al. 1997). The models range in complexity from those that use steady-state flow fields coupled with analytical solutions (Roy and Griffin 1991; Zaidel and Russo 1993) to others that use steady-state flow fields and numerical transport solutions (Massmann and Farrier 1992; Johnson et al. 1990). More complex models consider geologic heterogeneity while still assuming steady-state flow conditions (Baehr et al. 1989; Benson et al. 1993).

The next level of more complex models incorporates non-steady-state, single-phase air flow with contaminant transport. Nonequilibrium models in one dimension have been implemented (Brusseau 1991; Armstrong et al. 1994), but most of these models (e.g., Metcalf and Farquhar 1987) have been implemented in two dimensions (Abriola et al. 1997).

Few models are available that model transient multiphase, multicomponent flow and also include transport and interphase mass transfer (Abriola et al. 1997). Abriola studied these processes in a series of models (Abriola 1984, 1988; Abriola and Pinder 1985).

Abriola et al. (1997) developed a model specifically for SVE design and analysis that considered two-phase flow (air-water), multicomponent transport (including a number of VOC materials), rate-limited transfer for interphase mass exchange, and biodegradation kinetics simulation. This model, developed with the U.S. Environmental Protection Agency (EPA), is called the Michigan Soil Vapor Extraction Remediation (MISER) model. However, this model is only two-dimensional, either Cartesian or radial, and cannot be used to study either the well interactions that result from three-dimensional geometry or the geological complexity of a three-dimensional field situation. In addition, this model does not include a mobile NAPL phase; NAPL can be present, but movement is neglected. Bensen (1994) developed a series of models, VENT2D and VENT3D, which are similar to MISER but do not include the biokinetics. VENT3D is fully three-dimensional.

A series of more complex models was also developed. These models incorporate equations to describe three-phase flow, multicomponent transport, and heat transport in full three-dimensional space (Sleep and Sykes 1989; Falta et al. 1989). However, the models have not been extensively applied to SVE systems (Abriola et al. 1997).

This study used the model T2VOC (Falta et al. 1995), which is an extension of Falta et al. (1989), to determine if it could be effectively applied to SVE operation and analysis. T2VOC is described in detail in Section 4.1. T2VOC is a complex computer code that includes most of the physical processes that are thought to influence SVE systems. It includes fully mobile air, water, and oil phases and allows VOC to exist as free phase oil, dissolved in the aqueous phase, evaporated into the vapor phase, or sorbed onto the solid phase. The model is fully three-dimensional and includes thermal and density effects as well as several different ways to define the relative permeability and capillary pressure relationships. T2VOC can model long time periods with changing well and boundary conditions, and the code is in the public domain. The application of T2VOC to SVE system engineering operation has not been reported in the literature. For these reasons, T2VOC was chosen for this study.

1.2 STUDY APPROACHES

This study modeled an SVE system at TCAAP and developed recommendations for its future operation. The study evaluated the advanced, complex computer code, T2VOC, to determine if it could be used to help make engineering decisions for SVE systems. The study also extrapolated the results of the TCAAP analysis and developed general guidelines that can be applied to other SVE systems.

This study used SVE operational data from TCAAP SVE systems for detailed analysis. The analysis included state-of-the-art computer simulations of one TCAAP SVE system. The T2VOC model was used to evaluate the effectiveness of the SVE system and to develop future operational scenarios. The findings and methods from this site-specific analysis were used to develop general guidelines and recommendations that can be used for similar sites at other Army installations.

For almost 14 years, two SVE systems have been operating at TCAAP. Monitoring these systems has produced extensive data on extraction contaminant flux. These data show that extraction rates have declined significantly since operations began; measurable contaminants (0.5 to 1 kg per day) are still being removed from the subsurface. Detailed descriptions of these systems, along with the operation data, are presented in Section 2.

Several hypotheses have been presented to explain the long-term tailing behavior in contaminant extraction rates observed at TCAAP. One possible explanation is that the continued low VOC flux from the TCAAP SVE systems is the result of local contamination in tight soils near the surface. Another is that contaminated soil might remain at a depth below the influence of the SVE system. Or perhaps the SVE system could be extracting VOCs from contaminated groundwater beneath the system and removing them at the surface.

Two of the proposed hypotheses use a rate-limited mass transfer mechanism to account for the observed behavior. These hypotheses assume that there are either contaminants trapped in soil near the surface or contaminants in soils below the influence of the SVE system. The only mechanism that would allow the contaminants to move to the extraction wells is gaseous diffusion, either through the tight material near the surface or through the material that separates the deep contamination from the SVE system. VOC contamination in tight soils near the surface would move to the SVE system by gaseous diffusion through the low-permeability soils into the more rapid air flow in the looser soils. This process is slow and might result in system behavior similar to that measured in the field. VOC contamination in soils below the area of influence of the SVE system could produce similar behavior. VOCs from this deep contamination zone could move upward by gaseous diffusion until they were captured by the air flow of the SVE system. These deep contaminants would not necessarily be located in low-permeability soils.

The assumption that contamination might exist below the influence of the SVE system is based on the original design. A pilot study was conducted to design the SVE system (Weston 1985). It assumed a relatively shallow radius of influence for the extraction wells. On the basis of the pilot test data for the SVE system, some current reports argue that long-term tailing behavior at the TCAAP sites is a result of deep, residual contamination below the influence of the SVE systems (Wenck Associates, Inc. 1995). On the basis of this argument, the installation of deep vents to remove the contaminants was recommended (Wenck Associates, Inc. 1995).

The third hypothesis relies on a different mechanism to reproduce the observed field behavior. This hypothesis assumes the effective range of the SVE system reaches the contaminated groundwater. As the air, mobilized by the SVE system, sweeps across the surface of the contaminated groundwater, it volatilizes the contaminants, which are then transported to the extraction wells.

The determination of what processes are causing the long-term tailing behavior at TCAAP is critical. If contamination exists below the range of influence of the SVE system, installation of deep vents would be beneficial and would produce a more effective cleanup. However, if contamination exists only in small zones of tight soil near the surface or if the observed flux is a result of contaminated groundwater, the installation of deep vents would not appreciably affect the cleanup of the site. If VOC contamination exists in this manner, continued operation of the SVE system may not be necessary. Small regions of contamination near the surface would probably pose little risk to either human health or the environment because they would be relatively immobile and would not move to the groundwater. Natural attenuation processes, including biodegradation and continued vaporization, might remove VOCs existing in this manner before they could reach the groundwater.

If continued removal of VOCs by the SVE system is a result of the volatilization and transport of contaminants from the groundwater, other operational issues would need to be considered. An SVE system might not be the most efficient method to remove contaminants from groundwater.

The computer model T2VOC was used to simulate a variety of conditions and to evaluate the various mechanisms that could produce the tailing effect. Various material parameters, material distributions, and operational configurations for the SVE systems were studied. Within a simulation set, individual computer runs were designed to evaluate the model’s sensitivity to the various parameters under study. The results of each set of simulations were compared with the measured data to determine if the mechanism evaluated might be a cause of the tailing or if the mechanism was not a cause and should be neglected. The simulation sets were designed to isolate a single mechanism and evaluate whether it might be causing the tailing behavior. In addition, a number of simulation sets that combined various possible mechanisms were used to match the full history of the field data.

In summary, the goals of this project can be divided into two parts: (1) evaluating an existing multiphase, multicomponent transport code, T2VOC, to determine if it is applicable for modeling the long-term operation of SVE systems and (2) modeling an existing TCAAP SVE system to make recommendations for its future operation. In particular, three questions were addressed. Should system operation be modified? Should deep vents be installed? Should the system continue to operate?

This study also attempted to develop a method of analysis that would enable the results and numerical techniques developed for this site to be applied to similar sites to promote cost-effective, dependable restoration strategies.

2 TCAAP HISTORY

The TCAAP site is located north of Minneapolis-St. Paul, Minnesota. It is surrounded by the cities of New Brighton and Arden Hills. TCAAP construction began in 1941. The site formerly included 323 buildings, associated utilities, and services to support production activities. TCAAP produced small-caliber ammunition and related materials, proof-tested small-caliber ammunition, and handled or stored strategic and critical materials for other government agencies (Aberdeen 1991).

Investigations at TCAAP have focused on 14 areas that could be sources of contaminants resulting from releases and waste disposal activities (Aberdeen 1991). Some of these source areas caused groundwater beneath the TCAAP facility to become contaminated with VOCs. Two primary sources of the on-post and off-post groundwater VOC contamination are Site D and Site G. A pilot study was conducted in 1984 (Weston 1985) to determine the feasibility of using an SVE system at these sites. The Site D and Site G SVE systems were installed in 1985 as part of interim remedial actions (IRAs) to initiate contaminant source control. The data resulting from the long-term operation of these systems and future operational considerations are the focus of this report. Sites D and G are similar in geology and design but differ in size.

2.1 BACKGROUND ON SITES D AND G

The location of Site D is shown in Figure 2. Site D was used from about 1950 through 1968, and possibly as late as 1973, for the disposal and/or burning of wastes. The wastes, which included oil, solvents, rags, maizo, neutralized cyanide, mercurous nitrate, powder water, and scrap propellant powder, were put in up to five disposal pits (Aberdeen 1988). Soil borings used to characterize Site D revealed it was contaminated with VOCs, semivolatile organic compounds (SVOCs), metals, and polychlorinated biphenyls (PCBs). A clay cap had been installed over the site before the SVE system was installed to prevent infiltration of surface water through the source area, thereby minimizing impacts to groundwater. The clay cap also prevented short-circuiting of the SVE system (Aberdeen

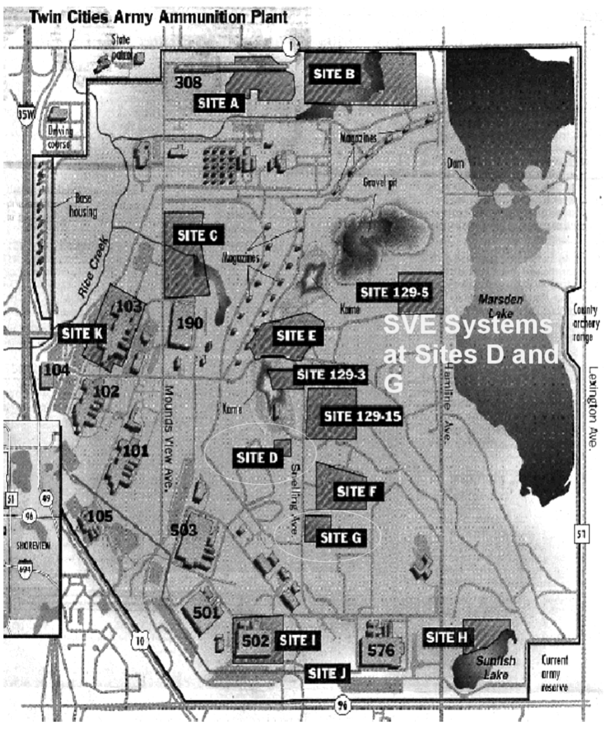

FIGURE 2 Locations of TCAAP SVE Systems

1991). An SVE system with 39 vents was installed in late 1985; it began operation on January 29, 1986.

The location of Site G is also shown in Figure 2. Site G was a landfill area that was used for disposing of concrete, rubble, asphalt pavement, railroad ties, barrels, oil filters, etc. The site was used from the early 1940s to 1976 (Aberdeen 1988). Characterization of the site revealed contamination with VOCs, SVOCs, and metals (Aberdeen 1991). A clay cap was installed over the site in late 1985. An SVE system with 89 vents was installed later in 1985. It began operation on February 20, 1986.

2.1.1 Geology

Detailed discussions of site geology and geologic cross sections can be found in the Remedial Investigation Report (Aberdeen 1991). In summary, Site D soils consist of approximately 120 ft of Arsenal Sand underlain by Hillside Sand that extends to a depth of approximately 430 ft. The Arsenal Sand and Hillside Sand do not have a distinctive lithologic break and consist of brown-gray, fine to coarse sands. In the Site D vicinity, disposal pits resulted in areas of stained sediment and residues extending from 4.5 ft to a maximum of 39 ft below ground surface. Groundwater beneath Site D occurs at a depth of approximately 130 to 150 ft and flows to the southwest (Aberdeen 1991).

Site G soils are heterogeneous. Generally speaking, a layer of silty sand or silty clay fill overlies the Twin Cities Formation, which overlies the Arsenal Sand. Layers and/or pockets of mixed fill and waste can be found within the fill layer or within the Twin Cities Formation. The Twin Cities Formation consists of glacial till (a mixture of clays, silts, sands, gravel, and boulders). The bottom of the Twin Cities Formation generally varies from 20 to 40 ft below ground surface. As such, most of the Site G SVE system vents extend into the Arsenal Sand, but some do not. The sand layers extend to a depth of up to 447 ft. Groundwater is present below the site at a depth of approximately 100 to 130 ft and flows to the southwest (Aberdeen 1991).

2.1.2 Contaminants of Concern

The principal contaminants of concern at Sites D and G that can be removed by SVE systems are VOCs. Other contaminants identified at Sites D and G (metals, SVOCs, etc.) are not the target of the SVE systems because they have low volatility or are nonvolatile.

Soil contamination at Site D was characterized by means of soil borings. Only a few of the soil borings were drilled deeper than 65 ft. The primary VOCs detected (in terms of frequency and magnitude of detections) were trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and trans-1,2-dichloroethene (T12DCE). Maximum concentrations of these three compounds were 7,000 µg/g at 4.5 to 6 ft, 1,000 µg/g at 4.5 to 6 ft, and 500 µg/g at 9.5 to 11.5 ft (Weston 1985; Aberdeen 1991). Other VOCs detected at Site D included 1,1-dichloroethene, 1,1-dichloroethane, chloroform, tetrachloroethene, methylene chloride, ethylbenzene, toluene, xylenes, and styrene.

Soil contamination at Site G was also defined by means of soil borings. Only a few of these soil borings were drilled deeper than 65 ft. As they were at Site D, the primary VOCs detected were TCE, TCA, and T12DCE. Maximum concentrations of these compounds at 4.5 to 6 ft were 400 µg/g, 100 µg/g, and 400 µg/g, respectively. Other VOCs detected at Site G included 1,1-dichloroethene, 1,1-dichloroethane, chloroform, and tetrachloroethene.

At Site D, VOCs detected in groundwater that were at levels above action criteria included TCE, TCA, 1,1-dichloroethene, and chloroform (Wenck Associates, Inc. 1994). At Site G, VOCs detected in groundwater above action criteria included TCE, TCA, and 1,1-dichloroethene (Wenck Associates, Inc. 1994). T12DCE was not detected above action criteria at either site.

2.2 SVE SYSTEM

2.2.1 Pilot Study

An SVE pilot study was conducted at Site D from November 1984 through February 1985 (Weston 1985). Two pilot-scale systems were installed. System 1 was installed in a zone of relatively low soil contamination (TCE less than 10 µg/g). System 2 was installed in a zone of relatively high soil contamination (TCE up to 7,000 µg/g).

In the pilot study, approximately 1,600 lb of TCE was removed, which indicated that SVE technology could be effective in removing VOCs at TCAAP. Also in the pilot study, design curves were developed to use for implementing full-scale SVE systems. In particular, a discharge rating curve that relates the vent flow rate to the required vacuum level at the vent and also a family of curves that describe the vacuum drop versus the radial distance from the vent were developed for various extraction vent flow rates. These empirically derived curves were used as the basis for the initial SVE design. Any modeling done as the basis for completing the design was restricted to empirical approaches and did not address long-term, low-concentration issues.

2.2.2 System Design and Construction

The objective of the SVE systems installed at TCAAP was to begin controlling the source areas contributing to VOC groundwater contamination. This objective was broad and did not address specific criteria, such as cleanup concentrations or depths, that could be used to justify a shutdown of the system (Wenck Associates, Inc. 1995). The SVE systems were meant for source control until the final remedy for TCAAP was determined. As such, the intent was for them to remove as much of the VOCs in shallow soils as possible and to prevent these VOCs from entering the groundwater. The systems were designed to address shallow contamination and not the possibility that contamination might exist in deeper soils.

On the basis of pilot study results, the design criteria selected were an air flow rate of 110 ft^3/min (cfm) per vent, a horizontal vent spacing of 25 ft, and an operating vacuum of 13 in. of water. The systems were over-designed on the basis of the pilot test results (i.e., closer vent spacing) for several reasons, including uncertainties associated with this new technology, heterogeneity of the sites (particularly Site G), and a desire to enhance the rate and effectiveness of remediation (Wenck Associates, Inc. 1995).

The layouts of the Site D and Site G SVE systems are shown in Figure 3 (Aberdeen 1991). Details of the SVE system design, including plan-size construction drawings, can be found in the Project Documentation Report (Wenck Associates, Inc. 1985). Construction of each SVE system is summarized in the text that follows (Wenck Associates, Inc. 1995).

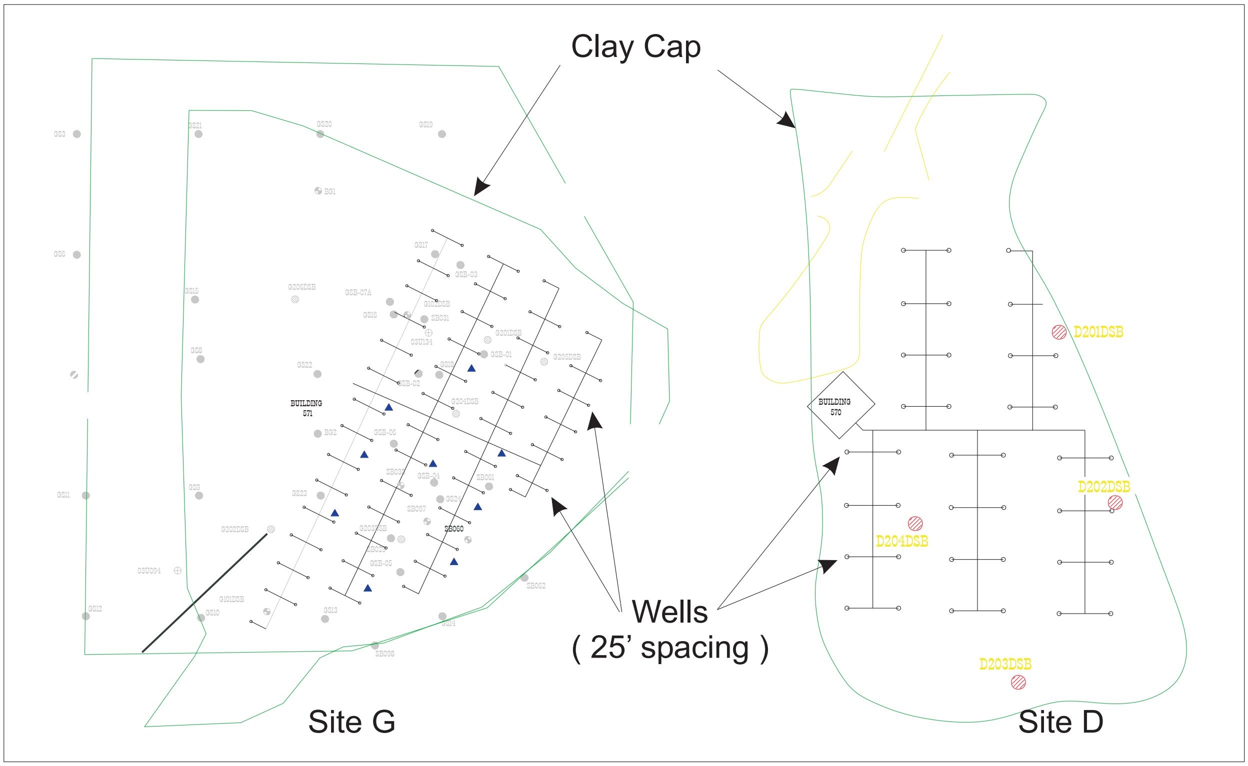

FIGURE 3 Design and Layout of the TCAAP SVE Systems at Sites D and G

Site D

- There are 39 vents constructed of 3-in.-diameter PVC (25-ft vent spacing).
- Vents are screened from approximately 7 ft below the ground surface to the vent bottom (vent depths range from 33 to 54 ft).
- Vent laterals are 8-in.-diameter steel pipe.
- Vent headers connecting the laterals are 18-in.-diameter steel pipe.
- Vent laterals and headers are insulated and heat traced.
- Four 20-hp blowers are connected to the vent header.
- Each blower's capacity is 2,200 cfm at 24 in. of water vacuum.
- Blowers and related electrical/control panels are housed in a heated building.
- The system's air flow rate and vacuum level are measured with a pilot tube at the building.
- Individual vent flow rates are controlled by a butterfly valve at each vent head.
- Access ports are installed at each vent head to allow sampling and vacuum/flow-rate monitoring.

Site G

- There are 89 vents constructed of 3-in.-diameter PVC (25-ft vent spacing).
- Vents are screened from approximately 7 ft below the ground surface to the vent bottom (vent depths range from 23 to 55 ft).
- Vent laterals are 12-in.-diameter steel pipe.
- Vent headers connecting the laterals are 24-in.-diameter steel pipe.
- Vent laterals and headers are insulated and heat traced.
- Four 40-hp blowers are connected to the vent header.

- Each blower's capacity is 5,700 cfm at 24 in. of water vacuum.
- Blowers and related electrical/control panels are housed in a heated building.
- The system's air flow rate and vacuum level are measured with a pilot tube at the building.
- Individual vent flow rates are controlled by a butterfly valve at each vent head.
- Access ports are installed at each vent head to allow sampling and vacuum/flow-rate monitoring.

The SVE system vents were installed by hollow-stem auger drilling. Vents were initially drilled to approximately 30 ft. If visual or field organic vapor screening indicated contamination at the 30-ft depth, the borehole was advanced to 40 ft. If contamination was still evident, vents were extended to a depth of 50 ft, which was the maximum vent depth installed in these initial SVE systems (Wenck Associates, Inc. 1995).

To minimize infiltration of surface water through the source areas, clay caps were installed over both Site D and Site G in late 1985 before SVE system installation. These caps which are shown in Figure 3, consist of 18 in. of clay compacted to a permeability of 1×10^{-8} cm/s with a 6-in. cover of granular native soils (Aberdeen 1991). The caps aid shallow SVE system operation; they cover areas larger than the SVE systems to provide adequate drainage and to ensure that off-cap infiltration does not enter the zone of contamination laterally. The caps restrict the flow of air from the ground surface in the capped areas, thus minimizing the short-circuiting of air flow to the vents and increasing the radius of influence of SVE system vents (Wenck Associates, Inc. 1995).

Measured SVE system flow rates average approximately 5,500 to 6,000 cfm at Site D and 6,000 to 7,000 cfm at Site G. Operating vacuums have typically been 18 to 20 in. of water (Wenck Associates, Inc. 1995). As expected, extraction air temperature was found to be similar to ground temperatures (50 to 65°F). Within this relatively narrow temperature range, increases in extraction air temperature do not seem to result in increased mass removal (Wenck Associates, Inc. 1988b).

2.2.3 System Operation

The SVE systems are currently in their 14th year of operation. System operation at Site D is summarized in Table 1. Long-term operational data are presented and discussed in Section 3.

TABLE 1 Historic System Operations at Site D

Date	Action
11/84-2/85	Pilot study conducted.
1/29/86	Full-scale system started up with 20 of 39 vents partially open.
3/6/86	System shut down by request of the MPCA because of high VOC emissions.
3/86-5/86	Need for VOC emission controls evaluated.
5/6/86	Best available control technology (BACT) for VOC emissions from Site G only requested by MPCA.
7/7/86	System started up with only one blower operating and 16 of 39 vents partially open to reduce VOC emissions (no emissions treatment was required).
7/9/86	Three additional vents (total of 19 of 39 vents operating) partially opened.
7/25/86	Four of the partially open vents fully opened.
9/17/86	All 39 vents at least partially opened.
10/3/86	Second blower turned on.
2/26/87	Third blower turned on.
4/9/87	Fourth blower turned on.
5/28/87	Most of the partially open vents completely opened.
6/25/87	All of the partially open vents completely opened.
8/21/87	System shut off at night and on weekends because of complaints about noise from neighboring residents.
11/5/87	Noise reducers installed.
11/6/87	Continuous operation resumed.
4/27/90	As a result of continued complaints about noise, seven-day timers installed to shut off the system between 10:00 p.m. and 6:30 a.m. on weeknights and on weekends.
5/7/90	Newly constructed, deep vent C1.5 opened.

3 TCAAP DATA

3.1 PRELIMINARY ESTIMATES OF VOC MASS

The initial mass of VOCs in the combined contaminated soils at Sites D and G was estimated to be approximately 20,000 lb (Wenck Associates, Inc. 1985). This estimate was based on existing data on VOC concentrations in soil and the estimated volume of soil containing VOCs. This estimate was used to design the SVE systems; however, at Site D alone, approximately 100,000 lb of VOCs was removed through 1994 (Wenck Associates, Inc. 1995; presented in the appendix).

3.2 DATA FROM SVE OPERATIONS

Historic data on SVE system operations are available from the beginning of system operations through the present. These data are in the form of an operational history, which provides details on when and how the system was operated and also on its measured air concentrations and flow rates. These data are contained in the appendix. At the beginning of system operation, measurements were taken about once a week; later they were taken every two weeks. Daily extraction rates and total extraction volumes were estimated on the basis of measurements of air concentrations and air flow rates, according to the equations below (Wenck Associates, Inc. 1995):

$$M = \frac{C M_w Q}{M_V}, \tag{1}$$

where

M = mass removed (kg/s),

C = volume fraction of the VOCs in air (parts per million or ppm),

M_w = molecular weight of the VOCs (kg/kg mol),

Q = gas flow rate (m^3/s), and

M_V = ideal gas volume (22.414 m^3/kg mol).

Before April 27, 1990, the cumulative extraction volume was computed as:

$$M_{cum} = \frac{\left(M_{daily} + M'_{daily}\right)N}{2} + M'_{cum}, \tag{2}$$

and after April 27, 1990, the cumulative extraction volume was computed as:

$$M_{cum} = \frac{\left(M_{daily} + M'_{daily}\right)N}{2}\left(\frac{5_{opdays}}{7_{wkdays}}\right) + M'_{cum}, \tag{3}$$

where

M_{cum} = cumulative amount of VOCs removed through the sampling date,

M_{daily} = mass of VOCs removed on the sampling date,

M'_{daily} = mass of VOCs removed on the previous sampling date,

N = number of days between the sampling dates, and

M'_{cum} = cumulative amount of VOCs removed through the previous sampling date.

After April 27, 1990, the system was operated only 5 days per week; thus, the cumulative volumes were scaled by five-sevenths.

This approach assumes a linear change between measurement periods and may introduce inaccuracies. However, no data are available to support a more advanced approach.

As shown in Figure 4, the daily extraction volumes varied significantly. This variation was probably partially a result of actual field conditions and partially a result of noise related to sampling error and the fact that sampling was relatively infrequent. Also shown in Figure 4 are the periods when Site D system did not operate.

3.2.1 Mass Removed

The total mass of VOCs removed from Site D through November 3, 1994, was approximately 100,000 lb. The peak mass removal rate for the Site D SVE system was about 1,300 lb/d on February 1, 1986 (third day of operation). The peak mass removal rate for the Site G SVE system was about 4,400 lb/d on February 20, 1986 (first day of operation) (Wenck Associates, Inc. 1995), when only a portion of the soil vents were open. If start-up had occurred with all vents open, peak rates would likely have been higher (Wenck Associates, Inc. 1995). These data are not included in the appendix. The appendix data begin on March 6, 1986, when construction operations were complete and normal operations began.

As shown in Figure 4, the mass removal rate at Site D in 1998 was approximately 2 lb/d and decreased two to three orders of magnitude from the initial rate. Cumulative mass removal is shown in Figure 5. On a mass basis, the VOCs removed at Site D consisted mainly of TCE and TCA. The relative percentages of these compounds varied but typically averaged 80% TCE and 20% TCA (Wenck Associates, Inc. 1995).

In May 1989 (after approximately three years of SVE system operations), soil borings were drilled at Site D to evaluate the effectiveness of the SVE systems (Weston 1994). The borings were drilled between depths of 31 and 36 ft (approximate depth of most vents at Site D), and samples were collected for laboratory analysis approximately every 10 ft.

Results indicated that the Site D SVE system effectively reduced VOC concentrations in the upper-zone soils. Pretreatment concentrations of TCE and TCA in soil were in the range of tens to hundreds of micrograms per gram. The samples from the 1989 borings showed contaminants in a range of approximately 0.001 to 0.029 µg/g. After approximately three years of operation, there was a reduction of approximately four to five orders of magnitude in measured concentrations of contaminants (Wenck Associates, Inc. 1995).

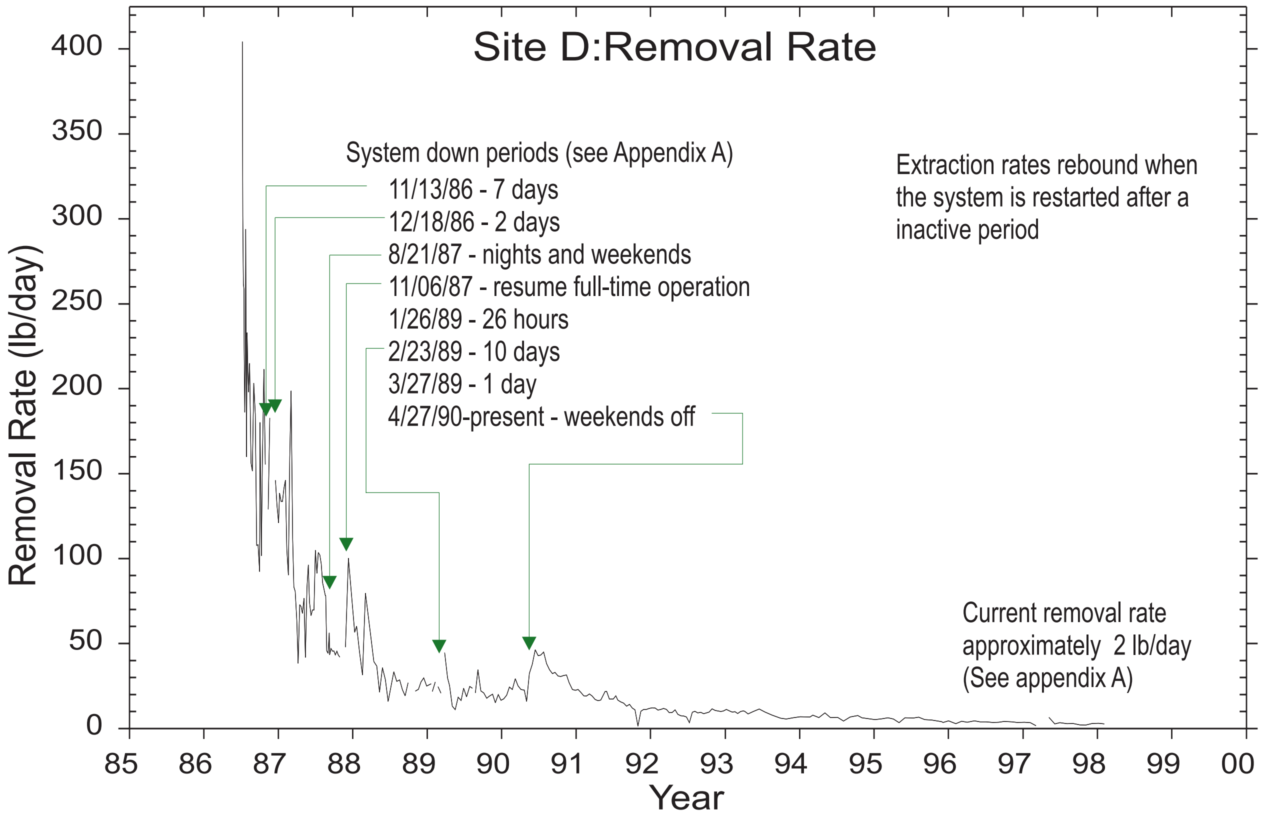

FIGURE 4 Mass Removal Rates for Site D

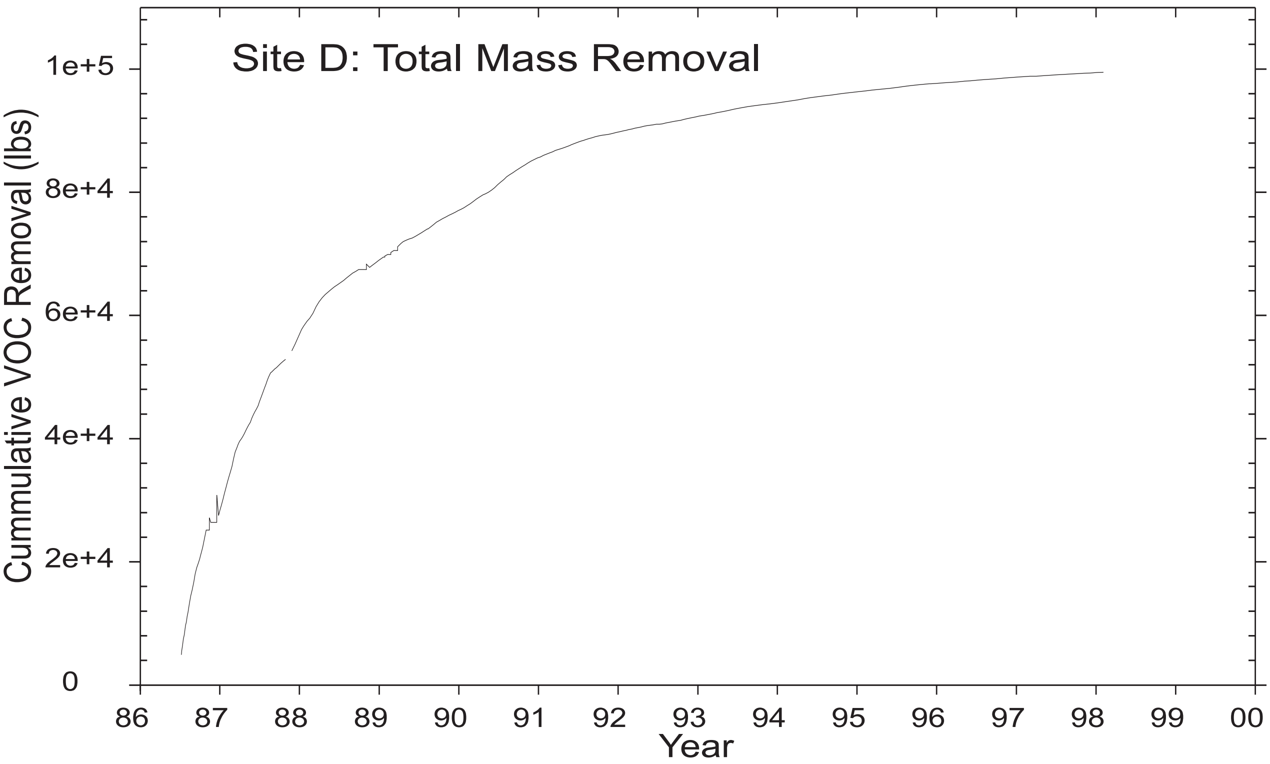

FIGURE 5 Cumulative Mass Removal for Site D

Deeper soil borings were also drilled at Site D. Contaminant concentrations were elevated in the southern portion of the SVE system. One soil boring completed as a soil vent with a screened interval of 125 to 150 ft was designated "C1.5." After its installation, the extraction flux doubled from approximately 20 to 40 lb/d (Wenck Associates, Inc. 1995). After about 10 months, system extraction fluxes returned to previous levels (Wenck Associates, Inc. 1995).

Samples from Site G showed similar results in the shallow zones, although reductions in contaminant concentrations were not quite as large, probably because the different soils that exist near the surface at Site G have a lower permeability and higher organic carbon content. Results from additional Site G borings showed no deep contamination (Wenck Associates, Inc. 1995).

3.2.2 Estimated Zone of Effective Influence

As a result of pilot study work, the design criterion for vent spacing was chosen to be 25 ft, which implies a 12.5-ft radius of influence. However, it was recognized that this spacing was conservative (Wenck Associates, Inc. 1995). A modeling study conducted by Colorado State University in 1989 indicated that the horizontal radius of influence was greater than 25 ft and that the SVE system's zone of influence when all vents were operating was almost the same as the zone when half or even one quarter of the vents were operating (while the same total system flow rate was maintained). The horizontal zone of influence for full system operation at Site D was shown to be at least 60 ft from the outermost line of vents. On the basis of this study, the radius of influence for a single vent can be 30 to 50 ft horizontally (Eisenbeis et al. 1989). Wenck Associates, Inc. (1995) states:

> *Based on theoretical derivations of flow fields for air extraction from porous media, the vertical extent of influence for the SVE systems is likely to be at least equal to the horizontal radius of influence if soil conditions are homogeneous. Given that the full system zone of influence is at least 60 feet horizontally, the estimated vertical zone of influence would be 60 feet below the bottom of the extraction vents. Thus for Site D, the vertical influence would be approximately 95 feet below ground surface (vent depths of approximately 35 feet plus 60 feet).*

However, these calculations do not consider the effects of the clay caps and the interaction of the wells in the well field. This interaction can significantly extend the vertical range of influence.

4 MODELING

Site D was the main focus of this modeling study. This site was used for other field studies, especially during the SVE system design stage. Colorado State University conducted several tests on the system and also developed an air flow model of the system (Eisenbeis et al. 1989). While the modeling effort discussed here focuses on site D, the results should generally apply to Site G and even more generally to other SVE installations.

The computer code T2VOC was selected for evaluation in this study on the basis of a review of the literature on available models and capabilities. T2VOC is a numerical simulator that can compute three-phase, three-component, nonisothermal, three-dimensional, heterogenous transport. The code, which was developed at Lawrence Berkeley Laboratory (Falta et al. 1995), was designed to model near-surface remediation processes such as steam-sweeping and SVE.

T2VOC models a multiphase system composed of three mass components: air, water, and a slightly water-soluble organic chemical (Falta et al. 1992a). Any of these components may be present in any of the phases (air, water, oil). Transport occurs by advection in all phases and also by gaseous diffusion in the air phase. All phases are in local chemical and thermal equilibrium. No other chemical reactions are modeled. The transform mechanisms for the organic chemical between the various phases include (1) evaporation and boiling, (2) dissolution into the water phase, (3) condensation from the air phase to the oil phase, and (4) equilibrium partitioning of the organic chemical between the solid, water, and gas phases. The transform mechanisms for water include (1) evaporation and boiling, (2) dissolution into the oil phase, and (3) condensation from the gas phase. The transform mechanism for air is equilibrium partitioning between the water and gas phases (Falta et al. 1992). The code includes modeling capabilities for heat transfer and heat transport, which were not used in this study. For a detailed description of the governing equations, code formulation, and capabilities, see Falta et al. (1992a,b, 1995).

4.1 GOVERNING EQUATIONS

This section uses equations from, and closely follows, Falta et al. (1995).

The T2VOC code is nonisothermal and contains three mass components. Three mass balance equations and an energy balance equation are required to define this system fully. The balance equations can be written for each component κ (κ = w for water, a for air, c for chemical, h for heat) in an integral for a flow region V_n that has a surface area Γ_n as follows (Falta et al. 1995):

$$\frac{d}{dt}\int_{V_n} M^{\kappa} dV_n = \int_{G_n} F^{\kappa} \times n dG_n + \int_{V_n} q^{\kappa} dV_n \ , \tag{4}$$

where

M^{κ} = mass of component κ (κ = w, a, c) per unit of porous media volume,

F^{κ} = mass flux of component κ into V_n,

n = inward unit normal vector, and

q^{κ} = rate of heat generation per unit volume.

4.1.1 Accumulation Terms

The mass accumulation terms for water and air (κ = w, a) sum over three phases (β = phase, g = gas, w = aqueous, n = NAPL).

$$M^{\kappa} = \phi \sum_{\beta} S_{\beta} \rho_{\beta} X_{\beta}^{\kappa}, \tag{5}$$

where

ϕ = porosity,

S_{β} = pore volume fraction (saturation) of phase β,

ρ_{β} = density of phase β, and

X_{β}^{κ} = mass fraction of component κ in phase β.

The chemical is allowed to sorb onto the solid phase according to the equations governing linear equilibrium partitioning:

$$M^{c} = \rho_b \rho_w X_w^{c} K_D + \phi \sum_{\beta} S_{\beta} \rho_{\beta} X_{\beta}^{c}, \tag{6}$$

where

ρ_b = dry bulk density of the soil,

X_w^c = chemical mass fraction in the aqueous phase, and

K_D = solid-aqueous distribution coefficient for the organic chemical.

The first term on the right-hand side of Equation 6 can be written as

$$C_s^c = \rho_b K_D C_w^c , \tag{7}$$

where $C_w^c = \rho_w X_w^c$ is the chemical concentration in the aqueous phase. If Equation 7 is used, some water must be present in the system, and the soil must be preferentially wetted by the aqueous phase. Using this equation can lead to errors in very dry systems.

Sorption of organic chemicals appears to depend on the amount of organic carbon in the soil. Thus, K_D is often defined as

$$K_D = K_{oc} f_{oc} , \tag{8}$$

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the organic carbon fraction in the soil.

Equation 6 is sometimes rewritten in an alternative form by using a retardation factor. If $\phi S_g \rho_g X_g^c$ is extracted from Equation 6, which is a standard form for gas accumulation with a single phase and no sorption, the following equation can be written:

$$M^c = \phi S_g \rho_g X_g^c R_g^c , \tag{9}$$

where R_g^c is the retardation factor for gas-phase transport. In a two-phase system (no NAPL present), this is given by

$$R_g^c = 1 + \frac{S_w C_w^c}{S_g C_g^c} + \frac{\rho_b K_D C_w^c}{\phi S_g C_g^c} . \tag{10}$$

This study does not consider the effects of heat transport. These equations are presented in Falta et al. (1995).

4.1.2 Flux Terms

The mass flux of the three components (water, air, chemical) includes a summation from each of the three possible phases (gas, aqueous, NAPL):

$$F^{k} = \sum_{\beta} F_{\beta}^{\kappa} . \tag{11}$$

The aqueous phase and NAPL phase fluxes, $F_{\beta}^{\kappa} = X_{\beta}^{\kappa} F_{\beta}$, are given by a multiphase extension to Darcy's law:

$$F_{\beta} = -k \frac{k_{r\beta} \rho_{\beta}}{\mu_{\beta}} \left(\nabla P_{\beta} - \rho_{\beta} g \right) , \tag{12}$$

where

k = absolute permeability,

$k_{r\beta}$ = relative permeability of phase β,

μ_{β} = phase β dynamic viscosity,

P_{β} = fluid pressure in phase β, and

g = gravitational acceleration vector.

Aqueous-phase and gas-phase pressures are related by

$$P_{w} = P_{g} + P_{cgw} , \tag{13}$$

where $P_{cgw} < 0$ is the gas-water capillary pressure. The NAPL pressure is related to the gas-phase pressure by

$$P_{n} = P_{g} + P_{cgn} , \tag{14}$$

where $P_{cgn} < 0$ is the gas-NAPL capillary pressure. Most geologic materials have a wetting order of (1) aqueous phase, (2) NAPL phase, and (3) gas phase. Thus, the gas-water capillary pressure is usually stronger (more negative) than the gas-NAPL pressure. The NAPL-water capillary pressure, P_{cnw}, from Equations 13 and 14 is

$$P_{cnw} = P_{cgw} - P_{cgn} = P_w - P_n. \tag{15}$$

The mass flux in the gas phase includes both advection and diffusion of each of the gas-phase components and can be described by the equation

$$F_g^{\kappa} = -k_o \left(1 + \frac{b}{P_g}\right) \frac{k_{rg}\rho_g}{\mu_g} X_g^{\kappa} \left(\nabla P_g - \rho_g g\right) + J_g^{\kappa}, \tag{16}$$

where k_o is the absolute permeability at large gas pressures (equal to the single-phase liquid permeability) and *b* is the Klinkenberg *b*-factor, which is used to model slippage of the gas phase, effectively increasing the gas permeability at low pressures. J_g^k is the diffusive mass flux of component κ in the gas phase.

The diffusive mass fluxes of water vapor and organic chemical vapor, J_g^c and J_g^c, are described by

$$J_g^{\kappa} = -\phi S_g \tau_g D_g^{\kappa} \rho_g \nabla X_g^{\kappa}, \tag{17}$$

where D_g^{κ} is the multicomponent molecular diffusion coefficient of component κ in the gas phase when no porous medium is present. τ_g is the gas-phase tortuosity found by using

$$\tau_g = \phi^{1/3} S_g^{7/3}. \tag{18}$$

Water and chemical diffusive fluxes are described by Equation 17. The air diffusive flux, J_g^a, is determined by

$$J_g^a + J_g^w + J_g^c = 0. \tag{19}$$

Equation 19 ensures that the total gas-phase diffusive mass flux, summed over the three components, is zero with respect to the mass average velocity. Thus, the total gas-phase mass flux is the product of the gas-phase Darcy velocity and the gas-phase density.

4.1.3 Sink and Source Terms

T2VOC has the ability to approximate biodegradation of the VOCs in the aqueous phase according to the exponential decay law:

$$dM_w^c = -\lambda M_w^c dt \tag{20}$$

where λ is the rate constant and is related to the half-life of the VOC, $T_{1/2}$, as $\lambda = \ln 2/T_{1/2}$. This is incorporated into the governing Equation 4 with a sink term ($q^c < 0$):

$$q^c = -\lambda M_w^c = -\lambda \phi S_w \rho_w X_w^c . \tag{21}$$

T2VOC incorporates a number of sink-source term options to specify the production or injection of either fluids or heat. Any of the three mass components (air, water, chemical) can be injected in either a constant or time-dependent fashion. Specific enthalpy of the injected fluid can also be either constant or time-dependent. In addition, heat sink-source terms without mass injection can be included and be either constant or time-dependent.

Fluid can be produced from an element at either a constant or time-dependent mass rate. The phase composition of the fluid can be determined by the relative mobilities of the various fluids in the element, or it can be specified to be the same as the phase composition of the producing element. The mass fractions of the components in the produced phases are the same as the corresponding mass fractions in the producing element.

T2VOC also includes a deliverability model for extraction wells where production occurs against a prescribed well bore pressure, P_{wb}. This method is the one used to model vapor extraction wells in the SVE system. The mass production rate of phase β from a grid block with a phase pressure $P_\beta > P_{wb}$ is described by

$$q_\beta = \frac{k_{r\beta}}{\mu_\beta} \rho_\beta PI \left(P_\beta - P_{wb} \right). \tag{22}$$

For radial flow, the productivity index, *PI*, for a given layer is given by

$$PI_l = \frac{2\pi \left(k\Delta z_l \right)}{\ln\left(r_e / r_w \right) + s - 1/2}, \tag{23}$$

where

Δz_l = layer thickness,

r_e = grid block radius,

r_w = well radius, and

s = skin factor.

If the well is producing from a grid block that does not have a cylindrical shape, *PI* can be approximated by using an effective radius as follows:

$$r_e = \sqrt{A/\pi}, \tag{24}$$

where *A* is the grid block area.

The rate at which each mass component is produced is described by

$$\hat{q}^{\kappa} = \sum_{\beta} X_{\beta}^{\kappa} q_{\beta}. \tag{25}$$

For wells that are completed in more than one model layer, T2VOC corrects the flowing well bore pressure to account for gravity and other effects. Details can be found in Falta et al. (1995).

For numerical simulations, the nonlinear coupled equations described by Equation 4 are descretized in space and time. The space discretization is performed by using an integral finite difference method, which is similar to conventional finite difference discretization schemes but offers more flexibility. Time discretization is fully implicit and uses first-order backward finite differences. A Newton-Raphson iteration is used to solve the nonlinear equations. The resulting linear equations are then solved by a number of user-chosen methods that include both direct solution techniques and frontal solvers. Details on the various solvers are available in Falta et al. (1995).

T2VOC also has the capability to include double and multiple porosity formulations.

4.2 MODEL DEVELOPMENT[1]

4.2.1 Conceptual Model

To develop the numerical model of the Site D SVE system, the TCAAP site geology was conceptualized as a layered system. The top layer consisted of the clay cap and, outside the cap, a relatively clean, fine sand. The next vertical 7 m of the model were assumed to be a mixed clayey-sand environment such as that documented by field investigations at Site G. For some model simulations, the stratigraphy was implemented as a layered system with both sand and clayey-sand layers. For other model runs, a more heterogeneous implementation was developed, in which clayey-sand, silty-sand, and sand materials were assigned to the various elements in a random process. This work is detailed below in the discussions about specific runs. Below the 7 m of mixed sand-clay geology, the remainder of the model was assumed to be clean, fine sand. The water table was located approximately 34 m below the surface.

Figure 6 shows the general conceptual model described above. The top 7 m of the model are represented by seven vertical elements on a 1-m vertical spacing in the computational grid. Below this, the spacing gradually increases until the water table is met. Horizontal descritization is 3 m by 3 m. Details of the mesh geometry are described below.

4.2.2 Model Symmetry

Figure 7 shows a plan view of the Site D SVE system. Also shown is the lateral extent of the model. The area modeled by T2VOC is the square shown in the figure. The lower portion of the SVE system has a twofold symmetry. The modeled square can be flipped along its left side or along its top or bottom edge. Any of these transformations result in a model identical to the one used (if the geology of the site is symmetrical). Geologic investigations of the site determined that the subsurface was relatively homogeneous (Aberdeen 1991); thus, the assumption of symmetry is valid.

Because the size of a mesh that can be solved by current computer systems is limited, an assumption of symmetry was required to develop the model. The modeled area is approximately 1/13th (3 of the 39 vents) of the entire SVE domain. A model 13 times as large as the one used in this study would have been impractical for T2VOC to solve on available computer systems because of time limitations. Minimal investigations on using larger grid sizes (more elements) were conducted, but the computer code was never able to run with these larger grids. Even though only 1/13 of the area was represented in this study, an IBM SP supercomputer used up to 3 days of computer time to simulate the entire 15-year period of SVE operations.

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[1] In this report, all field-measured data are in English units, while all model-generated data are metric.

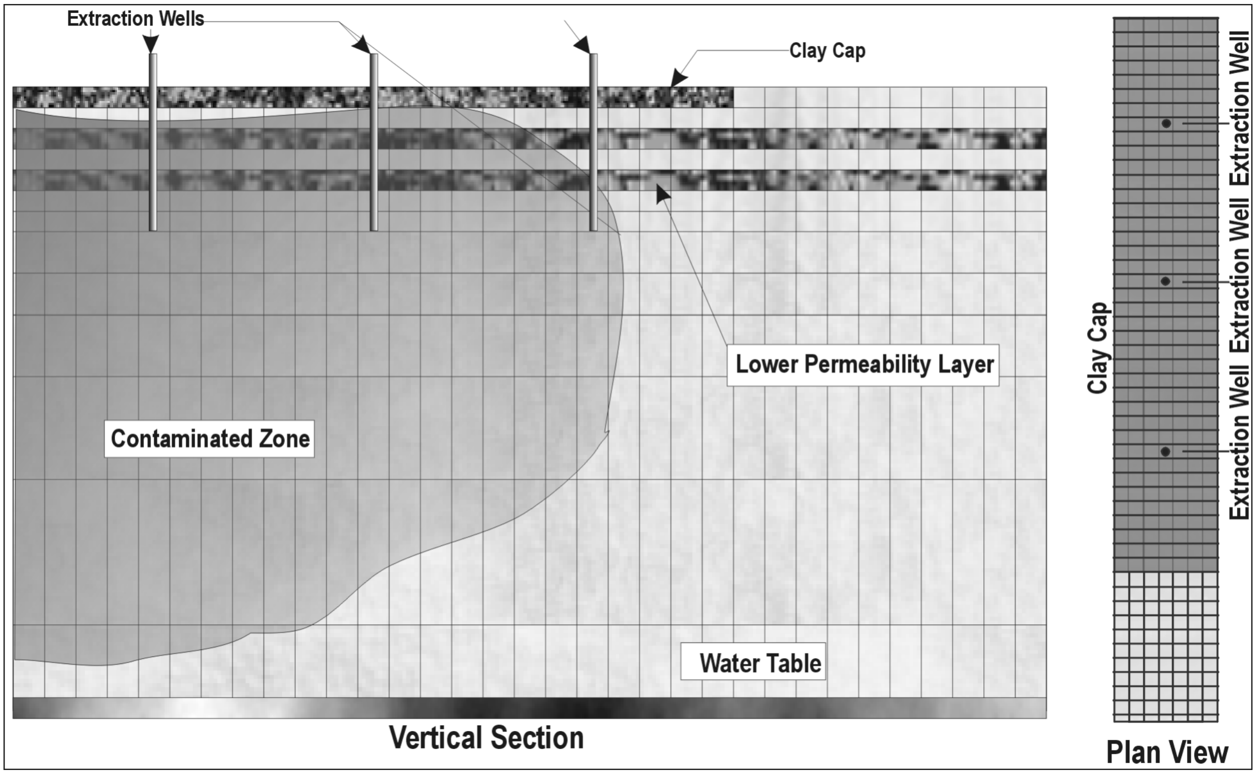

FIGURE 6 Conceptual Model and Computation Grid for the T2VOC Simulation

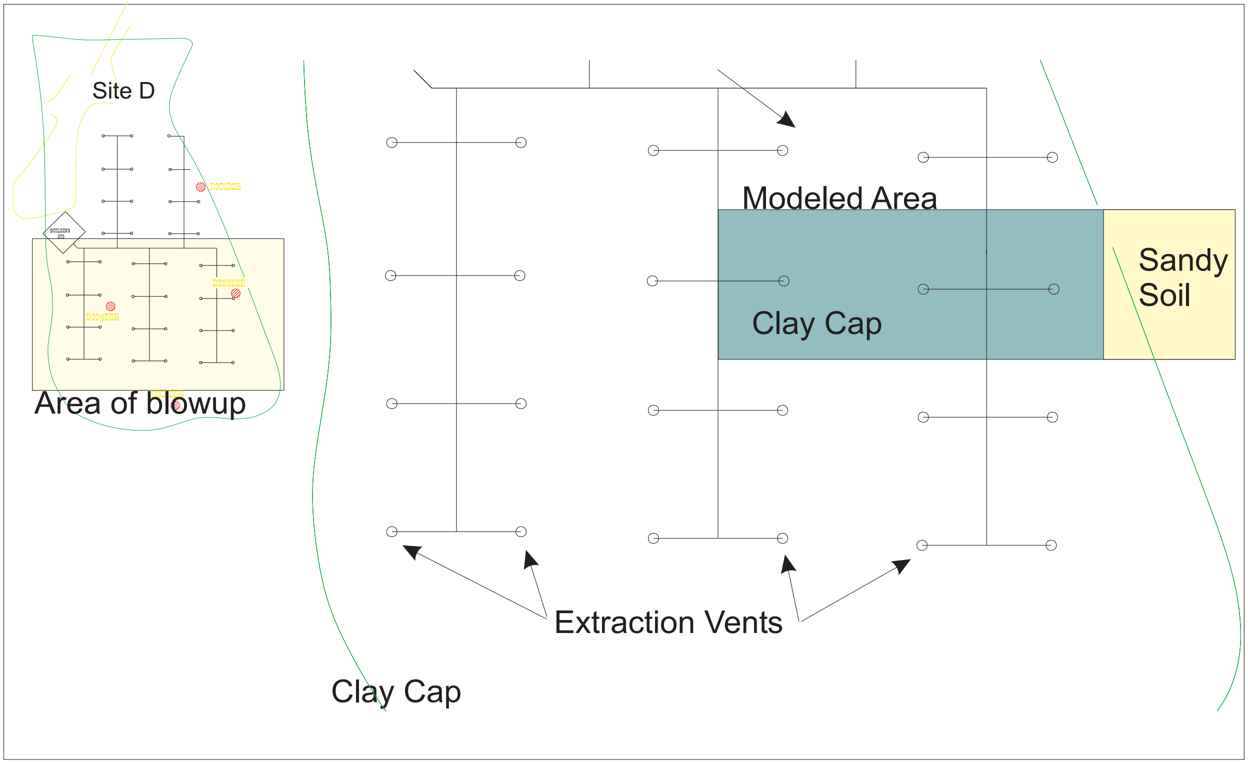

FIGURE 7 Site D Layout Showing the Area Modeled in the T2VOC Simulation

Multiphase, multicomponent flow is described by a set of equations that are highly nonlinear. Significant numerical difficulties occur when large systems of nonlinear equations need to be solved. By minimizing the model size, the model could be run in a reasonable amount of time on available computer systems and still include three full model phases.

4.2.3 Mesh Geometry

A T2VOC model of the TCAAP Site D was implemented by using a three-dimensional mesh that enclosed an area 33 m in the X direction, 7 m in the Y direction, and 34 m in the Z direction. This mesh is shown in Figure 6.

The mesh was divided into 33 components in the X direction, 7 components in the Y direction, and 13 vertical layers, as shown in Figure 6. A number of different materials were assigned to the various grid elements and used in simulation runs. Details on materials used in each run and the spatial distribution of the materials assigned to the elements are provided in the following sections.

4.3 MATERIAL DESCRIPTION

The parameters used to define the geologic materials used in the model are listed in Tables 2 and 3. Table 2 lists the general parameters that were the same for all the materials; Table 3 lists parameters that were different.

The relative permeability and capillary pressure parameters used to define the constitutive relationships for fluid movements in this study were taken from an article by Carsel and Parish (1988) and modified slightly. A number of studies (e.g., Guymon 1994; Kaleris and Croise 1999) use soil parameters from Carsel and Parish (1988); however, the values cited in the Carsel and Parish article can be misleading. The article uses the descriptive term "clay" for a soil that contains only 30% clay-size particles. It also uses the descriptive term "sandy-clay" to describe a soil that is approximately 35% clay and has a higher residual water content than that

TABLE 2 General Material Parameters

Parameter	Value
Compressibility (Pa^{-1})	0
Expansivity (1/temperature)	0
Tortuosity	0.25
Klinkenberg parameter (Pa^{-1})	0.005
Rock grain density (kg/m^3)	2,650
Formation heat conductivity (saturated) (W/m)	3.1
Formation heat conductivity (dry) (W/m)	3.1
Rock grain-specific heat (J/kg)	1,000

TABLE 3 Material-Specific Parameters[a]

Parameter	CLAY1[b]	DRT_1	MAT_1	MAT_2	MAT_3	MAT_4	DRT_2
Organic carbon fraction	0.000	0.001	0.005	0.005	0.001	0.001	0.001
Porosity	0.59	0.30	0.59	0.30	0.30	0.30	0.30
Permeability (m^2)	2.2×10^{-16}	1.6×10^{-11}	2.2×10^{-16}	2.1×10^{-13}	1.6×10^{-12}	1.6×10^{-11}	1.6×10^{-11}
Relative permeability parameters[c]							
S_m	0.109	0.109	0.109	0.110	0.088	0.078	0.078
n	1.419	1.56	1.419	1.275	1.36	1.56	1.56
Capillary pressure function parameters							
S_m	NA[d]	0.109	0.110	0.110	0.088	0.078	0.078
n	NA	1.56	1.275	1.275	1.36	1.56	1.56
α_{gn}	NA	9.9	20.8	10.8	9.9	9.9	9.9
α_{nw}	NA	11.0	15.0	7.0	11.0	11.0	11.0

[a] Different combinations of materials were used for different computational scenarios.

[b] This was the material used for the cap.

[c] Values for relative permeability parameters were taken from Parker et al. (1987).

[d] NA = not applicable.

of the “clay” soil. For this study, field-measured permeabilties for TCAAP were compared to the permeabilties given in Carstel and Parrish, and parameters from the soil that matched those of Carstel and Parish most closely were used.

This study, in addition to using the literature cited above, used the 1987 study performed by Colorado State University to help define material parameters. In the Colorado study, an air-flow model, CSU-GAS, was used to calculate the air-flow field for the TCAAP SVE systems. This study used three different materials and field-measured pressures to develop a calibrated model of the site (Eisenbeis et al. 1989).

The relative permeability functions from Parker et al. (1987) that follow were used to define the three-phase flow problem.

$$
\begin{aligned}
m &= 1 - 1/n \\
\bar{S}_g &= S_g/(1 - S_m) \\
\bar{S}_w &= (S_w - S_m)/(1 - S_m) \\
\bar{S}_l &= (S_w + S_n - S_m)/(1 - S_m) \\
k_{rg} &= \sqrt{\bar{S}_g}\left[1 - \left(\bar{S}_l\right)^{1/m}\right]^{2m} \\
k_{rw} &= \sqrt{\bar{S}_w}\left\{1 - \left[1 - \left(\bar{S}_w\right)^{1/m}\right]^{m}\right\}^{2} \\
k_{rn} &= \sqrt{\bar{S}_l - \bar{S}_w}\left\{\left[1 - \left(\bar{S}_w\right)^{1/m}\right]^{m} - \left[1 - \left(\bar{S}_l\right)^{1/m}\right]^{m}\right\}^{2},
\end{aligned}
\tag{26}
$$

where k_{rw}, k_{rg}, and k_{rn} are the relative permeabilties of the water, gas, and NAPL, respectively, and are limited to values between 0 and 1. S_w is the water saturation, S_g is the gas saturation, and S_n is the NAPL saturation. S_m and n are parameters used to fit the model (Falta et al. 1995). The Parker model is attractive because only two parameters are required; it was used for the majority of the model simulation.

For some initial simulations, a modified version of Stone's model was used (Falta et al. 1995). This model is defined as follows:

$$
\begin{aligned}
k_{rg} &= \left[\frac{S_g - S_{gr}}{1 - S_{wr}}\right]^{n} \\
k_{rw} &= \left[\frac{S_w - S_{wr}}{1 - S_{wr}}\right]^{n} \\
k_{rn} &= \left[\frac{1 - S_g - S_w - S_{nr}}{1 - S_g - S_{wr} - S_{nr}}\right]\left[\frac{1 - S_{wr} - S_{nr}}{1 - S_w - S_{nr}}\right]\left[\frac{1 - S_g - S_{wr} - S_{nr}\left(1 - S_w\right)}{\left(1 - S_w\right)}\right]^{n},
\end{aligned}
\tag{27}
$$

where S_{wr}, S_{nr}, and S_{gr} are the irreducible saturations for water, NAPL, and gas, respectively. The remainder of the variables are as described above. This model requires four parameters but seemed to converge better than the Parker model when doing oil injection.

The three-phase capillary pressure function used in this study was from Parker et al. (1987). Capillary pressures were not considered in the material used to define the clay cap. The Parker model of capillary pressures is as follows:

$$
\begin{aligned}
& m = 1 - 1/n \\
& \overline{S}_w = \left(S_w - S_m\right)/\left(1 - S_m\right) \\
& \overline{S}_l = \left(S_w + S_n - S_m\right)/\left(1 - S_m\right) \\
& P_{cgn} = -\frac{\rho_w g}{\alpha_{gn}}\left[\left(\overline{S}_l\right)^{-1/m} - 1\right]^{1/n} \\
& P_{cgw} = -\frac{\rho_w g}{\alpha_{nw}}\left[\left(\overline{S}_w\right)^{-1/m} - 1\right]^{1/n} - \frac{\rho_w g}{\alpha_{gn}}\left[\left(\overline{S}_l\right)^{-1/m} - 1\right]^{1/n},
\end{aligned}
\tag{28}
$$

where

P_{cgn} = pressure function for two-phase system of gas-NAPL,

P_{cgw} = pressure function for two-phase system of gas-water,

ρ_w = density of water,

g = gravitational acceleration,

α_{gn} = fitting parameter that approximates the residual gas saturation in the gas-NAPL system

α_{nw} = fitting parameter that approximates the residual NAPL saturation in the NAPL-water system.

The remainder of the parameters are defined above.

Care must be taken when these constitutive relations are used because although the different models use the same notation for the required parameters, they use different values. For example, a sand might require an *n* value of 1.3 in the Parker relative permeability model and a value of 3.1 in the modified Stone model. In addition, the *n* value used for a given material in the Parker relative permeability function may be different from the *n* value used for the same material in the Parker relative capillary pressure function. The sensitivity of the simulation to small changes in these parameters was not evaluated in the study, but the impact of larger variations (e.g., sand versus clayey-sand) was studied.

4.4 EXTRACTION WELLS

Three extraction wells were included in the model, as shown in Figures 6 and 7. The wells are screened and thus active in the first layer immediately below the clay cap (model Layer 2) and extend to model Layer 7, a depth of 7 m. Extraction fluxes for the various fluid constituents were calculated by using a deliverability model (see Equation 29). A constant pressure of 98,000 Pa was assigned to the wells, and an atmospheric pressure of 101,035 Pa was used as a boundary condition. The result is a well vacuum of approximately 3,000 Pa (13.0 in. of water), depending on the depth of the screen.

The deliverability model computes production against a prescribed flowing wellbore pressure, P_{wb}, with a productivity index, *PI* (Falta et al. 1995). The mass production rate of phase β, q_β, from a grid block with phase pressure $P_\beta > P_{wb}$ is

$$q_\beta = \frac{k_{r\beta}}{\mu_\beta} \rho_\beta PI \left(P_\beta - P_{wb} \right), \tag{29}$$

where

$k_{r\beta}$ = relative permeability of material r,

μ_β = viscosity of phase β, and

ρ_β = density of phase β.

For radial flow conditions, the value of *PI* is given by

$$(PI)_l = \frac{2\pi (k\Delta z_l)}{ln(r_e / r_w) + s - 1/2}, \tag{30}$$

where

Δz_l = layer thickness,

$k\Delta z_l$ = permeability-thickness product in layer l,

r_e = grid block radius,

r_w = well radius, and

s = skin factor.

If the well is producing from a noncylindrical grid block, an approximate *PI* can be computed by using the effective radius

$$r_e = \sqrt{A/\pi}, \tag{31}$$

where *A* is the grid block area (Falta et al. 1995). Wells were assumed to be 3 in. in diameter. The effective radius was computed by using the horizontal area of a computational cell, 9 m^2.

4.5 INITIAL CONDITIONS

Numerical modeling of three-phase flow requires an accurate description of the initial conditions. Because the problem is highly nonlinear, if initial conditions are not relatively accurate, numerical instability can result. For the large grids used in this study, if the initial conditions were not consistent, the model would not run. To define the initial conditions for this model, a one-dimensional model of the soil system was developed and exercised with a series of boundary conditions.

Calculation of the initial conditions was a multistep process. The one-dimensional model that was used to compute the initial conditions is shown in Figure 8. Initially the elements on the top and bottom of the soil column were designated as no-flow elements. The element immediately above the bottom of the soil column was assigned a constant boundary condition with a water saturation value of 50% (Figure 8). This boundary condition represents a field condition in which the water table is within the second element of the soil column. This configuration was run until equilibrium conditions existed. At the completion of this model run, the conditions in the top and bottom elements were noted and used as boundary conditions for the next run.

The one-dimensional model was next run to define the initial conditions calculated boundary within the soil column under these calculated boundary conditions. The model was relatively insensitive to starting water saturation values when the values were above residual saturation. The model converged quickly to an equilibrium condition. However, initial pressures in the boundary blocks needed to be close to actual equilibrium pressures or numerical problems occurred. On the basis of the results from this first run, the top and bottom elements of the one-dimensional model were assigned the pressure and saturation conditions calculated in the first one-dimensional model run, and the model was run again. The resulting saturation and pressure values were used to define the initial conditions for the soil columns in the full model. This process was done for both the area under the clay cap, with a clayey-sand material assigned to the top element, and for the area outside the clay cap, with a sand material assigned to the top element.

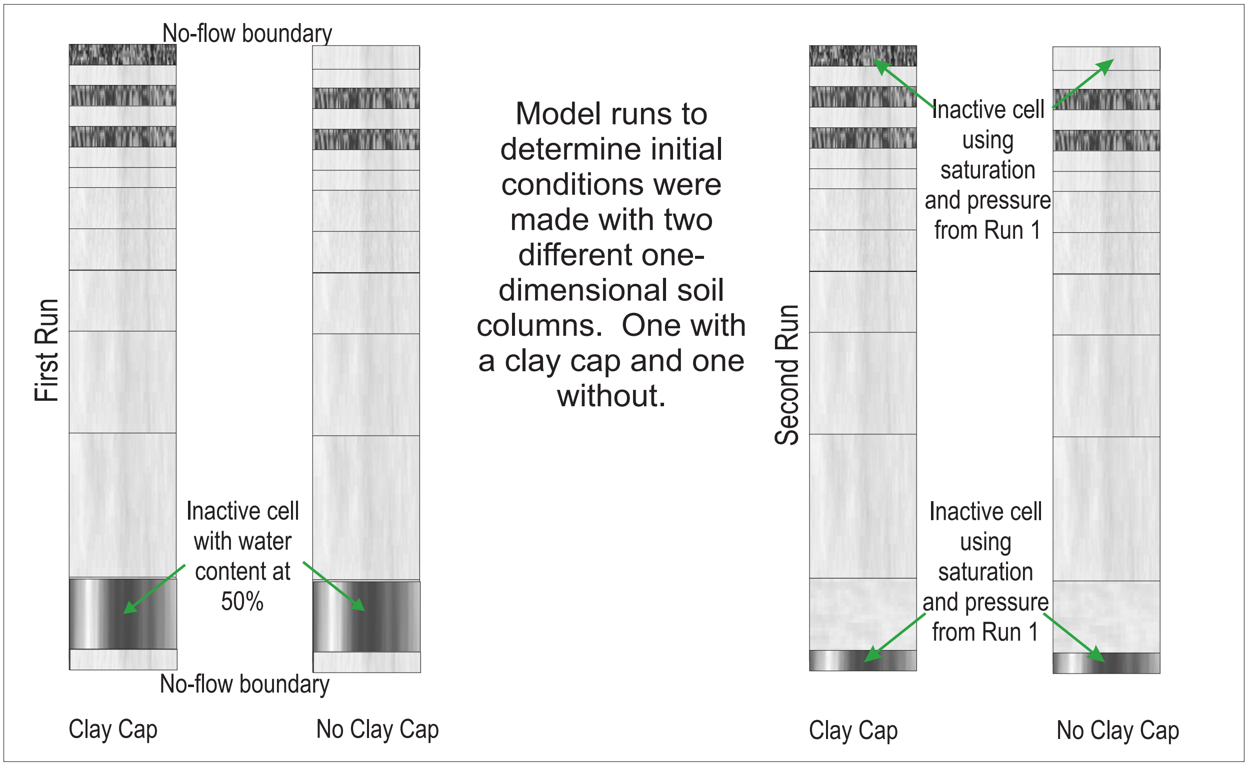

FIGURE 8 One-Dimensional Soil Column and Steps Used to Compute the Initial Conditions

4.6 NUMERICAL SOLVERS

T2VOC contains four numerical solvers: (1) The MA28 sparse direct solver; (2) DSLUBC, a bi-conjugate gradient solver; (3) DSLUCS, a preconditioned conjugate gradient solver; and (4) DSLUGM, a generalized minimum residual preconditioned conjugate gradient solver. A number of short initial runs were made to determine which solver was most efficient for this problem. The DSLUGM solver nearly always converged for any conditions; however, many cases required extremely small time steps, which rendered the DSLUGM code inefficient for larger runs. The DSLUCS solver proved to be most efficient in the majority of the cases and was used for nearly all runs. However, the DSLUGM solver was used to model the injection of oil into the subsurface. Subsurface injection of oil resulted in sharp oil-saturation and pressure fronts. Experience showed that under such conditions, the model required the DSLUGM solver for convergence.

4.7 CHEMICAL CONTAMINANT PROPERTIES

As described above, TCE is the cause of the majority of the contamination at the TCAAP site. The T2VOC code can model only one NAPL at a time. The majority of runs used TCE as the

NAPL. In addition, other contaminants such as TCA, toluene, and DCE were modeled as shown in Table 4.

T2VOC uses a series of complex equilibrium equations to define the phase transformations of NAPL in the subsurface. Details of these models can be found in Falta et al. (1995). In addition, Reid et al. (1987) is the source for the majority of the parameters used to define the various NAPLs for the T2VOC model.

4.8 SIMULATION APPROACH

The modeling was done in phases. T2VOC is configured so that at the end of a model run, a restart file is created. This file can be used for initial conditions in the next model run. Each time a material distribution in the model was changed, T2VOC was run for one year to establish equilibrium water and air saturation-pressure values. Initial conditions were also regenerated when any material properties were changed.

This study did not attempt to develop a calibrated model of the TCAAP Site G SVE system. Rather the model was configured to match the Site G SVE system as much as possible, and extensive sensitivity studies were conducted to determine which parameters were most important in defining SVE system behavior. It was found that SVE system behavior could be divided into short-term behavior (less than three or four years) and long-term behavior (more than six or seven years). Both TCAAP systems exhibited a rapid decline in extraction rate in the short term and an asymptotic approach to a nonzero extraction rates in the long term. This behavior was used as a base case for evaluating and validating the model results.

Field investigations showed that initial TCE contamination levels were between 100 and 1,000 mg/kg. For this study, the 1,000-mg/kg value was used. Two different approaches were used to introduce the contaminant into the system. The first approach used a series of injection wells that introduced NAPL directly into the grid blocks. This was done for Layers 2 through 7 in the area beneath the clay cap. Injection generally occurred over a period of approximately one week, with injection rates chosen so that the total amount of NAPL introduced into the cell would result in a NAPL concentration of approximately 1,000 mg/kg. Following this injection period, the system was run without any additional stresses to allow the three-phase oil-water-air system to come to equilibrium. This approach was problematic. One problem was the limitation of the T2VOC computer code, which allows only 50 injection wells to be operational at any time. Since injection had to occur in each gridlock within the top six layers, many more injection wells were required. This problem was solved by using several simulation runs to introduce oil into the system, one run for each model layer. The oil injection process also experienced some numerical difficulties.

TABLE 4 Properties of the NAPLs Used in the Study

Constant	TCE	TCA	Toluene
Molecular weight M^c_{wt} (g/mol)	131.4	98.96	92.14
Critical temperature T_{crit} (K)	572.0	566.0	591.8
Critical pressure P_{crit} (bars)	50.5	43.0	41.0
Critical compressibility Z_{crit}	0.265	0.0259	0.263
Critical volume V^c_{crit} (cm^3/mol)	256.0	293.1	316.0
Normal boiling point T_b (K)	360.4	347.2	383.8
Pitzer's acentric factor *w*	0.213	6.217	0.263
Dipole moment η_d (debyes)	0.9	1.7	0.4
Aqueous solubility χ^c_w	1.51×10^{-4}	9.7×10^{-5}	1.01×10^{-4}
Vapor pressure constants			
a	-7.38190	-7.313	-7.28907
b	1.94817	2.046	0.38091
c	-3.03294	-3.775	2.83433
d	-5.34536	-0.04548	-2.29168
Ideal gas heat capacity constants			
a	30.17	6.32	24.55
b	0.2287	0.343	0.5125
c	-2.229×10^{-4}	-2.96×10^{-4}	-0.276×10^{-3}
d	8.244×10^{-8}	9.79×10^{-8}	0.49×10^{-7}
Reference liquid density T_r = 293.0 K (kg/m^3)	1,462.0	1,339.0	867.0

The second approach used to introduce oil into the simulation model modified the T2VOC restart files. Restart files allow the user to define the amount of oil present in a cell in a number of different methods, depending on the amount of contaminant present. If NAPL exists as a separate phase, water and air saturation values are specified, and the code computes oil saturation. If oil concentrations are such that oil exists only (1) sorbed onto the solid phase, (2) dissolved into the aqueous phase, or (3) evaporated into the gas phase, the aqueous-phase oil concentration is specified as a mole fraction. Field samples at the TCAAP sites indicated that contamination existed in a range below 1,000 mg/kg. At these levels, oil does not exist as a separate phase but exists (1) sorbed onto the solid phase, (2) dissolved into the aqueous phase, or (3) evaporated into the gas phase.

Field data did not characterize existing contamination at the TCAAP site well. The volumes of contaminants extracted by the SVE system have exceeded the initial estimates of the total amount of contaminants in the subsurface by a factor of about five. Thus, there are large uncertainties about the contamination level that existed in the subsurface when the SVE systems were put into operation.

An initial contaminant concentration in the gas phase of 0.02 molar fraction was used to simulate field conditions. Depending on the amount of organic carbon present in the soil materials, this simulation resulted in different total contamination volumes in the study area.

It was found that the system response was more sensitive to the fraction of organic carbon present in the soil materials than to the initial aqueous-phase concentration. Because of these model sensitivities, and the large uncertainties in the actual field values, no further changes were made in the initial level of contamination.

5 SIMULATION RESULTS

In this study, a large number of computer simulations were run to evaluate the TCAAP SVE system under various scenarios. Detailed results from the runs are presented in this section. A number of additional simulations were performed to determine the numerical characteristics of the problem, choose the appropriate numerical solver, and modify the T2VOC source code. Detailed results from these additional runs are not presented but are instead briefly discussed in various sections of this report.

For this study, no attempt was made reproduce the periods when the field system was not operating. While the effects of these relatively short shutdown periods can be seen in historical data, they are not significant for predicting long-term trends. The period following April 27, 1990, the beginning of nonoperational weekends, when the system only operated five days per week, was of interest. However, the VOC extraction rates were so low during this period that the impacts of this operational change were expected to be minimal.

For this study, a number of changes were made to the T2VOC source code. First, the source code was modified to allow larger-than-standard arrays. The mesh size used for this study was larger than that typically implemented for a T2VOC model. Second, output routines were modified to facilitate analysis and visualization. Finally, a number of postprocessing and preprocessing programs were written to manipulate and modify the data for later use. None of these changes affected model computational routines.

This section presents the results from a series of simulations that explored the effects of various parameters and conceptual models on SVE operations. It then presents results from a set of simulations with a homogeneous material distribution to evaluate air flow. The impact of f_{oc} was explored next. Then layered material distribution was studied, and the effects of random sand inclusions in the clayey-sand layers were evaluated. To explore the impacts of heterogeneous material distributions more fully, a set of simulations with varying amounts of heterogeneity in the top 7 m of soil were evaluated.

The effect of contaminated groundwater beneath the site on SVE operations was evaluated. These effects have not been reported in the literature. The simulations showed that this phenomenon is the most likely cause of the long-term behavior of the TCAAP SVE systems. This phenomenon was first evaluated by using a homogenous material distribution and then by using a layered system. Finally, both initial vadose zone contamination and contaminated groundwater processes were implemented in a set of simulations to duplicate observed data. This section concludes with a discussion of the various simulation sets and comparisons of simulation results to field-measured values from the TCAAP SVE systems.

5.1 FRACTION OF ORGANIC CARBON COMPARISON

T2VOC uses the fraction of organic carbon (f_{oc}) levels to compute VOC partitioning between solid and aqueous phases. T2VOC requires that the user input an initial VOC concentration in the air phase, so the f_{oc} levels also determine the initial mass in all three phases. The partitioning between the solid and aqueous phases retards the advective transport of VOC in the gas and aqueous phases. This retardation effectively makes the advective transport velocity slower than the velocity of either the gas or aqueous phase itself. This apparent retardation can be significant and can greatly affect the results of the simulations. In addition, the f_{oc} levels for the various geologic materials at TCAAP are not well known. Because of these factors, the sensitivity of the simulation results to f_{oc} levels was examined before any attempt was made to model the TCAAP SVE system.

Four simulations were performed to determine the f_{oc} impact on SVE operations and results. These simulations defined Layers 4 and 5 as clayey-sand, as shown in Figure 9. The remainder of the model, with the exception of these clayey-sand layers, was sand. The base-case simulation

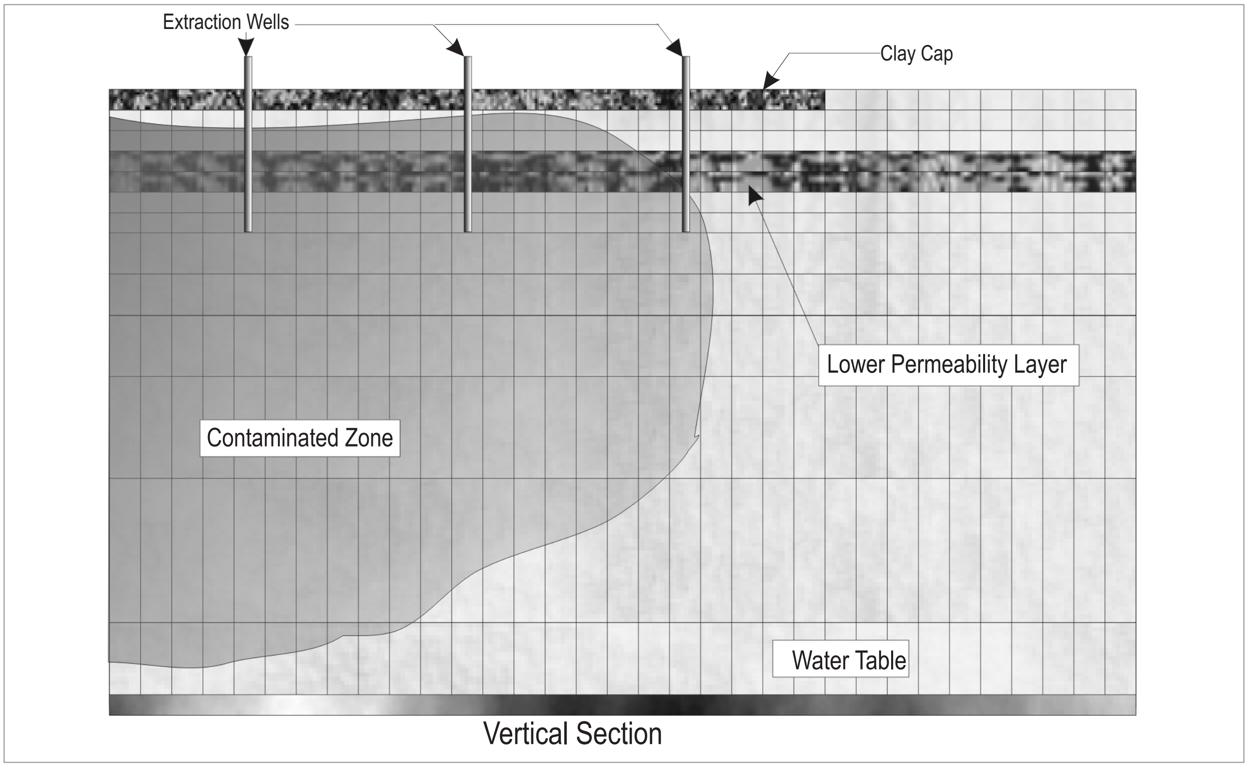

FIGURE 9 Mesh Used to Compare the Effects of the Fraction of Organic Carbon Present (Mesh Layers 4 and 5 are clayey-sand materials.)

assumed that clayey-sand material had a f_{oc} of 0.005, while the sand material had a f_{oc} of 0.001. The high f_{oc} simulation had a f_{oc} of 0.01 and the low f_{oc} simulation had a f_{oc} of 0.001 for the sand. In addition, a simulation was performed with the sand f_{oc} set to 0.002 and the clayey-sand f_{oc} set to 0.005.

Initial VOC concentrations were set to 0.02 molar in the gas phase. As shown in Table 5, the f_{oc} levels determined the quantity of VOC present in the subsurface. Amounts and concentrations of VOC in the air and aqueous phases were the same, but the amount of VOC present sorbed onto the solid phase (and thus the initial mass of VOC in the simulation) varied with the fraction of organic carbon present. Because of the assumption of local chemical equilibrium, the code computed the amount of VOC required in the solid phase to achieve equilibrium conditions for the user-defined aqueous-phase concentrations.

To facilitate the comparison of these values with field-measured concentrations, the approximate dry mass concentration of VOCs in the subsurface was computed and is presented on the last line of Table 5 as:

$$C_{voc} = \frac{M_{voc}\, 1 \times 10^{6}\, mg/kg}{V_{soil}\, r_{soil}} \tag{32}$$

TABLE 5 Initial Amounts of VOCs by Phase

Phase	Base Case	High Clay f_{oc}	Low Clay f_{oc}	High Sand f_{oc}
Gas (kg)	0.98×10^{2}	0.98×10^{2}	0.98×10^{2}	0.98×10^{2}
Aqueous (kg)	0.13×10^{3}	0.13×10^{3}	0.13×10^{3}	0.13×10^{3}
NAPL (kg)	0.00	0.00	0.00	0.00
Adsorbed (kg)	0.50×10^{3}	0.70×10^{3}	0.34×10^{3}	0.12×10^{4}
Total (kg)[a]	0.73×10^{3}	0.93×10^{3}	0.57×10^{3}	0.14×10^{4}
Sand f_{oc}[a]	0.001	0.001	0.001	0.002
Clayey-sand f_{oc}[a]	0.005	0.010	0.001	0.005
VOC conc. (ppm)[b]	105	134	82	202

[a] The amount of f_{oc} in the various materials changes equilibrium partitioning, resulting in differing total volumes. All runs have an initial gas-phase concentration of 0.02 (molar fraction) in the cells beneath the clay cap.

[b] VOC concentrations in parts per million were found by dividing the total mass of VOCs present in this volume (in milligrams of TCE) by the total dry soil mass (in kilograms).

where

C_{voc} = concentration of VOCs in the soil (ppm),

M_{voc} = mass of VOCs in the model domain (kg),

V_{soil} = volume of soil present in the model domain (cm^3), and

ρ_{soil} = bulk density of the dry soil (kg/m^3).

The area beneath the clay cap had a volume of 3.85×10^3 m^3. Assuming the bulk dry density of soil is 1,800 kg/m^3, the total soil mass is about 6.93×10^6 kg. VOC concentrations were computed by dividing the total mass of VOCs present in this volume by the total dry soil mass. Concentrations ranged from approximately 80 ppm to slightly more than 200 ppm and were in the range of values found for the TCAAP field samples from the preliminary site characterization, although some TCAAP samples had higher concentrations. VOCs present at this concentration level were not present as a pure oil phase but partitioned among the solid, aqueous, and air phases.

Figure 10 shows the results of these simulations as a set of four graphs. These graphs include both the mass of VOCs remaining in the subsurface over time and the calculated VOC extraction rate. These data are presented in both linear and log scales.

The extraction rate curves show some variation because these rates were computed by using the difference approximation and the mass change of VOCs over time. The change in mass over one model time step was divided by the model time step. These rates are not as accurate as the model-calculated extraction rates that are used in the remainder of this study.

The linear-scale plots show that the initial extraction rates were highest for the High Sand f_{oc} at approximately 54 kg/d for the three extraction wells in the model. If all the wells were to behave similarly, this rate would be the equivalent of about 700 kg/d for the entire SVE system of 39 wells. This value is almost twice the measured initial extraction rates for the system, which were approximately 400 kg/d. The initial rate was 26 kg/d for High Clay f_{oc}, Low Clay f_{oc}, and Base Case. These initial rates correspond to an equivalent rate of approximately 340 kg/d for the entire system, which is about 85% of the measured initial rate. These initial rates indicate that the VOCs are extracted from the sand material, which has a high permeability and low f_{oc}, first. VOCs in the clayey-sand take more time to reach the extraction wells.

As the simulations continue in time, differences between them become more pronounced. Rates for the High Sand f_{oc} case continue to be highest for approximately a year and a half, which can best be seen in the linear scale plot of the extraction rates. After this, the High Clay f_{oc} case has the highest extraction rates. This behavior is best seen in the log scale plot. The three cases that have

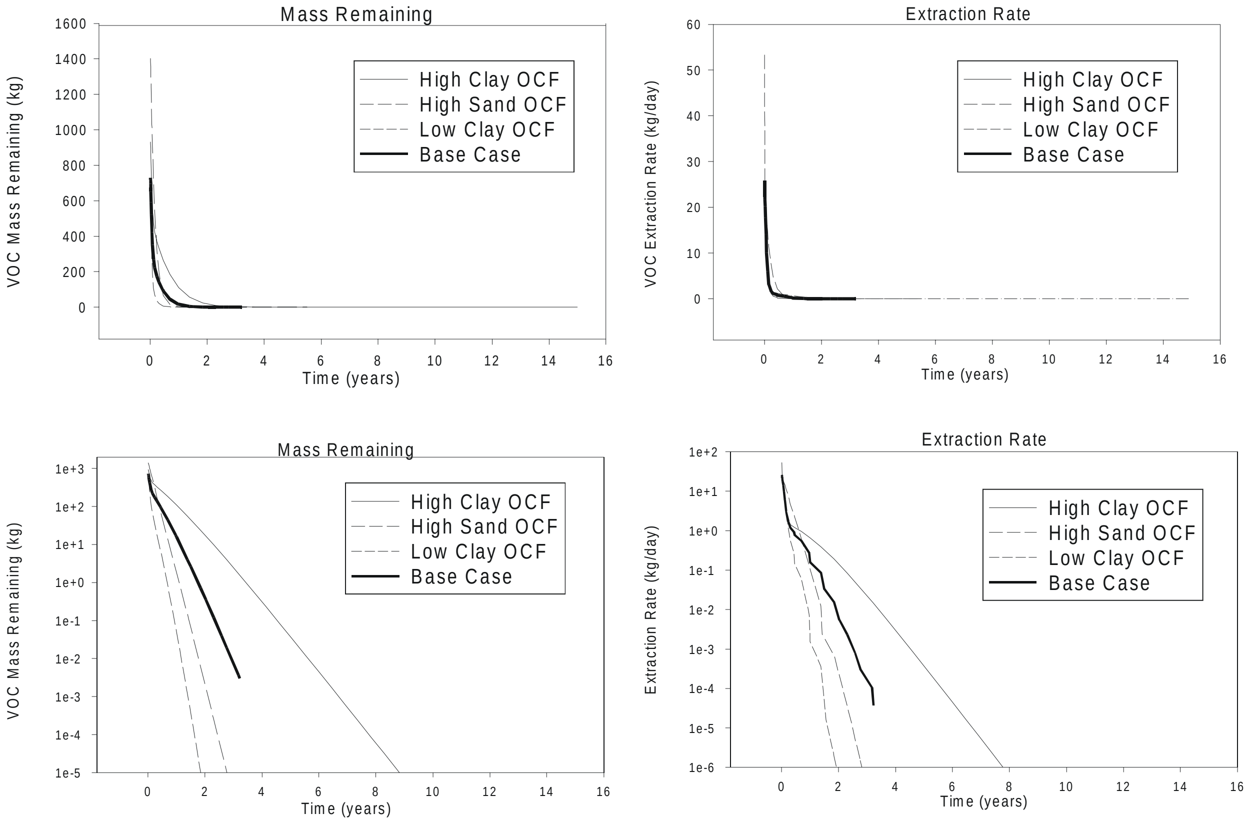

FIGURE 10 VOC Extraction Rates over Time for Various Amounts of Organic Carbon Present in the Sand and Clayey-Sand Materials

a sand f_{oc} of 0.001 behave almost identically over the first year and a half. This observation indicates that during this period, the majority of the VOCs are extracted from the sand. At longer times, the curves diverge as the effects of the clayey-sand become more apparent.

The plots showing the amount of VOCs remaining in the subsurface (top plots, Figure 11) indicate that the Low Clay f_{oc} and High Sand f_{oc} cases remove the majority of VOCs quickly, in about 2 years and 2 ½ years, respectively. The Base Case continues for approximately 4 years (best seen in the log scale plot of the mass VOC remaining). The High Clay f_{oc} case exhibits tailing behavior and has measurable extraction rates over the entire 15-year simulation period, although after about 8 years, these rates are below 10^{-4} kg/d, which would be equivalent to approximately 10^{-3} kg/d for the entire system. This value contrasts sharply with the measured values of between 0.5 and 1.0 kg/d extracted in the field system after nearly 15 years.

The results from these simulations do not match the initial or final behavior of the field system well. The field-measured extraction rates do not decrease as rapidly as the rates exhibited in these simulations. In addition, the long-term tailing behavior does not match well. The simulations do not exhibit the magnitude of tailing behavior observed at TCAAP.

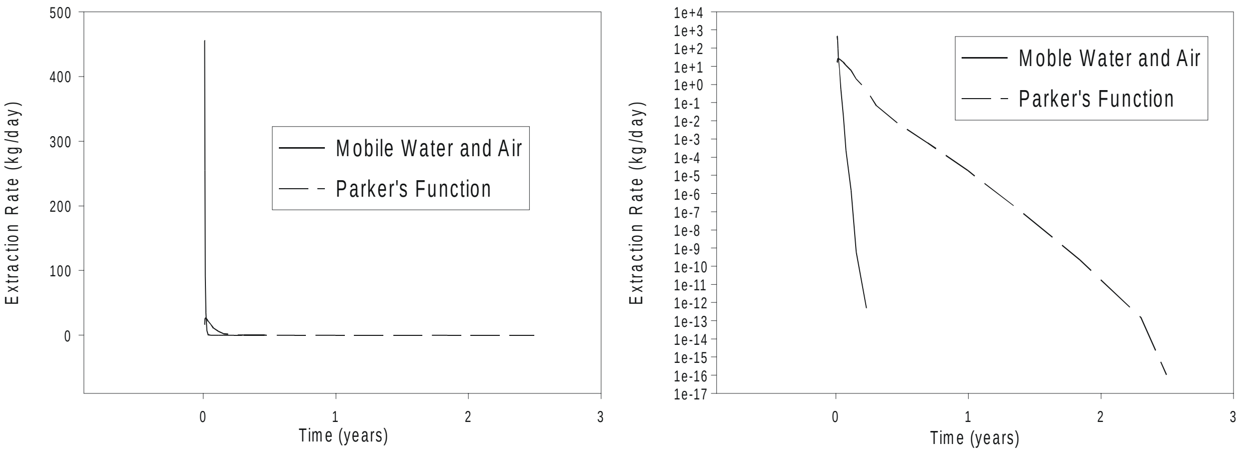

FIGURE 11 Extraction Rates for a Homogeneous Model, Showing the Effects of Different Relative Permeability Functions

Although these runs did not reproduce the behavior of the TCAAP SVE system, they did demonstrate the sensitivity of the model to the f_{oc} present in the various materials. They also showed how the f_{oc} of the various materials affects the different time periods of the simulation; sand values affect the early periods the most, while the tailing behavior is dominated by the clayey-sand parameters. Also, f_{oc} levels have a significant impact on the total amount of VOCs initially present in different materials with the same aqueous-phase concentration and can govern the long-term extraction rates.

5.2 HOMOGENEOUS MATERIAL

The initial approach to modeling the TCAAP SVE system was to develop a homogeneous model (Figure 11). The model used the grid presented in Figures 6 and 9, without the presence of the clayey-sand layers depicted in these figures. The geologic material used in the model was assigned a permeability of 1.6×10^{-11} m^2, which gives a saturated hydraulic conductivity of approximately 1.6×10^{-4} m/s, the range of a clean to slightly silty sand (Freeze and Cherry 1979). Field investigations estimate the materials at TCAAP to have a permeability that ranges from 1×10^{-10} to 1×10^{-13} m^2, with values in the silty-sand at D measured at 1.8×10^{-12} (Stone and Webster 1998).

The effect of the relative permeability function used was investigated. The modified version of Stone's three-phase method was used to define the relative permeability function (Equation 27) with S_{wr}, S_{nr}, S_{gr} and n set to 0.78, 1.56, 0.05, and 3.0 respectively, for one simulation. In the second simulation, the n value was set to 0, which effectively makes the gas, water, and NAPL phases mobile (relative permeability of 1). The capillary pressure function of Parker et al. (1987) was used

(Equation 28), with S_m, n, α_{gn}, and α_{nw} set equal to 0.078, 1.56, 9.9, and 11.0, respectively. These values follow the data presented in Carsel and Parish (1988) for a material with a hydraulic conductivity in the range of 1.5×10^{-4} m/s.

Initial VOC concentrations were set to 0.02 molar in the gas phase in the elements beneath the clay cap and above the water table. This resulted in 0.98×10^{2} kg of VOCs in the gas phase, 0.13×10^{3} kg of VOCs in the aqueous phase, and 0.34×10^{3} of VOCs sorbed onto the solid phase, for a total of 570 kg of VOCs in the model domain.

The homogeneous model simulation was configured to run for 15 years. Two simulations were run. One run included the effects of relative permeability. The water, air, and NAPL phases were mobile in the other run. Model simulations showed that the total mass of VOCs in the subsurface was reduced to negligible amounts within less than 2 years, and daily extraction rates fell below 1×10^{-5} kg/d within one year. The simulation was completed to a time of slightly more than 2 years for the material with relative permeability effects, and to a time of less than 1 year for the other material. The simulations were terminated at these points of time because extraction rates became essentially zero. This situation is shown in Figure 11, which shows the daily extraction rates for two runs of a homogeneous material in both a linear and semi-log scale.

The relative permeability function has a large impact on the model results. With three mobile phases, the daily extraction rates were essentially 0 within 2–3 days. A steady-state condition was reached within less than 6 months. Using a best estimate of the parameters for Parker's relative permeability functions (Equation 26) resulted in measurable extraction rates for 2 ½ years, although these rates dropped to below 1×10^{-7} kg/d after approximately 1 ½ years (Figure 12). Because of the amount of time required to run the model and the lack of any means to calibrate these parameters, no further study was made of these parameters. The best estimates of the parameters needed to define the relative permeability functions for the various materials were taken from the literature, relying heavily on Carsel and Parish (1989).

These plots do not show the entire 15-year period because the simulation is terminated once the model reaches an apparent steady state.

Varying the f_{oc} and the permeability of the material either shortened or extended the period required for cleanup. However, the change was not enough to match the extraction rates observed after 15 years. In these simulations, the VOC mass in the subsurface quickly reached negligible amounts.

The main objective of the homogeneous simulation set was to evaluate the range of influence of the extraction vents. As stated above, initial design calculations for the SVE system did not take into account the interaction of the multiple vents and the clay cap. The simulations show how these interactions affect the flow field.

Figure 12 shows how air is drawn into the system from beyond the clay cap and how it moves to the three extraction wells. Air flow into the well nearest the edge of the cap is relatively shallow, while air flow to the well furthest from the edge of the cap is deep and sweeps the surface of the water table. The clay cap effectively extends the vertical influence of the wells to a depth significantly below that predicted by simple one-well models. This effect was also noted in early gas-flow modeling conducted by Argonne National Laboratory and Colorado State University as part of the preliminary system feasibility study (Eisenbeis et al. 1989; Sabadell et al. 1991).

The initial TCAAP SVE system design assumed that the wells would have a vertical influence of approximately 14 m (7-m vent depth plus an additional 7 m of vertical influence) and did not use the Colorado State University results. The simulations presented in this section suggest that the TCAAP SVE system has influence over the entire vadose zone and reaches to the water table, as suggested by the Colorado State University reports (Eisenbeis et al. 1989; Sabadell et al. 1991) This larger zone of influence results from interacting effects from the other wells and the way in which the clay cap changes the air flow patterns.

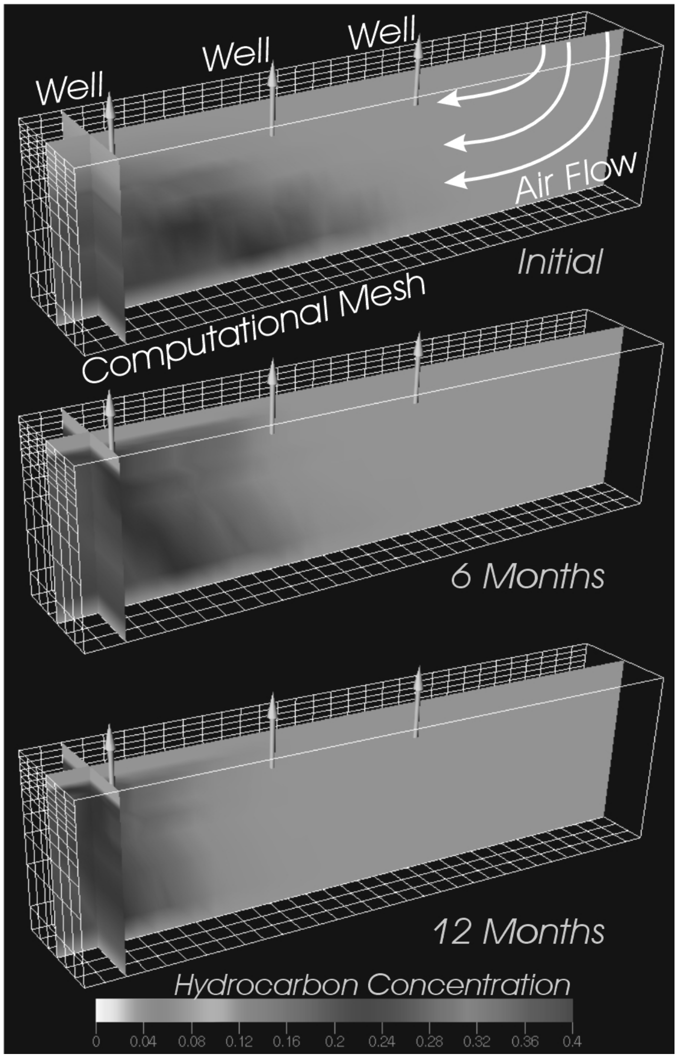

FIGURE 12 Homogeneous Model Results Showing How Air Enters from Beyond the Clay Cap, Sweeps along the Groundwater Surface, and Is Extracted by the Wells

Figure 12 shows that the SVE system removed the subsurface VOCs rapidly. The top image shows the subsurface VOC concentrations in the aqueous phase after a short initial period of only 1 day. The VOC levels near the outside well were already visibly decreasing, especially near the vent. After 6 months, the area outside the clay cap had low VOC concentrations, and the area near the outside well was relatively clean. The area near the middle well was also starting to become clean.

The VOC concentrations show the effect of the air flow patterns: the air swept in from the outside and down along the surface of the groundwater table. This flow pattern is evident from the sequential removal of the VOCs. Initially, the shallow contamination near the edge of the clay cap was removed. Next the deeper contamination and the contaminants in shallow areas near the middle of the model were removed. Then the contaminants from the area near the inside model boundary were removed. The last area swept free of VOC contamination was the deep part of the interior of the model. In addition, the concentration gradient shows how the material was swept up from the bottom of the modeled area to the interior well in the last image.

5.3 LAYERED MATERIAL

Site G at TCAAP consists of relatively homogeneous sand overlain by approximately 7 m of silty sand or silty clay fill that extends to the water table at Site D (Section 2). This geology was simplified and implemented in the model as a layered system. The top 7 m contained clayey-sand layers, and the remainder of the model consisted of sand. Figures 6 and 9 show the general configuration of the mesh used for this model. Different mesh layers were defined as clayey-sand for different simulations. In addition, the method used to develop the initial VOC contamination levels was also varied (Table 6). Simulations L1, L3, and L4 used an initial gas concentration of 0.02 molar in the elements beneath the clay cap. Simulation L2 was completed in phases in which a NAPL was injected directly into the subsurface in the area below the clay cap. This approach created significant demands on computer resources; several days of computer time were needed to complete the modeling of the injection process and subsequent SVE system operation. The injected NAPL was allowed to come to an equilibrium state over a period of 5 years. At the end of this period, the extraction process was started. By the end of the 5-year period, all the injected NAPL mass was partitioned among the solid, aqueous, and gas phases, and no free-product NAPL remained in the system. This approach resulted in a contaminant distribution similar to the distribution that results from setting initial gas concentrations. Because of these limitations, this approach was not used for other simulations. Instead, initial gas concentrations were specified.

Four different simulations were run to evaluate the impact of clayey-sand layers on SVE operations. The configurations used for these runs are presented in Table 6. Simulation L1 had Layers 4 and 6 defined as a clayey-sand and used an initial VOC gas concentration of 0.02 molar in the elements beneath the clay cap. Simulation L2 defined mesh Layers 4 and 5 as clayey-sand and used a NAPL injection process

TABLE 6 Layer Definitions and Material Parameters for the Layered Model Simulations

Run	Clayey-Sand Layers	VOC Method	Clayey-Sand[a] f_{oc}	Sand[b] f_{oc}
L1	4, 6	0.02 m	0.005	0.001
L2	4, 5	Inject	0.005	0.001
L3	4, 5	0.02 m	0.015	0.002
L4	2, 3, 4, 5, 6	0.02 m	0.010	0.001

[a] Clayey-sand permeability = 2.1×10^{-13} m^2.

[b] Sand permeability = 1.6×10^{-11} m^2.

to determine the initial VOC concentrations. Simulation L3 also defined Layers 4 and 5 as clayey-sand and set initial gas concentrations to 0.02 molar. In addition, Simulation L3 also set the clayey-sand f_{oc} to 0.015 and the sand f_{oc} to 0.002, compared to the values of 0.005 and 0.001 used for the clayey-sand and sand f_{oc} in the L1 and L2 simulations. Simulation L4 defined the entire top five mesh layers of the model (approximately 7 m, not including the clay cap layer) as a clayey-sand material with an f_{oc} of 0.010. For this simulation, the initial VOC concentrations were set to 0.02 molar in the gas phase.

Three extraction wells were modeled by using a vent pressure of 97,797 Pa, which is equivalent to approximately 13 in. of water (atmospheric pressure was set to 107,035 Pa). The simulations were run for 15 years.

Table 7 summarizes the results of these simulations. The table presents the initial amount of VOCs present in the modeled domain. This value includes VOCs sorbed onto the solid phase, dissolved into the aqueous phase, and volatilized into the air phase. No free NAPL was present at these concentrations. Simulation L2 used direct injection of 1,750 kg of NAPL into the subsurface to create the initial NAPL distribution. This injection process was modeled over 30 days. After the initial injection, the simulation was run for an additional 5 years with no additional system stresses to allow the subsurface NAPL to reach an equilibrium distribution. At the end of this period, the 1,750 kg of NAPL in the subsurface had partitioned between the various solid, liquid, and air phases, and no free NAPL remained.

Table 7 presents the initial mass of VOCs in the subsurface, the final mass of VOCs in the subsurface, and the percent of mass remaining in the subsurface after 15 years of SVE operations. The first two simulations, L1 and L2, essentially demonstrate a complete removal of the VOC from the subsurface; although the L2 simulation has a slight mass remaining, it is only 0.000085% of the initial mass. Both of these simulations had a clayey-sand f_{oc} of 0.005 and a sand f_{oc} of 0.001. Simulation L1 had a sand layer between two clayey-sand layers. This arrangement exposes more of the clayey-sand surface to the higher-velocity gas flow that occurs in the sand and provides a shorter diffusion length than do the simulations in which the clayey-sand layer was continuous. This configuration produced a rapid cleanup.

Figure 13 shows the model-calculated extraction rates over time compared with the field-calculated values. The field-calculated values drop off more quickly than those calculated by the model.

TABLE 7 Initial and Final VOC Mass in the Layered Simulations

Run	Initial VOC (kg)	Final VOC (kg)	Percent Remaining
L1	675	0.0	0.00
L2	1,750	1.5×10^{-5}	0.00
L3	1,250	0.20	0.02
L4	1,200	118.00	9.80

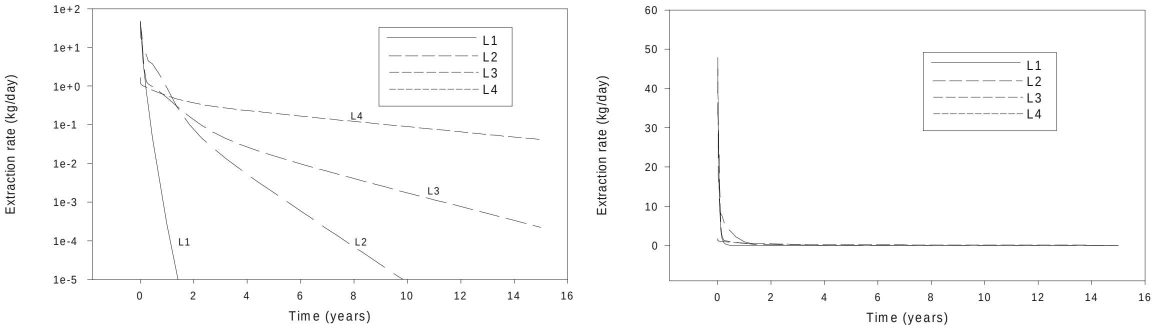

FIGURE 13 Daily Extraction Rates for the Layer Simulation Models Plotted on Linear and Semi-Log Scales

Figure 14 shows the phenomenon that produces this tailing in extraction rates. This figure is a three-dimensional visualization of the results of the layer model. It shows that small contaminated areas exist in the clayey-sand layers after years of system operation. These small areas are located between the extraction wells at the stagnation points of the flow field. Under these conditions, the only way that the contaminants can be transported to the wells is by a slow process of gaseous diffusion that moves the contaminants in the air phase out of the clayey-sand layer and into the sand, where the air can be advectively transported to the extraction well.

These results demonstrate that some of the long-term tailing behavior observed in field SVE systems may be caused by three-dimensional effects and material geometry. However, they do not account for the magnitude of the behavior observed in the field. The simulations were able to produce significant tails for only a short period of 4 to 7 years. They could not duplicate the 15 years of tails observed at TCAAP.

5.4 DISCONTINUOUS LAYERS

Continuous horizontal clayey-sand layers in subsurface sand can generate regular flow fields that bring air into contact with the entire clayey-sand layer surface. On the other hand, discontinuous clayey-sand layers can provide preferential flow paths for air, resulting in isolated regions of tight materials that may cause long-term tails. To evaluate the effect that discontinuous clayey-sand layers would have on the extraction rate, a processor was written that replaced random grid elements in Layers 4 and 5 (a clayey-sand layer) with a sand material. The remaining elements in these two layers were assigned the parameters that describe a clayey-sand. Clayey-sand was defined as having a permeability of 2.1×10^{-13} m^2 and an f_{oc} of 0.015. Sand was defined as having a permeability of 1.6×10^{-11} m^2 and an f_{oc} of 0.002.

Figure 15 shows model Layers 4 and 5 in plan view after this processing. The light colors represent the sand, and the dark colors represent the clayey-sand. The top of Figure 15 lists the percentage of sand that was present in the two layers as a whole. The top row of rectangles represents Layer 4. The bottom row of rectangles represents Layer 5. VOC concentrations were set to 0.02 molar in the gas phase for the elements below the clay cap. The model was configured for a 15-year simulation, and all the simulations were completed except for the 95% sand simulation. The 95% sand simulation ran for slightly more than 4 years until nearly all the VOC contamination in the model domain was removed and the extraction concentrations were too low to continue.

The results of this set of simulations are shown in Figure 14. The 95% sand simulation showed the most rapid cleanup, followed by the 85% and 50% sand simulations. Unexpectedly, the pure clayey-sand layer simulation, 0% sand, was the next most rapid cleanup. The reason was probably because a regular flow field resulted from the regular material distribution, and it did not cause any isolated clayey-sand mesh blocks, which occurred in the other simulations. The 5% sand simulation showed the least change and the slowest cleanup until approximately the 7-year point. The 10% sand and 15% sand simulations had nearly identical daily

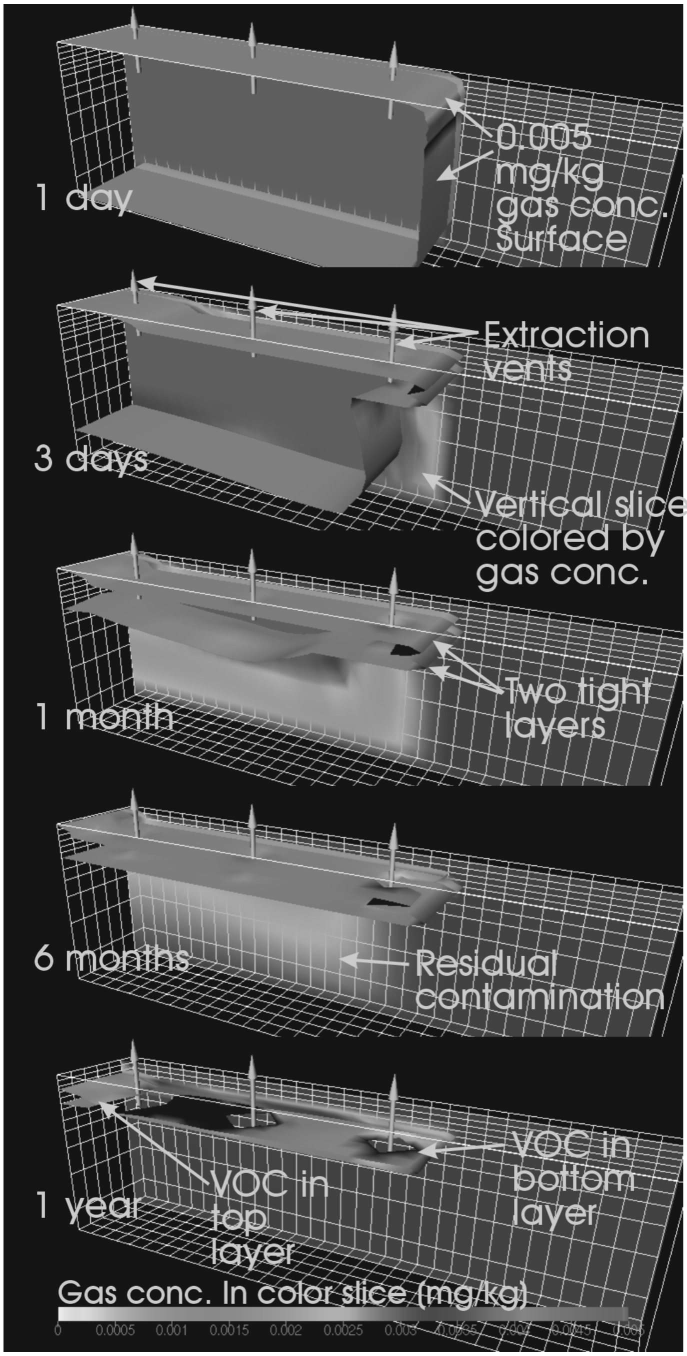

FIGURE 14 Three-Dimensional Visualization of the Results of Simulation L1 (The surfaces represent constant vapor concentrations.)

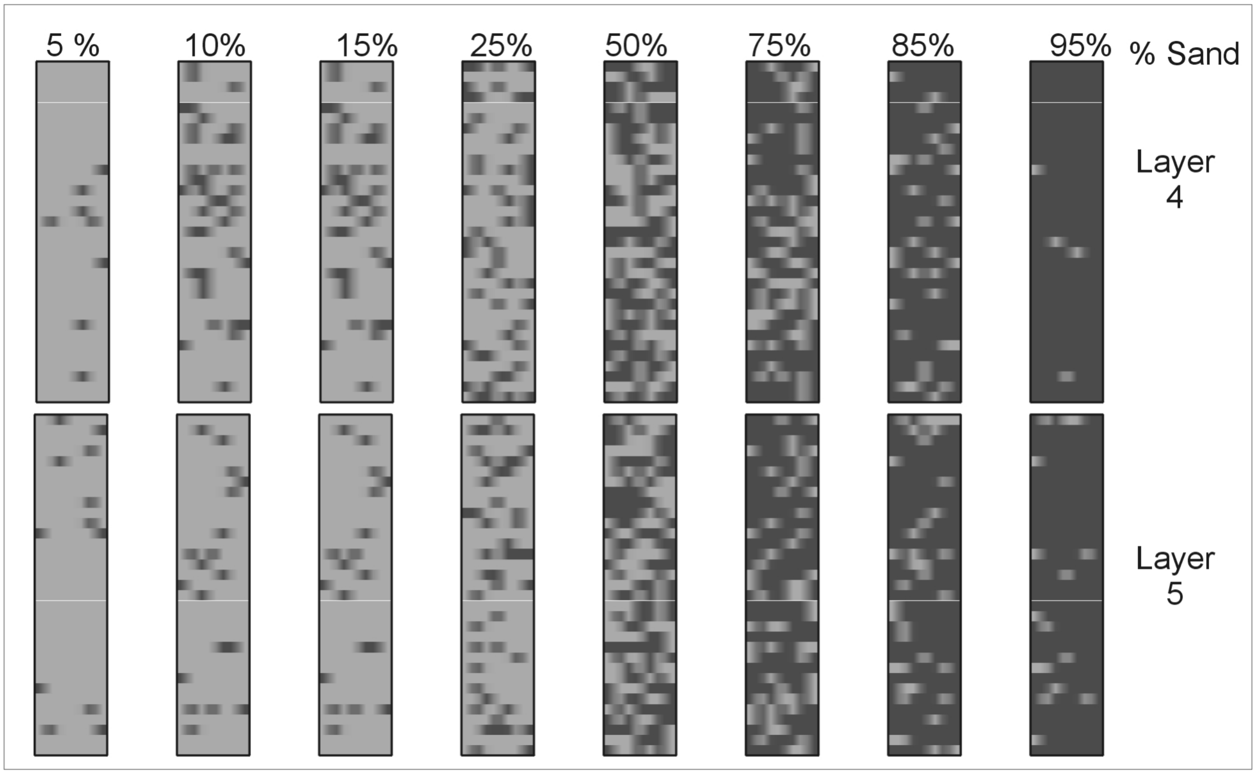

FIGURE 15 Plan View of the Material Extracted in Two Discontinuous Layers Model (Layers 4 and 5 were assigned random amounts of sand to determine the effect that discontinuous layers had on extraction rates.)

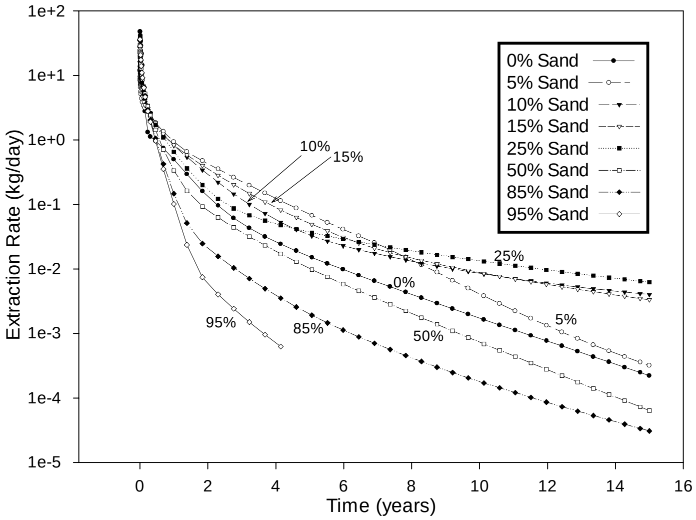

FIGURE 16 Extraction Rates over Time for Various Amounts of Sand in Two Clayey-Sand Layers Model

extraction rates at the end of the 15-year period: approximately 3×10^{-3} kg/d for the three vents in the model. This value corresponds to an approximate rate of 3.9×10^{-2} kg/d total for the entire SVE system, which is significantly below the 0.5- to 1-kg/d extraction rates that were measured. While these two simulations of 10% and 15% sand were nearly identical at 15 years, they showed differences before the 10-year mark. The 15% sand simulation extraction rates did not decrease as quickly as those from the 10% sand simulation. The 25% sand simulation exhibited a rapid decrease in extraction rates, more rapid than those from the 0%, 10%, or 15% sand simulations. However, even though the initial decrease was rapid, the rate of decrease dropped quickly at about the 2-year mark. The extraction rate at the end of the simulation for the 25% sand simulation was 1×10^{-2} kg/d, which is the equivalent of approximately 0.13 kg/d for the entire SVE system, a value that was slightly below the field measured values.

The behavior of the these simulations can be explained in reference to the amount of contact the tight clayey-sand materials had with the air flowing through the sand. The 95%, 85%, and 50% sand simulations exhibited the most rapid decrease in extraction rates. VOCs in the clayey-sands in these simulations were in close contact with the sand, where air flow is high. In these simulations, the clayey-sand layer was discontinuous, and each individual clayey-sand element was surrounded by sand with high air flow rates. This situation is shown in Figure 15. The next most rapid decrease occurred in the 0% sand, or pure clayey-sand layer, simulation. In this simulation, the air flow was regular and in contact with each element of the clayey-sand layers on both the upper and lower faces. The decrease in extraction rates was not as rapid as that found in the 95%, 85%, and 50% sand simulations because these simulations had single, disconnected clayey-sand elements exposed to air flow on all sides, which resulted in a more rapid movement of the VOCs out of the clayey-sand elements.

The 10%, 15%, and 25% sand simulations all behaved similarly. In these simulations, there was enough sand present to short-circuit the air flow through preferential pathways in the clayey-sand layers. This situation resulted in contaminated zones that were isolated from the air flow and retained VOCs for the entire simulation period. VOCs from the isolated element had to move by diffusion out of the clayey-sand material. This effect was probably sensitive to the mesh size used in the model if the mesh elements were too large. The effect of mesh size was not investigated in this study because of limitations in the number of elements that the model could run.

Table 8 presents the initial and final amounts of VOC present for each of these simulations. The initial mass of VOCs was relatively constant. The smallest VOC mass was approximately 75% of the largest. However, the mass remaining after the simulation ranged from a few hundredths of a kilogram (0.05 kg) to more than 16 kg, a range of three orders of magnitude for the standard simulations. The last simulation, which had 25% sand and the clayey-sand f_{oc} increased to 0.025, had almost 60 kg of NAPL remaining. This result shows how disconnected areas of VOC contamination in isolated areas can persist over long periods. It should be noted that this mass of contaminant in the volume represented by the model was actually quite low. If this amount of contaminant were

TABLE 8 Initial and Final VOC Mass (kg) for the Various Amounts of Sand Present in Two Clayey-Sand Layers

Simulation (15 years)	Initial Mass (kg)	Final Mass (kg)	% Mass Remaining
0% Sand	1,250	0.196	0.015
5% Sand	1,260	0.282	0.022
10% Sand	1,230	0.374	0.030
15% Sand	1,230	9.000	0.732
25% Sand	1,210	16.600	1.372
50% Sand	1,090	0.048	0.004
75% Sand (did not run)			
85% Sand	970	0.035	0.003
95% Sand (4 years)	930	0.26	0.020
25% Sand (high f_{oc})	1,750	59.400	3.400

distributed through the model area, it would be the equivalent of approximately 2 ppm dry weight (16.6 kg of TCE per 6,930,000 kg of soil).

These small isolated areas of VOC remaining in the isolated clayey-sand elements did not duplicate the observed daily extraction rates in the long term. Although there was tailing behavior, it was not of the magnitude observed in the field. Even the last simulation, with nearly 60 kg of NAPL remaining in the model domain, had an extraction rate of only 0.015 kg/d at the end of the 15-year simulation. This value is the equivalent of approximately 0.2 kg/d for the entire site, lower than the extraction rates observed in the field. Perhaps more importantly, the initial extraction rates for this simulation were much too low and did not decrease rapidly enough to match the measured values.

By using discontinuous layers, the long-term tailing was able to be duplicated at magnitudes similar to those observed at TCAAP. However, in order to induce tailing behavior of this magnitude, the extraction rate curves were relatively flat and did not match the initial behavior of the TCAAP systems.

5.5 HETEROGENEOUS MATERIAL

The heterogeneous simulation set was constructed in an attempt to model more realistic conditions than those represented by the layered model described in Section 5.4. This set assumed a random distribution of materials in the volume of elements that make up the top seven layers of the model (7 m), excluding the top layer, which represents the clay cap and a soil surface. Material properties were assigned by using a random number generator. The percentage of each material used is presented in Table 9. The first four simulations (H1, H2, H3, and H4) used the same distribution of materials, with the material properties changing as shown in Table 10. For these simulations, the majority of the material present was a sand, and only a small percentage, 1.9%, was a clayey-sand. These simulations represent field conditions in which the majority of the materials are a sand or a silt, with small pockets of a clayey-sand or other tight material. Simulations H5 and H6 used only two materials in the spatial distribution: a majority (91.6%) of clayey-sand and only 8.4% sand. The last simulation, H7, used 100% clayey-sand.

TABLE 9 Percentage of Material Present in Various Simulations

	Percent of Material Present			
Run	Mat 1	Mat 2	Mat 3	Mat 4
H1	1.9	8.5	30.7	58.9
H2	1.9	8.5	30.7	58.9
H3	1.9	8.5	30.7	58.9
H4	1.9	8.5	30.7	58.9
H5	91.6	0	0	8.4
H6	91.6	0	0	8.4
H7	100	0	0	0

Table 10 presents the material properties used in Simulations H1 through H7. Both the permeability and the f_{oc} for each material were modified for the various simulations. Simulations H1 and H2 used the same material parameters, with only the permeability of Mat 1 changed by a factor of two. H3 used the same permeabilties as H1, but the f_{oc} parameter was changed significantly for each material, from 0.01 to 0.05, 0.005 to 0.050, 0.001 to 0.02, and 0.001 to 0.01 for Mat 1, 2, 3, and 4, respectively. Simulation H4 modified the permeability of Mat 2 from that of Simulation H1, and it also modified the f_{oc} values, raising them slightly, though not as much as did Simulation H3. Simulations H5 and H6 used only two materials rather than four. For both of these simulations, the permeabilties were set to 2.1×10^{-13} m^2 for the clayey-sand and 1.6×10^{-11} m^2 for the sand. Both simulations had a sand f_{oc} of 0.002, while the clayey-sand f_{oc} was set to 0.010 and 0.005 for the H5

TABLE 10 Material Parameters for the Heterogeneous Simulations That Used Random Material Distributions in the Top 7 Meters of the Model

	Permeability (m^2)				Fraction Organic Carbon (f_{oc})			
Run	Clayey-Sand Mat 1	Clayey-Sand Mat 2	Silty-Sand Mat 3	Sand Mat 4	Mat 1	Mat 2	Mat 3	Mat 4
H1	0.5×10^{-13}	2.1×10^{-13}	1.6×10^{-12}	1.6×10^{-11}	0.010	0.005	0.001	0.001
H2	1.0×10^{-13}	2.1×10^{-13}	1.6×10^{-12}	1.6×10^{-11}	0.010	0.005	0.001	0.001
H3	0.5×10^{-13}	2.1×10^{-13}	1.6×10^{-12}	1.6×10^{-11}	0.050	0.050	0.020	0.010
H4	0.5×10^{-13}	1.1×10^{-13}	1.6×10^{-12}	1.6×10^{-11}	0.008	0.007	0.005	0.004
H5	2.1×10^{-13}			1.6×10^{-11}	0.010			0.002
H6	2.1×10^{-13}			1.6×10^{-11}	0.005			0.002
H7	2.1×10^{-13}				0.010			

and H6 simulations, respectively. Table 11 lists the initial and final amounts of VOCs in the simulations. Simulations with large amounts of clay or high f_{oc} values have high residual VOC values.

TABLE 11 Initial and Final VOC Mass in the Heterogeneous Material Simulations

Run	Initial VOC (kg)	Final VOC (kg)	Percent Remaining
H1	603	0.047	0.008
H2	603	0.013	0.002
H3	2,740	11.800	0.430
H4	814	0.027	0.003
H5	1,150	1.020	0.090
H6	847	0.023	0.003
H7	1,250	118.000	9.440

This heterogeneous simulation set was set up to try to determine the impact of small-scale, local, low-permeability zones on the long-term tailing behavior of the SVE system. If a small, low permeability zone were to be located near a stagnation point in the flow field, the tailing effects noted in the layered model would increase. As a result, the model might match the rapid drop-off evidenced by the field- measured extraction rates while still duplicating the long-term tailing behavior observed at TCAAP.

Figures 17 and 18 present the results of these heterogenous simulations over time. Figure 17 presents the results on a semi-log scale, while Figure 18 presents the same results on a linear scale. The semi-log scale is best used for evaluating the tails of the extraction rate, while the linear scale is more appropriate for investigating the initial extraction rates.

These figures show that simulations H3, H5, and H7 had the highest tails, ranging from 10^{-3} to 10^{-2} kg/d. H5 had the lowest tail of this group, while H7 had the highest. The tailing effects in Simulations H5 and H7 resulted from their large percentage of clayey-sand, 91.6% and 100%, respectively. The other simulation that had a high tail, H3, had a very high f_{oc} combined with a low clayey-sand permeability of 0.5×10^{-13} m^2. The f_{oc}s for simulation H3 were 0.05, 0.05, 0.02, and 0.01 for Mat 1, 2, 3, and 4, respectively. These values are essentially an order of magnitude higher than the f_{oc} values used for the other simulations, and they had the effect of slowing advective transport because of high retardation.

In general, there are two areas in which the simulation data need to match the field-measured data: (1) the initial extraction rates to approximately 3 or 4 years and (2) the long-term tail. The tailing behavior seems the most difficult to match, and when it was duplicated, the initial extraction rates, and also the dramatic decrease in extraction rates observed over a short term period in the field, were not duplicated.

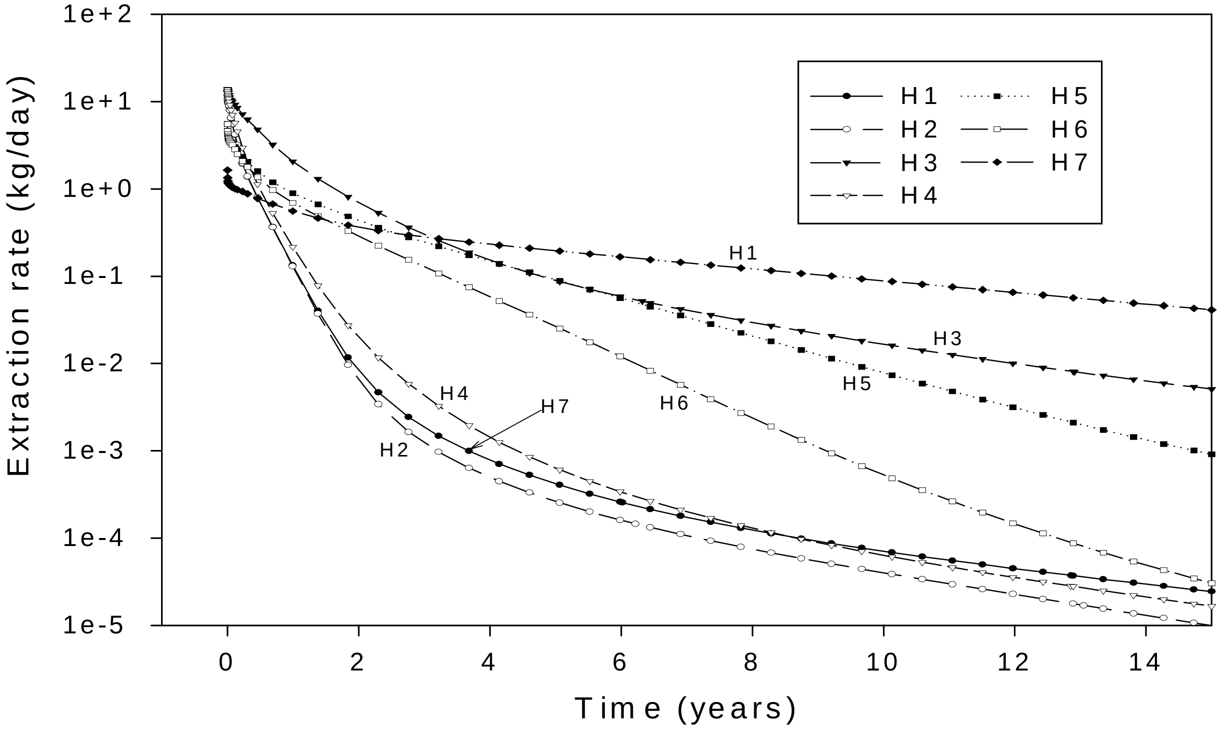

FIGURE 17 Results of the Series of Simulations Exploring the Impacts of a Heterogeneous Material Distribution in the Top 7 Meters of the Model Plotted on a Semi-Log Scale

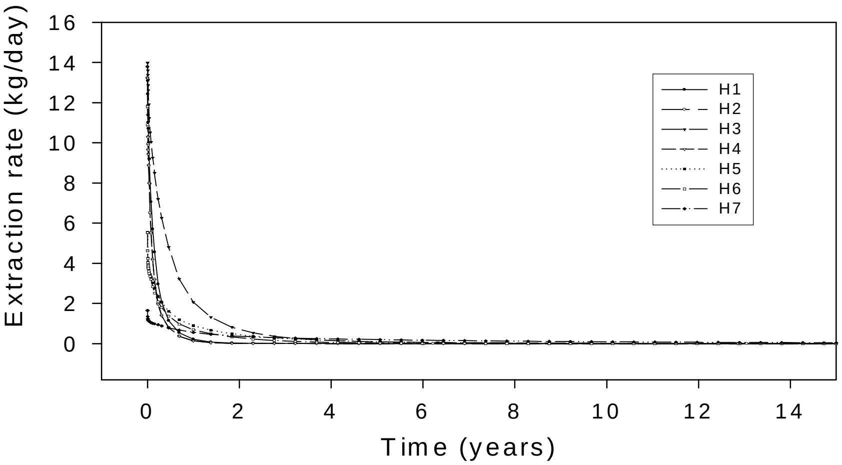

FIGURE 18 Results of the Series of Simulations Exploring the Impacts of a Heterogeneous Material Distribution in the Top 7 Meters of the Model Plotted on a Linear Scale

In Simulations H1, H2, and H4, initial extraction rates were quickly reduced; they fell below 10^{-2} kg/d within approximately 2 years. The final simulation, H6, exhibited behavior between these two groups: the initial decrease in extraction rates was not quite as rapid, and the flat tails of the other group did not occur.

Figure 17 shows that Simulation H7 had the highest tail; it represented solid clayey-sand in the top 7 m. While this tail is in the range of the data collected from the field, Figure 18 clearly shows that Simulation H7 did not have high enough initial extraction rates nor the dropoff required to match field data.

Simulation H3 matched the initial behavior of the field system quite well, with the extraction rate dropping slowly for the first 3 to 4 years. However, it did not match the tailing behavior noted in the field data. With the exception of Simulations H7 and H2, the remaining simulations did not match any of the field data well. Table 12 shows the effect of f_{oc} on the partitioning between the aqueous and gas phases. If these phases are not taken into account, estimates of initial contaminant mass may be significantly in error.

5.6 CONTAMINATED GROUNDWATER

Many of the approaches tried above could approximate the shape of the extraction rate curve for limited periods. However, the only simulations that closely matched the tailing behavior observed in the field had parameters that were unrealistic (e.g., 100% clayey-sand for the top 7 m). In addition, the simulations that exhibited long tails did not duplicate the initial rapid drop in extraction rates that had been observed; thus, they could not match the initial behavior of the field systems.

One possible explanation is that two different physical processes produced the observed behavior. One was dominant during the early period (1 to 4 years), and the other became increasingly important later (7 to 15 years).

The simulations presented above suggest that the long-term tailing behavior did not result from isolated regions of trapped NAPL or from contaminants trapped in small dead zones, although these possibilities have not been entirely ruled out. Tailing behavior at the magnitude

TABLE 12 Groundwater TCE Contamination Values for the Aqueous Phase and Gas Phase, Showing the Effect of f_{oc}

Aqueous Phase Concentration (mg/kg)	Gas Phase Concentration (molar fraction)
2.6	7.6×10^{-5}
1.3	3.8×10^{-5}
0.65	1.9×10^{-5}
0.26	7.6×10^{-6}
0.13	3.8×10^{-6}
0.065	1.9×10^{-6}
0.026	7.6×10^{-7}
0.013	3.8×10^{-7}
0.0026	7.6×10^{-8}

observed at TCAAP could be matched, but only when parameters were unrealistic or only when the initial part of the extraction rate curve did not match well.

Another possible source for the long-term continued removal of VOCs from the TCAAP SVE systems is contaminated groundwater beneath the SVE system. If an SVE system generates air that flows and comes in contact with contaminated groundwater, VOC may volatilize from the groundwater and be transported to the vents.

To explore the effect of contaminated groundwater on the operation of SVE systems, a series of simulations were run in which no VOCs were initially present in the vadose zone, but the groundwater beneath the SVE system was assumed to be contaminated with VOCs at various levels. To implement these simulations, the boundary condition that represents the water table (Figures 6 and 9) was set to various constant aqueous concentrations. This boundary condition ranged from 2.6 ppm (7.6×10^{-3} molar) to 0.0026 ppm (7.6×10^{-6} molar) TCE (Table 8).[2] A total of nine simulations were run.

T2VOC accepts either aqueous-phase or gas-phase molar concentrations for initial conditions, depending on the number of phases present in the mesh block. Initial conditions were such that the code used gas-phase concentrations in the blocks representing the groundwater table. Initial estimates of the gas-phase concentration required to bracket the observed aqueous-phase concentration resulted in model aqueous-phase concentrations in a range of 2.6 to 0.0026 ppm. Because these concentrations spanned the range of interest, the simulations were not rerun with more traditional values (e.g., 0.001 to 10 ppm).

The simulations were configured to run for 15 years, but most reached an approximate steady-sate condition in less than 1 year. The model was configured as a homogeneous sand with a permeability of 1.6×10^{-11} m^2 and an f_{oc} of 0.002, which is relatively high for a clean sand. Parker's relative permeability functions were used (Equation 26) with an S_m of 0.078 and an n value of 1.56 per Carsel and Parish (1989). Parker's three-phase capillary functions were also used (Equation 28) with an S_m of 0.078, n of 1.56, α_{gn} of 9.9, and α_{nw} of 11.0. The model vents had an applied pressure of 97,797 Pa, which gives an approximate vacuum of 3,238 Pa or about 13 in. of water. Atmospheric pressure was set to 101,035 Pa.

Table 13 presents the results of these runs showing the equilibrium extraction rates (kg/d) for the three vents in the model, the approximate total SVE system rate (assuming all 39 vents behaved as the three model vents), and the amount of VOC in place in the vadose zone when steady state was reached. Both the extraction rates and the amount of VOC in the vadose zone initially start at zero. These values asymptotically approached the steady-state value and were approximately 1% of this value within 2 weeks.

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[2] For example, 0.001 to 10 ppm.

TABLE 13 Results from Simulations with Contaminated Groundwater beneath the SVE System[a]

	Model (3 wells)		
Simulation (ppm)	Extraction Rate (kg/d)	VOC in Vadose Zone (kg)	Estimated SVE Extraction Rate[a] (39 wells) (kg/d)
2.6	7.7×10^{-1}	4.628	10.00
1.3	3.9×10^{-1}	2.333	5.10
0.65	2.0×10^{-1}	1.166	2.60
0.26	4.6×10^{-2}	0.375	0.60
0.13	3.9×10^{-2}	0.233	0.51
0.065	2.0×10^{-2}	0.116	0.26
0.026	7.9×10^{-3}	0.047	0.10
0.013	3.9×10^{-3}	0.023	0.05
0.0026	7.9×10^{-4}	0.005	0.01

[a] Measured values range from 1 to 2 lb/d (0.5 to 1 kg/d).

The results from this set of simulations show that the SVE system can extract significant amounts of VOCs from contaminated groundwater beneath the site. Groundwater contamination values between 0.026 and 1.3 ppm TCE resulted in daily extraction rates that were the same order of magnitude as those observed in the field, 0.5 to 1 kg/d, for the entire SVE system.

Table 14 presents the results of two simulations that were run to determine the impact that clayey-sand layers would have on the amount of VOC extracted from contaminated groundwater. Also included in the table are results from a comparative simulation that had no clayey-sand layers present. For these simulations, the groundwater contamination level was set at 0.026 ppm. A clayey-sand material with an f_{oc} of 0.015 and a permeability of 2.1×10^{-13} m^2 was used, along with a sand material with an f_{oc} of 0.001, and a permeability of 1.6×10^{-11} m^2.

The first simulation defined mesh Layers 9 and 10 as a clayey-sand material. This simulation corresponds to a clayey-sand layer 5 m thick that begins 9 m below the surface and 2 m below the extraction vents. Unlike the other simulations with contaminated groundwater, this simulation required almost 1 year to reach an approximate steady-state condition. Over this year, extraction rates gradually increased to a value of 1.7×10^{-3} kg/d, which is slightly over half the rate when no clayey-sand layers are present. Compared with the no-clayey-sand layer simulation, this simulation showed more than twice the amount of VOCs in the subsurface at steady-state conditions, 0.109 kg (versus 0.047 kg).

TABLE 14 Results from Simulations with Contaminated Groundwater beneath the SVE System and Clayey-Sand Layers Present at Various Locations

	Model (3 wells)		
Clayey Sand Layer[a]	Extraction Rate (kg/d)	VOC in Vadose Zone (kg)	Estimated SVE Extraction Rate[b] (39 wells) (kg/d)
None	7.9×10^{-3}	0.047	0.10
Bottom	4.7×10^{-3}	0.109	0.06
Top	7.9×10^{-3}	0.531	0.10

[a] Groundwater contaminant levels were set to 0.026 ppm.

[b] Measured values range from 1 to 2 lb/d (0.5 to 1 kg/d).

The second simulation defined mesh Layer 4 as a clayey-sand-type material. This simulation corresponds to a clayey-sand layer 1-m thick beginning 4 m below the surface and 3 m above the bottom of the extraction vents. Thus, the vents are completed in, above, and below this layer. This simulation showed almost no difference in extraction rates when compared with the simulation in which no clayey-sand layer was present. It did take slightly longer to reach steady-state extraction rates than did the simulation with no clayey-sand layers, approximately 1 month versus a little more than 1 week. Steady-state extraction rates were essentially the same.

The amount of VOCs in the subsurface for the second simulation that had top clayey-sand layers (0.53 kg) was more than 10 times the amount for the simulation without the clayey-sand layers (0.05 kg) and approximately 5 times the amount for the simulation with deep clayey-sand layers (0.11 kg). Clayey-sand material has a higher f_{oc} than sand, which results in more of the VOCs partitioning to the solid phase as the VOC vapor is transported up from the groundwater. This process explains the difference between the simulations with and without clayey-sand layers.

The difference between the two simulations that both included clayey-sand layers is not as easily explained. The first simulation with bottom (deep) clayey-sand layers was equivalent to 5 m of clayey-sand, but the second simulation with top clayey-sand layers equivalent to only 1 m of clayey-sand had the most total VOCs in place. This difference in the total amount of VOCs in the subsurface at steady-state conditions was probably caused by the same mechanism that caused the difference in the time required for the two simulations to reach a steady-state condition: the location of the clayey-sand layers with respect to the vents. In the first simulation, the clayey-sand layers were below the reach of the vents. Vents located in the interior of the model required air flow from below these clayey-sand layers, since all air flow above the clayey-sand layers was captured by the outside vent (nearest the edge of the clay cap). This situation resulted in small but significant air flow through the clayey-sand layer. This air flow lasted some time before the VOC concentrations in the vapor phase, transported from the groundwater, reached equilibrium partitioning conditions, as a result of the slower movement of air through this thick clayey-sand layer. The simulation with a 1-m clayey-sand layer behaved differently. Since the clayey-sand layer was located within the completion zone for the extraction vents, air flow could occur both above and below it. This situation resulted in little air flow in the areas of the clayey-sand layer that were distant from the vents. In this location, no transport of the VOCs occurred, which resulted in more material being sorbed onto the clayey-sands. The extraction rates were approximately equal to those of the simulation with no clayey-sand layers, because the lower portion of the vents extracted the majority of the air that had been in contact with the contaminated groundwater.

The movement of VOCs in the groundwater itself was not evaluated. If the SVE system were to remove sufficient amounts of VOC from the surface of the groundwater, this source could be depleted. A concentration gradient in the groundwater would be established, and additional VOCs would reach the surface of the groundwater, either by diffusion due to this concentration gradient or by mixing due to the movement of the groundwater itself. For these simulations, it was assumed that the groundwater was moving at a sufficient rate to keep the surface concentrations approximately equal to the concentrations deeper in the plume and to keep them constant over the duration of the simulations.

This effect of depleting the groundwater source on the modeled extraction rates could be explored by adding several mesh layers to represent to groundwater and evaluate movement of the dissolved VOCs from deeper in the groundwater plume to the surface of the groundwater plume. However, this modeling was not done because of time constraints.

These simulations indicate that the extraction of VOCs from the groundwater by the TCAAP SVE systems could be a cause of the observed tailing effect. The simulations presented here assumed that the groundwater contaminant plume extended under the entire SVE system, including the model area outside the clay cap. At TCAAP, the plume is present under only a portion of the SVE system; however, groundwater contaminant levels are in the 10- to 100-ppm range, well above the values used in the model to match field conditions. The numerical simulations show that it is possible to extract significant amounts of contaminant from the groundwater. If only a portion of the extraction wells were influenced by a plume contaminated at a higher level (1 to 10 ppm), the extraction rate could be in the 0.5- to 1.0-kg/d range. This situation could occur even if the majority of the SVE extraction system was not influenced by contaminated groundwater.

5.7 RESIDUAL VADOSE ZONE VOCS AND CONTAMINATED GROUNDWATER

The simulations of contaminated groundwater showed that the long-term tailing behavior observed at the TCAAP SVE systems could be duplicated if contaminated groundwater beneath the restoration system was assumed. However, although the long-term tailing behavior of the TCAAP systems could be explained by the existence of contaminated groundwater beneath the site and its effect on SVE system operation, another mechanism is required to replicate the short-term behavior of the TCAAP SVE system Small, tight soil zones located near the stagnation points of the flow field, such as those examined earlier, could constitute such a mechanism. A number of the initial simulations duplicated the short-term extraction rate behavior quite well. The simulations consisting of layers with random sand inclusions and heterogenous material in the top 7 m duplicated the behavior well in this respect.

Two different processes were probably responsible for the SVE behavior observed at TCAAP. The initial phase of operation (2 to 4 years) was dominated by extraction of VOCs initially present in the vadose zone. The final phase of operations (7 to 15 years) was dominated by extraction of VOCs from the contaminated groundwater and their advective transport to the SVE vents. The set of simulations discussed here was designed to explore this hypothesis.

Field measurements showed that initial conditions consisted of residual vadose zone contamination and a contaminated groundwater plume under the SVE system. A series of simulations was configured to examine these conditions; the simulations are described in Table 15.

These simulations were generally configured with the model elements beneath the clay cap assigned an initial VOC concentration of 0.02 molar in the gas phase and various material distributions as presented in Table 15. As shown in the table, these simulations were the same as those presented earlier in this report, with the addition of contaminated groundwater beneath the SVE system. Simulation CW1 had a homogeneous material distribution. Simulations CW2, CW3, and CW4 used material distributions and parameters from the heterogeneous section of simulation H3. Simulations CW5 and CW6 used material parameters and distributions from the random layer section simulations. Simulation CW5 used the parameters from the 5% sand simulation, and CW6 used the parameters from the 25% sand distribution. Simulations CW7, CW8, and CW9 also used the parameters from the 25% sand distribution, but they had a higher initial VOC concentration in the vadose zone than the other simulations: 0.03 molar rather than 0.02 molar. Simulations CW7, CW8, and CW9 had different concentrations of TCE in the groundwater. While f_{oc} levels were set higher for simulations CW7, CW8, and CW9 than for the other simulations, the levels were still within the range of values that could be expected at a field site.

These simulations were configured to run for 15 years. The simulation configured as a homogeneous sand had permeabilties of 1.6×10^{-11} m^2 and an f_{oc} of 0.002, which is relatively high

TABLE 15 Descriptions of Simulations that Evaluated Contaminated Groundwater in Addition to a Contaminated Vadose Zone

Run	Simulation Description	GW Conc. (ppm)[a]	Long-Term Rate (kg/d)[b]	Equiv. Rate (kg/d)[c]
CW1	Homogeneous material (sand) distribution	0.26	4.38×10^{-3}	0.06
CW2	Heterogeneous material distribution from H3	2.6	4.99×10^{-2}	0.65
CW3	Heterogeneous material distribution from H3	0.26	1.08×10^{-2}	0.14
CW4	Heterogeneous material distribution from H3	0.026	6.93×10^{-3}	0.09
CW5	Two-layer distribution; Layers 4 and 5 = 5% sand and 95% clayey-sand	0.26	5.55×10^{-3}	0.07
CW6	Two-layer distribution; Layers 4 and 5 = 25% sand and 75% clayey-sand (high VOC)	0.26	6.03×10^{-3}	0.08
CW7	Two-layer distribution; Layers 4 and 5 = 25% sand and 75% clayey-sand (high VOC)	0.26	2.21×10^{-3}	0.03
CW8	Two-layer distribution; Layers 4 and 5 = 25% sand and 75% clayey-sand (high VOC)	2.6	2.13×10^{-2}	0.28
CW9	Two-layer distribution; Layers 4 and 5 = 25% sand and 75% clayey sand (high VOC)	7.8	6.36×10^{-2}	0.83

[a] Groundwater concentration in ppm of TCE.

[b] Model extraction rate for the three vents modeled.

[c] Equivalent extraction rate assuming the remaining vents behave similarly to the modeled vents. Measured values range from 0.5 to 1.0 kg/d.

for a clean sand. Parker's relative permeability functions were used (Equation 26) with an S_m of 0.078 and an n value of 1.56 after Carsel and Parish (1989). Parker's three-phase capillary functions were also used (Equation 28) with an S_m of 0.078, n of 1.56, α_{gn} of 9.9, and α_{nw} of 11.0. The clayey-sand material used in the simulations had a permeability of 3.6×10^{-13} m^2 with an S_m of 0.110 and an n value of 1.275 for Parker's relative permeability functions. Parker's three-phase capillary functions were also used with an S_m of 0.110, n of 1.275, α_{gn} of 12.8, and α_{nw} of 12.0. The model vents had an applied pressure of 97,797 Pa, which gives an approximate vacuum of 3,238 Pa or about 13 in. of water. Atmospheric pressure was set to 101,035 Pa.

Simulation CW1 consisted of a homogeneous sand having a permeability of 1.6×10^{-11} m^2, a f_{oc} of 0.001, and groundwater contamination of 0.26 ppm TCE. Simulations CW2, CW3, and CW4 used the material distribution from the heterogeneous simulation H3, which consisted of four materials. This distribution is defined in detail in Tables 9 and 10. This distribution was defined over the top 7 m of the model, with the remainder of the model mesh defined as a sand material. CW2 had a groundwater concentration of 2.6 ppm, CW3 had a groundwater concentration of 0.26 ppm, and CW4 had a groundwater concentration of 0.026 ppm. CW5 was a two-layer discontinuous simulation that used the material distribution from the previously presented random layer simulation R5, which had mesh Layers 4 and 5 assigned as 5% sand and 95% clayey-sand, respectively. The sand was assigned a permeability of 1.6×10^{-11} m^2 and an f_{oc} of 0.002, the clayey-sand had a permeability of 2.1×10^{-13} m^2 with an f_{oc} of 0.015, and the groundwater contamination level was 0.26 ppm. In Simulations CW6, CW7, CW8, and CW9, Layers 4 and 5 were clayey-sand with a random 25% distribution of sand and the permeabilties were the same: 1.6×10^{-11} m^2 for the sand and 2.1×10^{-13} m^2 for the clayey-sand. The f_{oc} was set to 0.005 for the sand and 0.025 for the clayey-sand in CW7, CW8, and CW9. In simulation CW6, the f_{oc} was raised to 0.05 in the clayey-sand. In all these simulations, mesh Layers 2 through 7 (sand) were set to an f_{oc} of 0.005, but the remainder of the mesh was defined as a sand with an f_{oc} of 0.002. Simulations CW7, CW8, and CW9 had initial VOC gas-phase molar concentrations of 0.03 for contamination in the vadose zone. Simulations CW7, CW8, and CW9 had groundwater contaminations of 0.26, 2.6, and 7.8 ppm, respectively.

Figure 19 presents the results of these simulations plotted on a linear scale. It shows that the initial extraction rates dropped quickly for all the simulations and that all the simulations approached steady state within less than 8 years. Most of the simulations showed little variation after 4 years.

Figure 20 shows the period from 2 to 8 years after the start of SVE operations. The figure shows that although extraction rates were still decreasing at the 8-year mark, they were asymptotically approaching a steady-state value. Figure 21 also shows how initial behavior and long-term behavior differed. For example, CW5 was significantly lower than all the other simulations except CW1 (homogeneous case). However, by Year 8, long-term extraction rates in CW5 were very similar to those in a number of the other simulations. Early extraction rate behavior was governed by vadose zone contamination, while long-term behavior was governed by groundwater contamination. Material distribution and parameters affected both short and long time periods.

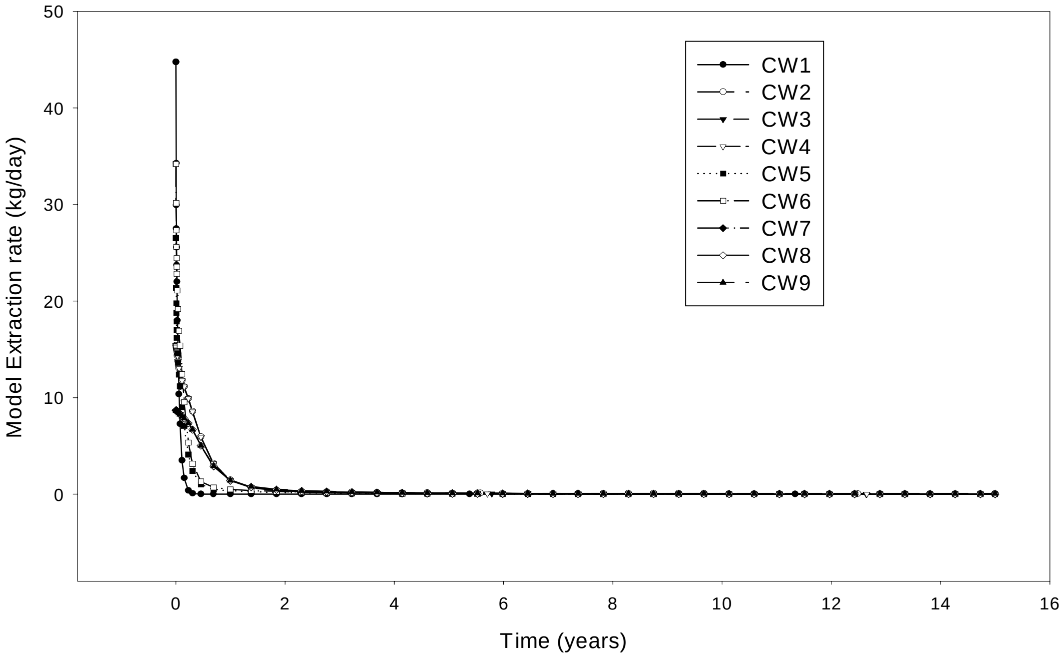

FIGURE 19 Results of the Simulations That Combined a Contaminated Vadose Zone with Contaminated Groundwater beneath the SVE System Plotted on a Linear Scale

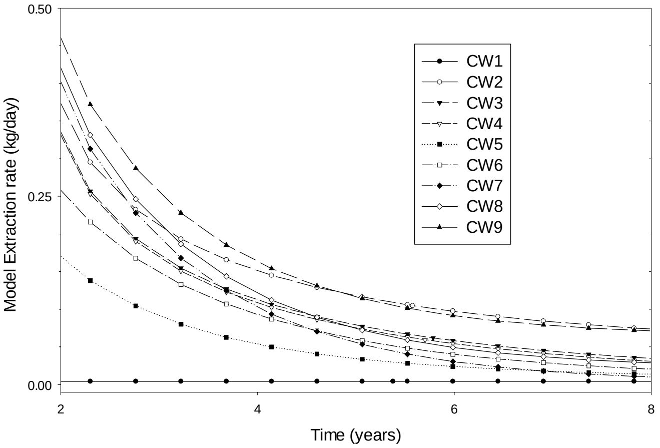

FIGURE 20 View of the 2- to 8-Year Time Period of the CW Simulation Set Plotted on a Linear Scale

Figure 21 shows the results of the simulations plotted on a semi-log scale. Simulations CW1, CW3, CW5, CW6, and CW7 had groundwater TCE concentrations of 0.26 ppm. As expected, CW1, the homogenous simulation, demonstrated rapid removal of the vadose zone VOCs; the removal rate dropped to a steady-state value in about 1 year, when steady-state extraction rates were driven by groundwater contamination.

A number of simulations, including CW1, had groundwater concentrations of 0.26 ppm. Simulations CW5 and CW6, two-layer simulations with 5% and 25% sand, respectively, asymptotically approached the steady-state condition exhibited by CW1, and both had nearly steady-state extraction rates at the end of the 15-year period. These two simulations behaved differently during the initial stages of system operation, with CW5 extraction rates dropping faster than those of CW6. CW3 appeared to be approaching a different steady-state value than that exhibited by CW1. It showed a lower rate of change and a flatter curve. This difference was due to the different material distributions; CW3 had more total clayey-sand than CW5 or CW6. CW3 might also approach the same value over a long time period, or the material distribution might change the long-term VOC extraction rate. However, differences are exaggerated by the semi-log scale. The difference between CW5 and CW6 was only 0.0005 kg/d, and the difference between CW6 and CW3 was only 0.005 kg/d.

Simulations CW7, CW8, and CW9 showed the effect of material distributions on long-term, groundwater-dominated extraction rates. CW7 approached a different steady-state value than the other simulations with a groundwater concentration of 0.26 ppm TCE. Figure 21 shows that CW7 approached a steady-state value of 2×10^{-3} kg/d, measurably lower than the other simulations with the same level of groundwater contamination, which approached values of about 6×10^{-3} kg/d. This same behavior was exhibited by CW8 and CW9, which had the same material distribution as CW7. CW8 had groundwater contamination of 2.6 ppm, the same as did simulation CW2, but it approached a steady-state value that was measurably lower. CW9 had a groundwater contamination level of 7.8 ppm but appeared to approach a steady-state value similar to that of CW2, which had a groundwater contamination level of only 2.6 ppm. These simulations showed that for a given material distribution, long-term extraction rates changed linearly with groundwater contamination levels. However, material distributions could affect these long-term values.

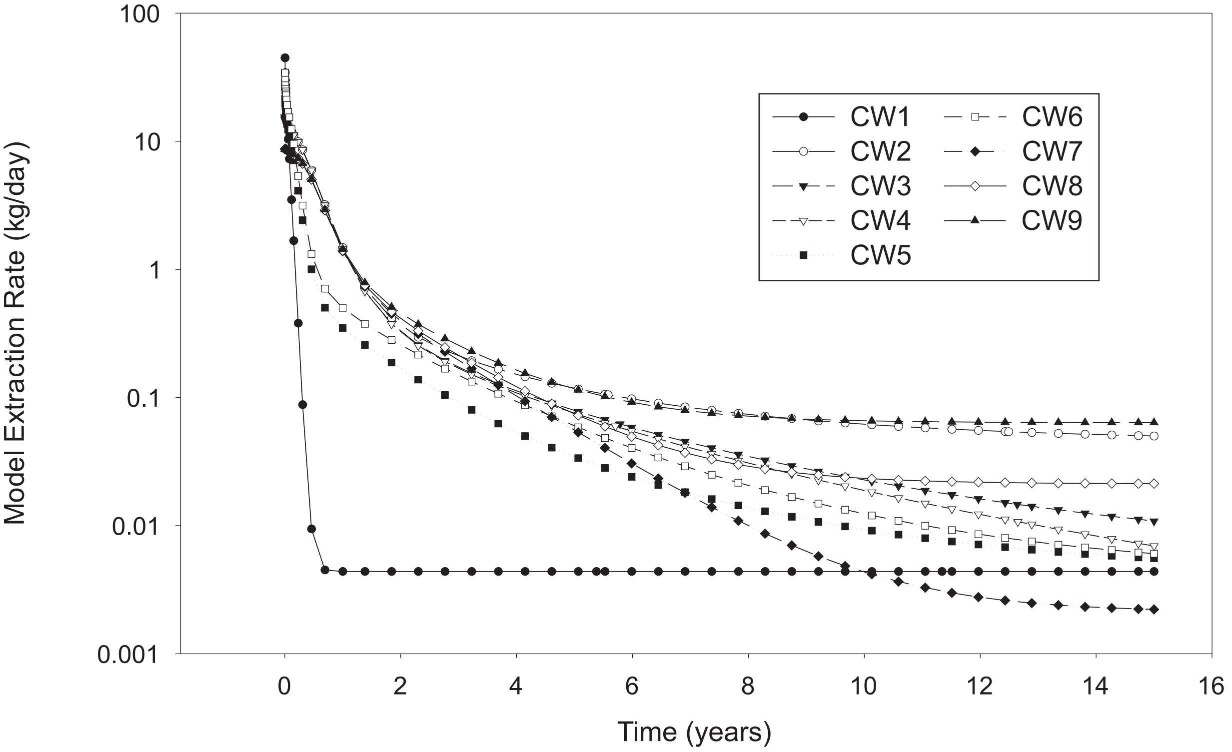

FIGURE 21 Results of the Simulations That Combined a Contaminated Vadose Zone with Contaminated Groundwater beneath the SVE System as Plotted on a Semi-Log Scale

Simulations CW6 and CW7 had different clayey-sand f_{oc} levels and initial vadose zone VOC contamination levels. Figure 21 shows how the CW7 extraction rates started higher than the CW6 rates as a result of the higher VOC levels. After about 4 years, this situation changed, and the CW6 rates became higher than the CW7 rates. CW6 approached a steady-state extraction rate that was 0.004 kg/d higher than that of CW7 because of the higher f_{oc}. These two simulations showed how different conditions affect different time periods of SVE operation.

These simulations showed that by combining initial contamination in the vadose zone with contaminated groundwater beneath the SVE system, the general results observed in the field could be duplicated. These simulations could reproduce both the short-term and long-term behavior of the TCAAP SVE system. Short-term behavior was governed by extraction of VOCs from the vadose zone, while long-term behavior was determined by VOCs extracted from groundwater. Both short-term and long-term behaviors were affected by the distribution of material parameters.

5.8 COMPARISONS WITH TCAAP DATA

Figure 22 shows the field-measured data overlain by the CW simulation set results. There was some question on how to scale the simulation results so they could be compared with the field-measured values. For the vent extraction rates, a simple ratio of the number of vents in the model to the number of vents in the TCAAP SVE system was used: 3/39. All plots displayed in this section have two scales, one showing the measured extraction rates in pounds per day, and one showing the model extraction rates in kilograms per day. The scales use a ratio of 3 modeled vents to 39 system vents and a ratio of 1 lb to 2.2 kg.

If the initial mass of VOCs in the subsurface had been known, this value could have also been used as a calibration/scaling measurement. However, this information was not available. The other option was to match initial model extraction rates with initial measured rates. Preliminary trials of this method indicated that it worked well but required a different scaling ratio for each simulation run. In addition, it was unclear what value to use for the initial field system extraction rate. In some pilot tests, VOCs were extracted at very high rates, while the rates at the start of the data period were lower.

We concluded it was valid to compare the long-term extraction rates by using a ratio of simulation vents to system vents. This method does not include as many unknown parameters. The results of the contaminated groundwater simulations showed that long-term extraction rates varied almost linearly with groundwater contamination levels of 0.1 to 10.0 ppm over the range of the simulations. Thus, in addition to scaling the number of vents in the model to the number of vents in the system, the number of vents could also be adjusted depending on the percentage of the SVE system that had contaminated groundwater beneath it. This adjustment was not done for this study.

No attempt was made to calibrate the T2VOC simulations to the measured data. The model simulation did not include the periods when the system was not operational or when the configuration was changed. Also, because field data were measured at the treatment system, the behavior of an individual vent was not documented. Only integrated values reflecting the operation of the entire system were recorded, making calibration of individual vents impossible.

This study did not require a calibrated model since its objective was not to make detailed predictions of the future behavior of the TCAAP SVE system. This study instead made use of various simulations to explore mechanisms that can influence SVE system behavior in both the short and long term. These simulations were employed to represent various possible conditions at TCAAP and used measured data for comparison purposes.

Figure 22 shows that the measured field results in both the short term and long term could be closely matched by several defensible model simulations. To match field results over both time periods required the inclusion of both initial vadose zone contamination and the existence of

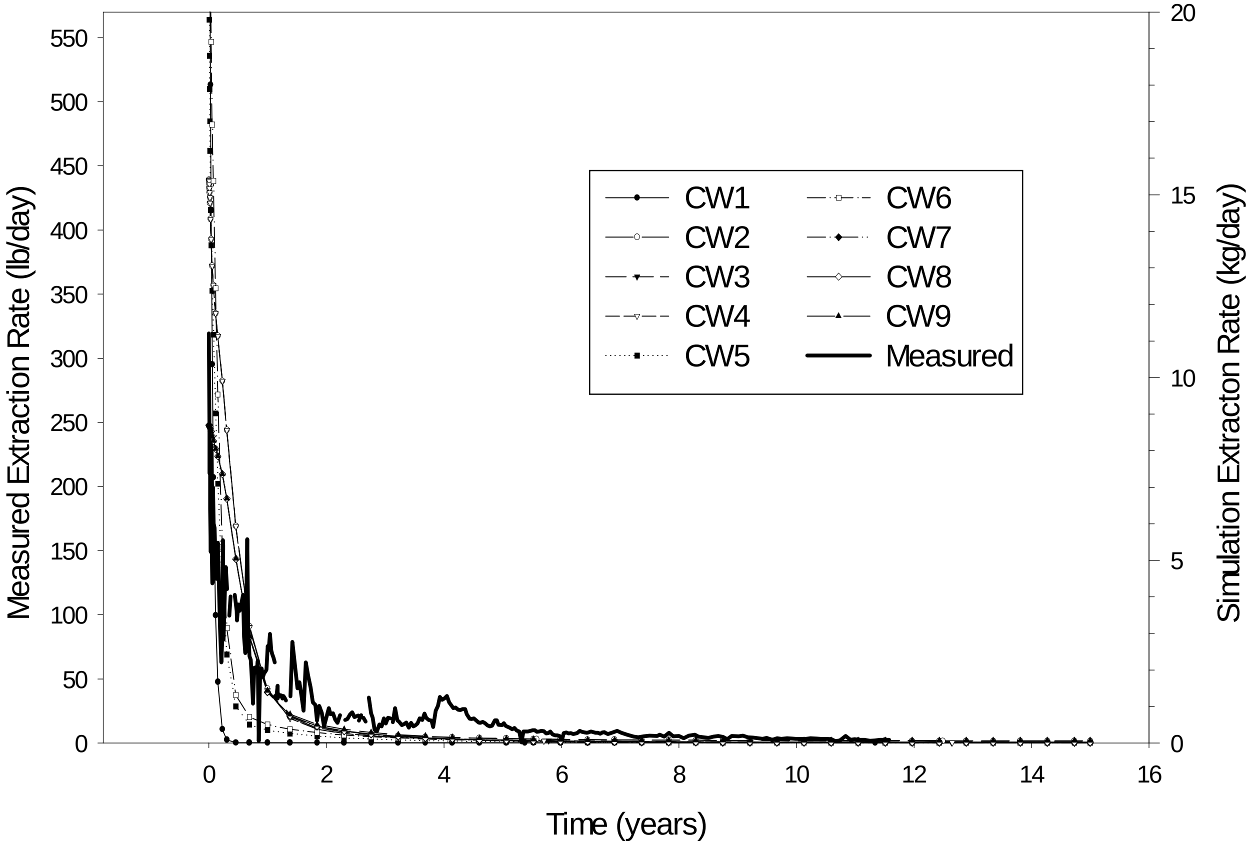

FIGURE 22 Comparison of CW Simulation Data with Field-Measured Data

contaminated groundwater beneath the SVE system. While other model simulations were able to duplicate the measured data for certain time periods, only simulations that included both vadose zone and groundwater contamination were able to match the system's behavior from initiation to the present day.

Figure 22 shows that field-measured rates matched simulations that had very rapid changes in the initial extraction rates until about 1 year after the start of SVE operations. After approximately 1 year, the field system operations underwent changes (Figure 4 and the appendix). After about 1 year, the field extraction rates matched the set of simulations that had a slower decrease in extraction rates. This match continued through the remainder of the modeled period.

After about 4 years, a deep vent was installed in a contaminated zone. Measured extraction rates increased significantly for about 1 year, then returned to values similar to those observed before the installation of the deep vent. With the exception of this time period, Figure 22 shows that the simulations presented here matched the field data over the full operational history of the SVE system.

Figure 23 shows the period from 3 years after SVE operations began until the end of the 15-year simulation period. This figure clearly shows the effect of the additional deep vent on the system and how the system returned to preinstallation values.

Four years after SVE operation began, the system was modified to shut down at nights and on weekends. This shutdown was not duplicated by the model simulations. Previous studies have shown that this type of pulsed pumping initially increases the VOC extraction rate, but over time, the rate eventually approximates the rate that would have occurred if continuous extraction had been used. Figure 23 seems to show this effect. Unfortunately, the last field data available were from February 1998. Figure 23 indicates that the field-measured values and the model simulations were coming into close agreement.

The two simulations that most closely matched the field data were CW2 and CW9. CW2 had a groundwater contamination level of 2.6 ppm and a heterogeneous material distribution in the top 7 m of the model. In CW9, the groundwater contamination level was 7.8 ppm, model Layers 4 and 5 were randomly assigned 75% clayey-sand, and the clayey-sand f_{oc} was slightly higher.

Figures 24 and 25 show the field-measured data and data from the two simulations CW2 and CW9 and an additional simulation, CW2a. CW2a had a groundwater contamination level of 7.8 ppm (compared to 2.6 ppm for CW2); otherwise, the simulations were identical. Figure 24 presents the entire 15-year simulation period, while Figure 25 presents Years 4 through 15 to emphasize the tailing behavior. All three simulations matched the field data well. Simulation CW2 and CW9 values were slightly below the measured data, and CW2a values were slightly above.

Figures 26 and 27 show three-dimensional representations of the distribution of VOCs in the subsurface for the CW2 simulation. Figure 26 shows the images from the full simulation period, while Figure 27 covers the first year. The images are rather complex. The white box represents the model domain. Each image has two iso-surfaces that define the surface in space that corresponds to a constant gas-phase concentration. They are the equivalent of three-dimensional contour lines. The two surfaces represent the 0.05- and 0.005-kg/m^3 concentrations of TCE. In addition, two sections are present in the image. One is a vertical slice near the back of the modeled domain, and the other a horizontal slice at mesh Layer 4. These sections are colored by TCE gas-phase concentrations.

This set of images clearly shows how the extraction process proceeded from the edge of the clay cap to the interior of the model. The initial contamination distribution is located below the clay cap and was evenly distributed throughout the model. As the extraction process started, the surface near the first well started to move toward the well as the VOCs were extracted. At slightly deeper levels, the surface moved even further back, because of gas flow to the other two wells. At this point, the effect of the heterogenous material distribution could be clearly seen in the iso-surfaces. Tight clayey-sand pockets retained the VOCs, while other sandy areas were rapidly cleaned up. This process continued through the remainder of the simulation.

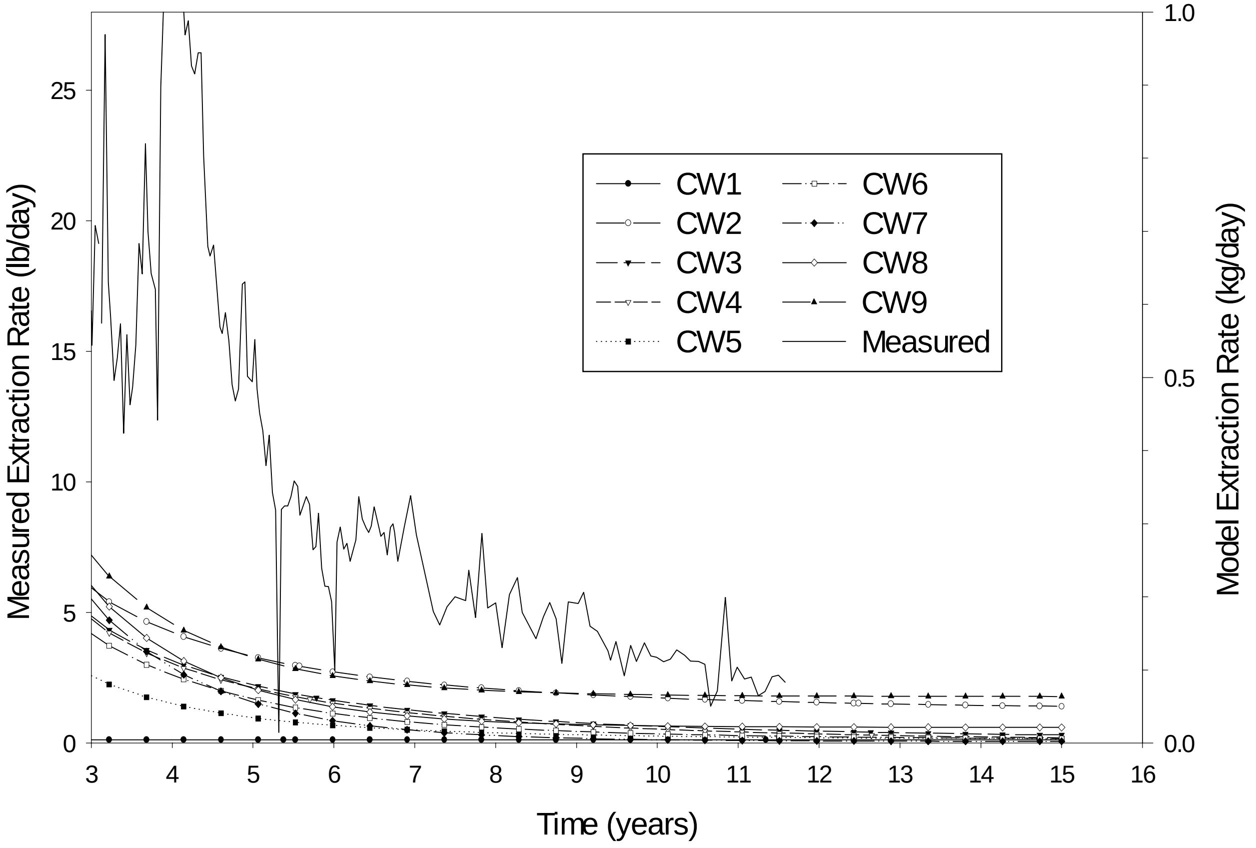

FIGURE 23 Field-Measured Data and CW Simulation Data for Year 4 to Year 15

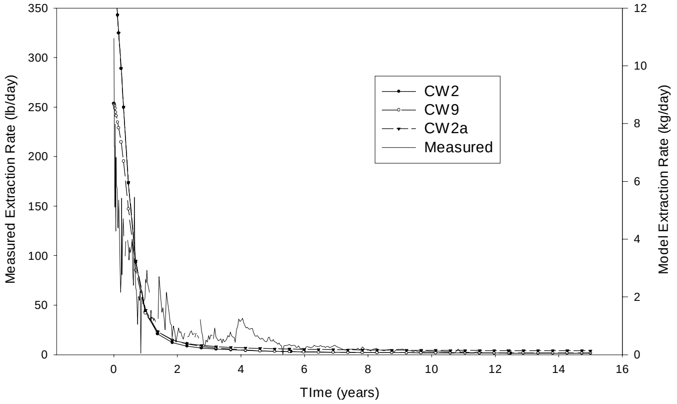

FIGURE 24 Field-Measured Data and CW2, CW9, and CW2a Data for Year 0 to Year 15

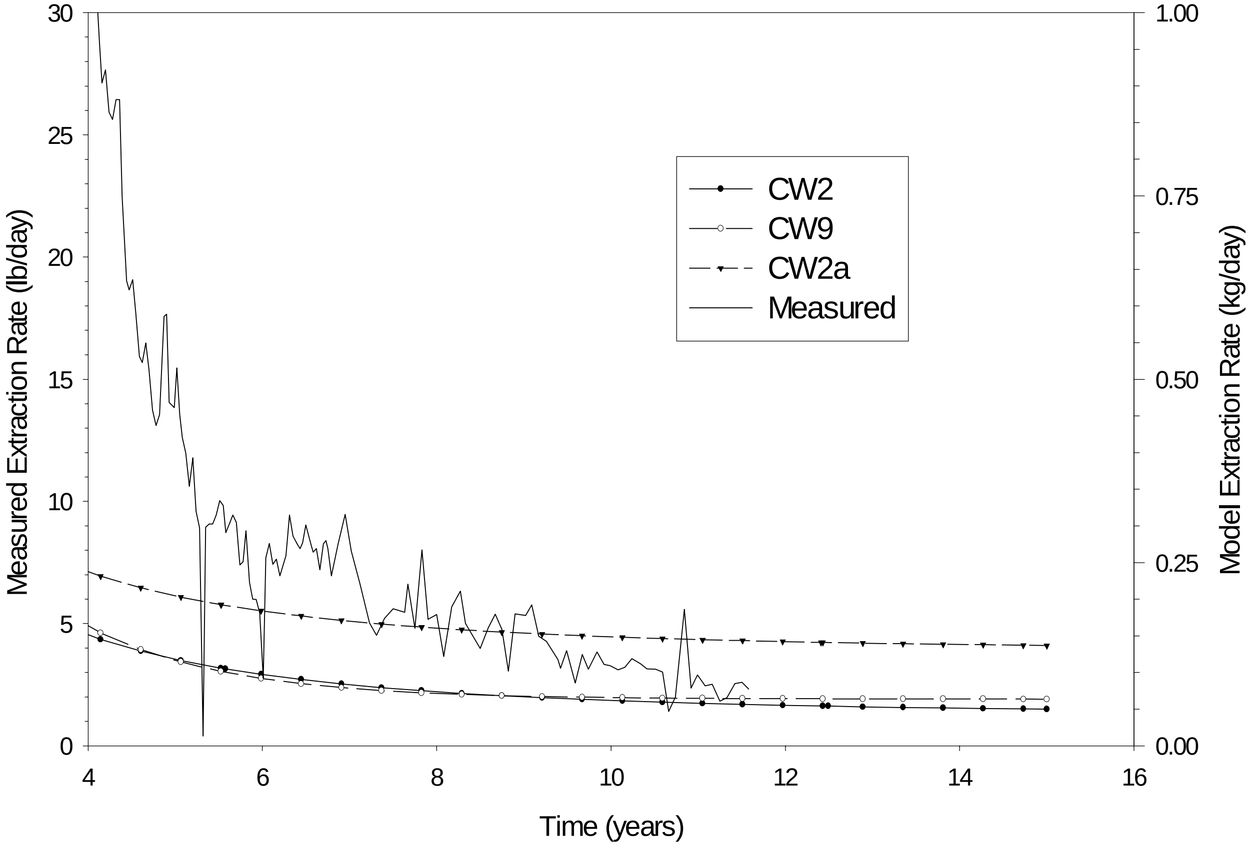

FIGURE 25 Field-Measured Data and CW2, CW9, and CW2a Data with a Groundwater Contaminant Concentration of 7.8 Parts per Million

The effects of the groundwater table can best be observed in the slices taken through the model. These slices are color-coded by VOC concentration in the gas phase (kg/m^3). Notice that the groundwater table at the bottom of the grid influenced the domain above it, providing noticeable VOC gas-phase concentrations.

Even at the end of the 15-year period, small pockets of residual VOC contamination existed, although they did not have an impact on the long-term extraction rates. This situation is evident in the three-dimensional visualization shown in Figure 26. The location and size of the residual VOC-contaminated areas changed very little over the last seven years of the simulation.

Figure 27 shows details of how the VOC extraction proceeded over the short term. Cleanup occurred first near the exterior well and immediately below the heterogenous part of the model (the top 7 m). Cleanup then proceeded in the deeper sand, from the outside of the clay cap toward the interior. After 1 year, the majority of the sand beneath the site was at low contaminant levels, represented by the light tan color. However, at the end of 1 year, the top 7 m still contained

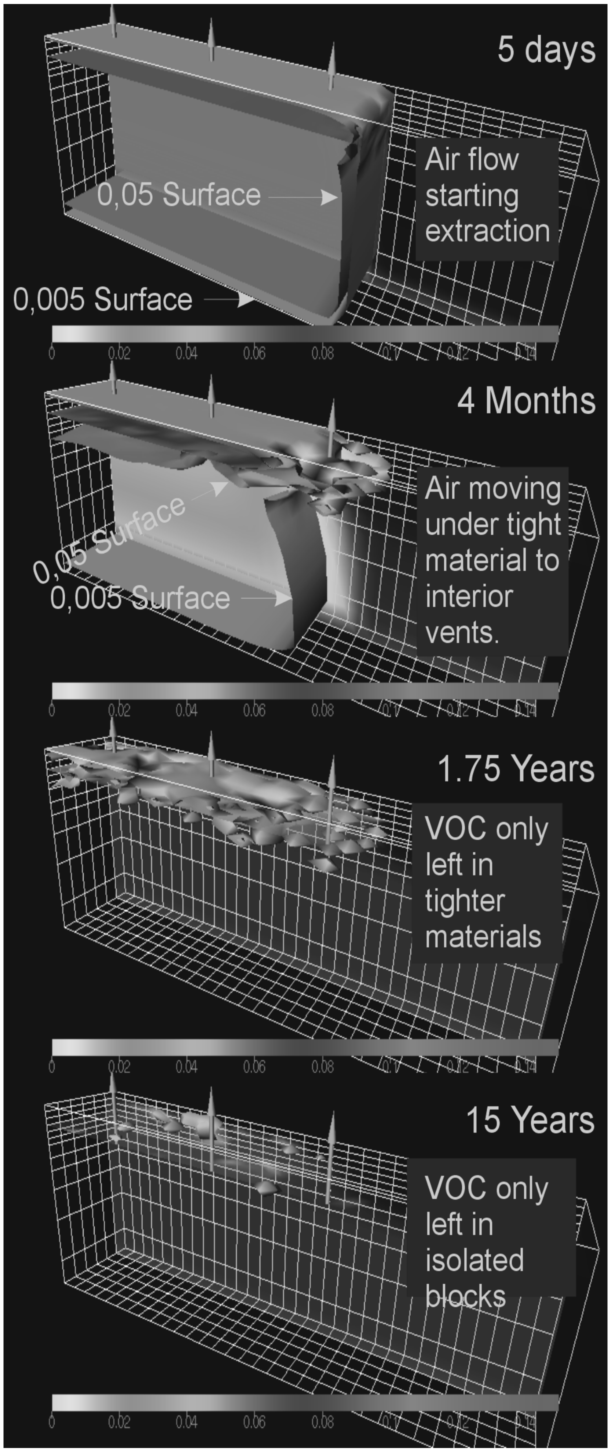

FIGURE 26 Spatial/Time Distribution of VOCs for the CW2 Simulation for Year 0 to Year 15

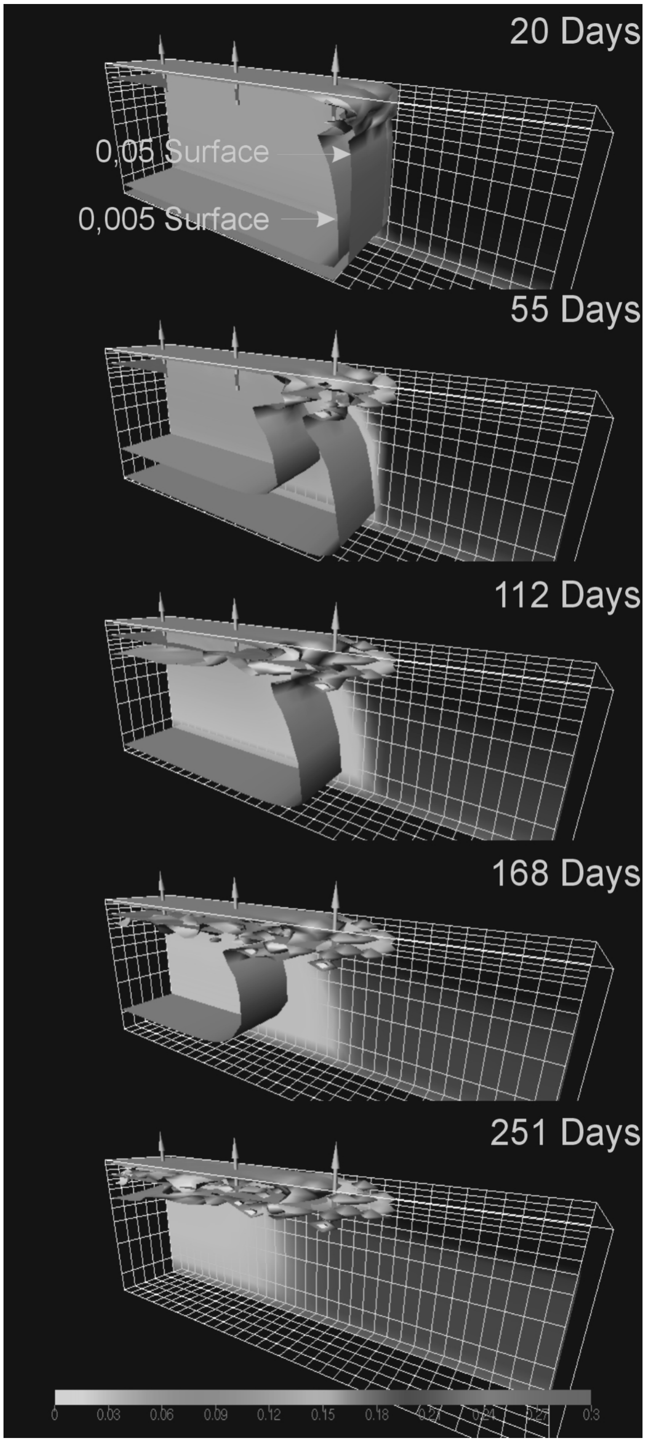

FIGURE 27 Spatial/Time Distribution of VOCs for the CW2 Simulation for Year 1

0.05 kg/m^3 of VOCs in the gas phase. Small pockets at this contamination level remained until the end of the simulation period, as shown in Figure 26.

Extraction from the deep sand was important in the first year for the model. The tighter contaminated area in the top 7 m of the model contributed to the model's behavior for 3 to 5 years. After approximately 5 years, there were still small contaminated zones in existence, but the majority of the contaminants that were extracted after this time came from the groundwater. Figure 26 shows how little change took place in these small contaminated zones over the later periods of the simulation.

5.9 DISCUSSION AND RESULTS

This study demonstrated how a simulation using a combination of initial vadose zone contamination and contaminated groundwater could match the entire extraction time history. While the data from the simulations presented here matched the field data well, the simulations did not represent calibrated models. For the purposes of this study, it was not necessary to develop a calibrated model. Such a model would have required a much more detailed time history of vent operations (shutdown periods, 24-hour operation history, etc.). However, this study demonstrated that if such a model was needed and the data were available, T2VOC could be configured and calibrated to match the entire time history of the TCAAP SVE system.

The results of this modeling study strongly indicate that the continued VOC extraction observed in the TCAAP SVE systems is a result of VOCs being mobilized and extracted from the groundwater beneath the sites. The geometry of the TCAAP SVE system could not be used to devise a case in which deep contamination remained in the vadose zone and contributed to long-term SVE tails.

The simulation results presented in the early sections and the arguments set forth here strongly indicate that the current VOC extraction rates observed at the TCAAP SVE system are almost entirely caused by the vaporization, mobilization, and extraction of VOCs from the groundwater beneath the sites.

5.9.1 Model Simulations

The various simulations discussed here in Section 5 evaluated a large number of model parameters. The simulations did not support a number of early hypotheses about SVE system operation at TCAAP. These hypotheses included the continued existence of near-surface contamination in tight materials that were near stagnation points in the flow field and the existence of contamination in the deep vadose zone, above the water table but below the area of influence of the SVE vents.

The simulation extraction rates could not match the observed extraction rates when only tight materials near the surface were assumed. Perhaps more importantly, the simulations showed that the SVE system's range of influence reached the groundwater table. The simulations showed that the existence of contamination in the deep vadose zone was not the likely cause of the continued tailing behavior observed at TCAAP.

A number of simulations showed that the area of influence for the SVE vents reached the water table. The modeled system was efficient in removing contaminants in this region. None of the simulations showed any tailing behavior that could be attributed to deep contamination. However, the impact of deep clayey-sand layers was not explored because the geology at TCAAP does not include clayey-sand at significant depths, and limits had to be set on the number of variations that could be considered. The model finding was supported by field sampling that took place before the start of this study, which also showed no contamination at depth (Wenck Associates, Inc. 1995).

In addition to field sampling, gas flow modeling was also performed for the TCAAP site. It was conducted by Colorado State University using a single-phase gas system. The model was calibrated to the field SVE system air extraction rates (Eisenbeis 1989; Sabadell et al. 1991). This model showed that the reach of the gas flow was deep, and it came into contact with the water table. These results were duplicated in the modeling study discussed in the report.

Since the start of this modeling study, additional data have become available. The SVE system at TCAAP had deep vents installed to remove any contamination that might exist in the vadose zone in the deep regions but above the water table. These vents are now operational, and extraction rates have not shown any significant increase, indicating that deep contamination does not exist at the TCAAP field site. These data help verify this modeling study.

There are two other possible explanations for the long-term tailing behavior observed. One is the existence of small pockets of free-product NAPL in cracks or fractures in the vadose zone. However, this explanation is unlikely (because of the 15-year time frame of the operation of the field system). Over this long a time period, free-product NAPL would slowly diffuse into the surrounding soil matrix, evaporate, and dissolve into the groundwater. In addition, several field sampling programs were devised to determine if this NAPL was the cause of long-term tailing in the SVE systems. None of them detected any contamination in the shallow vadose zone (0 to 7 m). This lack of samples showing contamination was what led to the initial hypothesis that the tailing was caused by deep contamination below the area of influence of the SVE system. This modeling study, combined with these field sampling programs, shows that vadose-zone contamination is not the likely cause of the observed behavior of the TCAAP SVE system.

The other mechanism that might have contributed to the observed behavior is nonequilibrium kinetics in the chemical reactions. Nonequilibrium kinetics manifest themselves when the chemical reaction is slow when compared to the time of interest (e.g., if measurements are taken before the reaction has had a chance to finish). Over long time periods, nonequilibrium reactions can be approximated by the assumption of equilibrium. A different value of k_d might have to be used to determine the partitioning in the model, but these partitioning behaviors will appear as equilibrium processes over long times. Since these nonequilibrium partitioning processes can be approximated by equilibrium models over long time periods, by varying the f_{oc} and hence the k_d values used in the model, the effects of nonequilibrium sorbtion on SVE operation were effectively evaluated. As stated above, the observed behavior could not be duplicated without introducing the effects of contaminated groundwater into the model simulations.

All of the simulations presented in this study support the conclusion that the continued tailing observed in the TCAAP SVE systems is the result of VOCs being extracted from the groundwater beneath the SVE systems, transported through the vadose zone, and extracted at the vents. It is possible, though unlikely, that the continued tailing could be caused by nonequilibrium processes or the existence of small pockets of oil-phase NAPL located in small cracks or fissures. However, field samples, local geology, and the simulations presented here do not support these potential reasons for long-term tailing behavior. The explanation that is most consistent with field data and these simulations is the influence of contaminated groundwater on long-term SVE operations.

5.9.2 Supporting Field Data and Simulations

In the spring of 1997, Stone and Webster Environmental Technology and Services conducted a sampling program and installed a pilot system with deep vents to determine whether contamination existed deep in the vadose zone and whether the installation of deep vents would be warranted. These efforts focused on Site D.

The field samples indicated that TCE occurred at concentrations between 5 and 50 µg/kg at depths near the water table (Stone and Webster 1998). These concentrations ranged from one to two orders of magnitude below the regulatory guideline value of 416 µg/kg (Stone and Webster 1998) and indicated very low levels of contamination in the soil. These samples were consistent with the assumption that the VOCs being extracted were derived from groundwater contamination.

In 1997, Stone and Webster installed a pilot SVE system with deep vents to evaluate the presence of deep residual contamination in the soil. A series of pressure measurements were made, and the results of these measurements were used with a computer model to estimate the permeability of the material. A permeability of 1.7×10^{-12} m^2 (Stone and Webster 1998) was estimated, which is the value that was used for silty-sand in this study.

Field tests provided additional evidence to support the assumption that groundwater contamination was affecting SVE operations. The well that showed the highest concentration of VOCs in the effluent had a screened interval immediately above the groundwater table. The Stone and Webster (1998) report states, “The higher concentration of VOCs seen at this well may be the results of VOCs partitioning from the liquid phase.” The conclusion section of the report also presents the possibility that SVE removes VOCs directly from the groundwater, but this explanation is discounted as “extremely limited and seasonal at best” (Stone and Webster 1998).

The Stone and Webster (1998) report further states that groundwater samples taken from wells downgradient of the SVE system indicate that TCE concentrations are decreasing. It states that this observation indicates that a stationary source of soil contamination does not exist. On this basis, Stone and Webster argue that further operation of the Site D SVE system would not significantly affect groundwater contamination or groundwater cleanup efforts.

In addition to these field data, which support this report’s conclusions, the Stone and Webster (1998) report also describes a three-dimensional gas flow model that was executed to estimate the zone of influence for the SVE vents. The report states that the modeling results indicated that the zone of influence extended over the entire vadose zone, which supports this report’s findings. Stone and Webster did not accept this result because it appeared to be unreasonable. Instead, they used an empirical method recommended by the EPA to recompute the zone of influence. This report argues that these results were valid and a result of the interaction of multiple vents and the clay cap, parameters not included in the empirical model. These simulation results also support the conclusion that the TCAAP SVE systems are affected by contaminated groundwater.

6 EXTENSION TO OTHER SITES

6.1 INFLUENCE OF GROUNDWATER

When one considers site restoration options, a number of different technologies are available. Each is suited to a particular set of parameters. SVE is an attractive technology when contamination is from VOCs in the vadose zone. Rathfelder et al. (1995) notes that 18% of the U.S. Superfund sites employ SVE for remediation. SVE systems are most effective in uniform soils with good conductivity and are not as effective in tighter soils (Rathfelder et al. 1995). These restrictions indicate that SVE systems will generally be installed in geologic conditions that are similar to those of the TCAAP SVE systems: a deep, relatively homogenous soil underlain by a contaminated groundwater plume.

An important aspect of this study may have applicability to other SVE installations. A number of researchers have noted the long-term tails characteristic of SVE systems and have attributed these tails to “diffusion controlled mass transfer of contaminants located in occluded regions” or “flow by-passing of zones of low permeability” (Rathfelder et al. 1995). But these researchers have not acknowledged the potential for contaminated groundwater to significantly affect the operation of SVE systems. If the geologic characteristics are similar to those at TCAAP, contaminated groundwater is a possible explanation for long-term tailing behavior observed in the field. Considering the geologic requirements for installing an effective SVE system, this phenomenon of extraction of VOCs from groundwater could be widespread.

Field data can be gathered to support this conclusion. If field data indicate a lack of deep contamination (i.e., contamination is below the area of influence of the SVE system but above the groundwater table), and if samples of the geologic conceptual model make the existence of VOCs in occluded local regions of sufficient volume to produce the observed tails, then contaminated groundwater is the most likely cause of the observed behavior.

While the influence of contaminated groundwater might not occur at every SVE installation, the knowledge that this process can occur and can have relatively significant impacts on long-term SVE operations can guide operators in their decisions. While this process is not significant initially, it can be the cause of long-term tailing behavior. By understanding this possibility, one can design field sampling programs to evaluate the other potential causes of long-term tailing behavior. If these other causes cannot be supported by the field data, then the most likely explanation for continued long-term tailing is contaminated groundwater. This conclusion can be supported by this study or further simulation work; it is difficult to prove by sampling. Sampling programs should instead be designed to eliminate the possibility of other causes. Once the most likely cause of long-term tailing is identified, future SVE operation decisions can be based on this knowledge, resulting in more efficient operation, or perhaps termination, of the SVE system.

6.2 SHUTDOWN CRITERIA

When long-term tailing behavior is observed in the field, one of the difficult questions to answer is when to terminate operation of an SVE system that is still extracting VOCs at measurable rates. If the conditions are such that the most likely cause of SVE system tailing is contaminated groundwater, then system operation should be reviewed, as discussed above. Field data that might exclude other causes can be gathered. If contaminated groundwater is the cause, using SVE systems for groundwater restoration is not efficient, and system operation should be terminated.

Two important questions must be asked to determine when to terminate operation of an SVE system. (1) When has an SVE system reached the “tailing” portion of the extraction rate curve? (2) When has the majority of initial contaminant in the vadose zone been removed?

One advantage of model simulations is that the total amount of VOCs in place at the beginning of the simulation is known. (In field systems, the total amount of VOCs in the subsurface can only be estimated). Table 16 presents interesting results obtained from the set of simulations presented in the heterogenous simulation section above. In this set of simulations, the top 7 m of the model were defined with various amounts of four different materials. No contaminated groundwater was considered in the model. Since the initial mass of VOCs in the model domain was known, the percentage of the initial mass remaining at any given time could be easily calculated. In addition, the ratio of the extraction rate at any given time to the initial extraction rate could be calculated. The ratio of the extraction rate at the point when 99% of the mass was removed to the initial extraction rate was computed and is presented as a percentage for different runs in Table 16. The percentages are remarkably constant for these runs, which covered a very wide range of conditions. Initial amounts of mass in place ranged from 600 kg (H1 and H2) to nearly 3,000 kg (H3). The final extraction rates ranged from relatively high tails (H7) to essentially no tails after 4 years (a number of simulations); see Figure 15.

TABLE 16 Percent of the Initial Extraction Rate When 99% of the Initial VOC Mass Is Removed from the Simulation

Simulation	% of Initial Extraction Rate
H1	0.3
H2	0.3
H3	0.1
H4	0.2
H5	0.3
H6	0.4
H7	Not reached

Table 16 shows that for all of these situations, when extraction rates fell below 0.3% to 0.1% of the initial rates, 99% of the initial mass had been removed from the subsurface. This indicator also worked well for simulation H7, in which, even after 15 years, there was still nearly 10% of the initial mass of contaminant in the subsurface. In this case, the extraction rate at the end of the 15-year period was 2.5% of the initial rate, a level well above the 0.3% to 0.1% cutoff value. The H7 simulation had a very flat extraction rate curve and 7 m of clayey-sand in the top of the modeled domain.

The rates provide an indicator of when to terminate operations at field SVE systems. If SVE extraction rates are below 0.1% of the initial rates, 99% or more of the mass has been removed. When the model simulations reached this level, further mass removal was slow, and the system showed asymptotic behavior.

Table 17 presents the percent of initial extraction rates reached when 90% of the initial mass of VOCs has been removed from the subsurface. The values range from about 2.5% to 4.5%, again a narrow range. The 90% point may be a better indicator of when to terminate SVE operations than the 99% removal point.

Table 18 presents data to explain why it might be useful to evaluate the system at a 90% removal point rather than a 99% removal point. In Table 18, the time required to remove the initial 90% of the mass of VOC initially in the subsurface is presented, along with the additional time to remove 99% of the initial mass. The time required to remove the last 9% is longer than the time required to remove the first 90%. When VOC contamination in the vadose zone reaches these levels, the extraction rate decreases. The VOCs are not mobile and are generally sorbed onto the solid phase, with smaller amounts partitioned into the aqueous and gas phases. From a risk perspective, contamination at these levels may pose little concern because of the lack of mobility and receptors. The cost to remove the additional 9% may not be justified by the subsequent reduction in risk.

TABLE 17 Percent of the Initial Extraction Rate When 90% of the Initial VOC Mass Is Removed from the Simulation

Simulation	% of Initial Extraction Rate
H1	4.4
H2	4.3
H3	3.5
H4	2.8
H5	3.0
H6	3.7
H7	2.6

TABLE 18 Comparison of the Time Required to Remove 90% versus 99% of the Initial Contamination

Simulation	Time for 90% (years)	Time for 99% (years)
H1	0.5	1.5
H2	0.5	3.5
H3	2.5	5.5
H4	0.5	10.0
H5	4.0	11.0

7 CONCLUSIONS

This study attempted to answer several questions about the SVE systems installed at TCAAP. These questions ranged from general ones (can the T2VOC code be used to model the long-term behavior of an SVE system?) to more specific ones (should deep vents be installed at TCAAP?).

The results of this modeling study show that both the short-term and long-term tailing behavior observed in SVE systems can be matched by models that do not contain nonequilibrium chemical processes. We were able to successfully match the short-term and long-term field behavior of the TCAAP system by using T2VOC and defensible modeling assumptions. It appears that over long time periods (several years), nonequilibrium processes can be approximated by local equilibrium assumptions.

The initial SVE system design for TCAAP was based on estimates that cleanup times would be on the order of 3 to 4 years. The model results from this study confirm this initial estimation. Figure 22 shows that 95% of the contaminants present in the vadose zone were removed during this time period. The modeling also shows that the persistent tailing behavior revealed by the TCAAP field is probably derived from contaminated groundwater beneath the site. This conclusion implies that the long-term tailing behavior is not a result of contamination located below the SVE site and that installation of deep vents is not needed. As was stated above, after this modeling study was started, these deep vents were installed, and they never did indicate the existence of any deep contamination.

Simulations showed that using SVE systems for the mass removal of VOCs from the subsurface is exponential in nature. Removal of the first 90% of the mass takes less time than removal of the next 9%. The simulations suggest that the percentage change in the later extraction rates from the initial extraction rate can indicate the percentage of mass that has been removed from the subsurface. These simulations show that when extraction rates drop below 2% to 5% of initial rates, approximately 90% of the initial mass has been removed. Continued operation of the system removes additional mass only very slowly.

This study was successful in demonstrating the following general conclusions:

- Advanced multiphase, multicomponent computer codes such as T2VOC can be used for engineering evaluations of field-scale SVE systems.

- Local equilibrium models are capable of duplicating observed field behavior.

- Contaminated groundwater beneath SVE systems can have significant impacts on the long-term tailing behavior. This finding has not been previously reported in the literature.

The study also provided answers to specific questions about future operations of the TCAAP SVE systems:

- Deep contamination does not exist at TCAAP, and deep vents are not needed. (This finding was supported by recent field data [Stone & Webster 1998].)
- The most likely cause of long-term tailing behavior at TCAAP is contaminated groundwater beneath the site.
- The TCAAP SVE systems have achieved their stated objective of source control.

The study was successful in developing some general guidelines for operation of other SVE systems, including these:

- Contaminated groundwater is a potential source of long-term tailing behavior. (This finding can be considered when designing field sampling programs.)
- The percentage change in extraction rates can be used as an indicator of the VOC mass remaining in the subsurface.
- Long-term operation of SVE systems becomes increasingly inefficient.
- SVE operations should be reviewed when extraction rates drop to about 5% of the initial rates.

Since none of these operational guidelines are absolute, they are best used to help determine when it would be reasonable to reevaluate SVE system operations. The study also provides important insight into physical processes that might be affecting long-term SVE system behavior.

Although the study was extensive, a number of further simulations could provide additional insight into long-term SVE operations and exit strategies. Some of these simulations could evaluate the effects of small pockets of free-phase NAPL trapped in fractures (including the effects that removing VOCs from groundwater could have on the groundwater-soil gas interface flux). Both these effects could be evaluated by using T2VOC. Nonequilibrium kinetics might also have an impact on long-term operations, but if the period of operation is long compared to the time required for the chemical reaction to finish, the effects could be approximated by equilibrium assumptions. T2VOC cannot evaluate the impact on nonequilibrium kinetics without significant modifications.

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APPENDIX: SITE D OPERATION DATA

		TCA Mol. Wt. = 133.4		TCE Mol. Wt. = 131.4		Total VOCs Removed	
Date	Flow Rate (ft^3/min)	Conc. (ppm)	Mass Removed (lb/d)	Conc. (ppm)	Mass Removed (lb/d)	Mass Rate (lb/d)	Cumulative (lb)
03/06/86							0.00
07/07/86	2,840	10	15.15	38	56.72	71.88	4,420.44
07/09/86	2,950	54	85.00	206	319.41	404.41	4,896.72
07/11/86	2,920	38	59.21	158	242.49	301.70	5,602.83
07/14/86	2,920	33	51.42	137	210.26	261.68	6,447.90
07/16/86	2,920	31	48.30	137	210.26	258.56	6,968.14
07/18/86	2,920	27	42.07	119	182.64	224.70	7,451.41
07/21/86	2,920	24	37.39	97	148.87	186.27	8,067.86
07/23/86	2,920	25	38.95	113	173.43	212.38	8,466.51
07/25/86	2,950	39	61.39	150	232.58	293.97	8,972.85
07/28/86	2,950	27	42.50	100	155.05	197.55	9,710.14
07/30/86	3,160	21	35.41	75	124.57	159.98	10,067.67
08/01/86	3,160	22	37.10	118	195.99	233.08	10,460.73
08/04/86	3,160	10	16.86	120	199.31	216.17	11,134.60
08/07/86	3,160	16	26.98	103	171.07	198.05	11,755.93
08/14/86	3,160	28	47.21	101	167.75	214.96	13,201.48
08/21/86	3,160	15	25.29	79	131.21	156.50	14,501.62
08/27/86	3,160	14	23.61	77	127.89	151.50	15,425.61
09/03/86	3,160	28	47.21	94	156.12	203.34	16,667.53
09/10/86	2,920	37	57.65	83	127.38	185.03	18,026.83
09/17/86	2,920	12	18.70	58	89.02	107.71	19,051.45
09/24/86	2,920	29	45.19	41	62.92	108.11	19,806.83
10/01/86	2,920	7	11.06	53	81.34	92.40	20,508.63
10/03/86	5,675	7	22.11	53	158.09	180.19	20,781.22
10/10/86	5,675	7	21.20	27	80.54	101.73	21,767.96
10/15/86	5,560	13	38.57	40	116.89	155.46	22,410.95
10/23/86	5,560	25	74.17	47	137.35	211.52	23,878.88
10/30/86	5,560	12	35.60	41	119.82	155.42	25,163.16
11/13/86	System off for 7 days to fence-in transformer					(903.19)	24,259.97
11/13/86	5,560	10	29.67	34	99.36	129.03	26,251.08
11/21/86	5,560	23	68.53	39	114.26	182.80	25,507.26
12/18/86	System off for 2 days to put in Petrex tubes (Site F)					(292.35)	25,214.91
12/18/86	4,780	12	30.61	46	115.57	146.18	29,656.05
12/26/86	4,780	11	28.06	41	103.01	131.06	26,323.87
01/02/87	4,780	10	25.51	38	95.47	120.98	27,206.01
01/08/87	4,780	12	30.61	43	108.03	138.64	27,984.86
01/15/87	4,780	12	30.61	41	103.01	133.61	28,937.74
01/22/87	4,780	11	28.06	42	105.52	133.58	29,872.91
01/29/87	4,780	12	30.61	44	110.54	141.15	30,834.46
02/05/87	4,780	12	30.61	46	115.57	146.18	31,840.11
02/12/87	4,780	9	22.96	33	82.66	105.61	32,721.37
02/19/87	4,780	8	20.15	28	70.10	90.24	33,406.87
02/26/87	5,200	12	33.85	46	125.45	159.30	34,280.28

		TCA Mol. Wt. = 133.4		TCE Mol. Wt. = 131.4		Total VOCs Removed	
Date	**Flow Rate (ft^3/min)**	**Conc. (ppm)**	**Mass Removed (lb/d)**	**Conc. (ppm)**	**Mass Removed (lb/d)**	**Mass Rate (lb/d)**	**Cumulative (lb)**
03/05/87	4,960	15	39.70	61	159.03	198.73	35,533.37
03/12/87	5,150	8	22.53	33	89.33	111.86	36,620.42
03/19/87	5,150	6	15.66	25	67.67	83.33	37,303.60
03/26/87	5,150	6	15.66	24	64.96	80.63	37,877.47
04/02/87	5,160	5	12.39	19	51.53	63.92	38,383.39
04/09/87	5,300	3	7.64	11	30.64	38.28	38,741.08
04/16/87	5,300	5	14.42	21	58.50	72.92	39,130.29
04/23/87	5,600	4	12.85	20	58.87	71.72	39,636.52
04/30/87	5,800	4	13.00	18	54.87	67.87	40,125.08
05/07/87	5,800	4	12.69	21	64.02	76.71	40,631.10
05/14/87	5,800	13	40.23	0.5	1.52	41.76	41,045.73
05/21/87	5,800	10	30.95	17	51.82	82.77	41,481.59
05/28/87	6,500	11	38.15	17	58.08	96.23	42,108.10
06/04/87	6,500	5	16.30	17	58.08	74.38	42,705.24
06/11/87	6,500	4	15.26	15	51.25	66.51	43,198.35
06/18/87	6,500	4	14.91	16	54.66	69.58	43,674.64
06/25/87	7,000	4	14.57	15	55.19	69.76	44,162.30
07/02/87	6,400	14	47.81	17	57.19	105.00	44,773.93
07/10/87	6,000	5	15.69	24	75.69	91.37	45,559.41
07/16/87	6,000	10	31.06	23	72.53	103.59	46,144.30
07/24/87	6,000	5.3	16.97	27	85.15	102.12	46,967.11
07/31/87	5,500	8.4	24.65	25	72.27	96.92	47,663.75
08/06/87	5,500	5.6	16.43	24	69.38	85.81	48,211.96
08/13/87	5,500	5.5	16.14	23	66.49	82.63	48,801.51
08/20/87	5,700	5.0	15.21	21	62.91	78.12	49,364.14
08/21/87	System shut off during nights and weekends					78.12	49,442.26
08/27/87	6,000	4.4	9.09	18	36.61	45.70	49,638.12
09/03/87	6,200	4.0	8.54	17	35.73	44.27	49,863.03
09/08/87	6,000	5.6	11.56	22	44.75	56.31	50,042.64
09/10/87	6,000	4.2	8.67	17	34.58	43.25	50,113.76
09/17/87	6,200	4.3	9.18	18	37.83	47.01	50,339.41
09/24/87	6,000	4.3	8.88	18	36.61	45.49	50,570.67
10/01/87	6,100	4.0	8.40	18	37.22	45.62	50,798.46
10/08/87	6,000	4.2	8.67	17	34.58	43.25	51,020.64
10/15/87	6,000	4.3	8.88	18	36.61	45.49	51,242.50
10/22/87	6,100	3.9	8.19	17	35.16	43.34	51,464.59
10/29/87	6,100	4.2	8.82	16	33.09	41.91	51,677.72
11/03/87	Noise reducers installed						
11/06/87	System resumed 24-hour operation.						
11/27/87	6,300	3.4	11.43	11	36.42	47.85	53,065.48
12/11/87	6,000	6.7	21.45	25	78.84	100.29	54,102.49
01/11/88	5,800	4.5	13.93	14	42.68	56.61	56,534.38
01/21/88	6,000	4.0	12.81	15	47.30	60.11	57,117.96
02/04/88	6,200	2.7	8.93	11	35.85	44.78	57,852.18
02/18/88	5,900	2.0	6.30	8.1	25.12	31.41	58,385.54

		TCA Mol. Wt. = 133.4		TCE Mol. Wt. = 131.4		Total VOCs Removed	
Date	Flow Rate (ft^3/min)	Conc. (ppm)	Mass Removed (lb/d)	Conc. (ppm)	Mass Removed (lb/d)	Mass Rate (lb/d)	Cumulative (lb)
03/03/88	5,700	5.5	16.73	21	62.91	79.64	59,162.94
03/17/88	5,600	4.6	13.75	18	52.98	66.73	60,187.52
03/31/88	5,500	3.5	10.27	15.0	43.36	53.63	61,030.04
04/14/88	5,500	2.6	7.63	11.0	31.80	39.43	61,681.48
04/28/88	5,800	2.3	7.12	9.7	29.57	36.69	62,214.30
05/12/88	5,500	1.4	4.11	6.0	17.34	21.45	62,621.30
05/26/88	5,600	2.3	6.87	9.8	28.84	35.72	63,021.50
06/09/88	5,400	1.9	5.47	8.2	23.27	28.75	63,472.76
06/23/88	5,700	1.0	2.92	4.3	12.88	15.80	63,784.61
07/21/88	6,200	1.9	6.29	8.3	27.05	33.33	64,472.51
08/04/88	6,200	1.6	5.29	6.9	22.49	27.78	64,900.29
08/18/88	5,700	1.8	5.47	7.7	23.07	28.54	65,294.54
09/01/88	6,000	1.4	4.48	5.8	18.29	22.77	65,653.76
09/15/88	6,100	1.1	3.58	4.9	15.71	19.29	65,948.21
09/29/88	5,800	1.7	5.26	7.1	21.64	26.91	66,271.58
11/03/88	System off for 360 hours to repair blowers					(331.18)	65,940.40
11/03/88	5,900	1.3	4.09	5.8	17.99	22.08	66,797.62
11/18/88	5,900	1.4	4.41	6.0	18.61	23.01	66,285.60
12/01/88	5,900	1.7	5.35	7.1	22.02	27.37	66,613.10
12/15/88	5,900	1.9	5.98	7.7	23.88	29.86	67,013.70
12/29/88	5,700	1.6	4.87	6.7	20.07	24.94	67,397.29
01/20/89	5,100	1.8	4.90	8.0	21.44	26.34	67,961.39
01/26/89	System off for 26 hours for Colorado State University (CSU) study					(23.64)	67,937.75
01/26/89	4,500	1.8	4.32	7.4	17.50	21.82	68,082.25
02/09/89	5,300	2.0	5.66	7.8	21.73	27.38	68,321.13
02/23/89	System off for 240 hours for Colorado State University (CSU) study					(245.74)	68,075.39
02/23/89	5,900	1.6	5.04	6.3	19.54	24.57	68,439.10
03/09/89	5,000	1.6	4.27	6.3	16.56	20.83	68,756.89
03/27/89	System off for one day due to power outage					(44.58)	68,712.31
03/27/89	5,600	3.1	9.26	12.0	35.32	44.58	69,300.99
04/11/89	5,800	2.1	6.50	7.6	23.17	29.67	69,857.87
04/21/89	5,900	1.8	5.67	6.3	19.54	25.20	70,132.23
05/04/89	5,900	0.9	2.83	3.3	10.23	13.07	70,380.99
05/18/89	6,000	0.7	2.24	2.8	8.83	11.07	70,549.95
06/01/89	6,000	1.2	3.84	4.6	14.51	18.35	70,755.89
06/15/89	6,100	1.1	3.58	4.0	12.82	16.41	70,999.17
06/29/89	6,300	1.3	4.37	5.8	19.21	23.58	71,279.03
07/13/89	6,300	1.0	3.36	4.6	15.23	18.59	71,574.21
07/28/89	6,500	1.4	4.86	5.8	19.82	24.67	71,898.70
08/10/89	6,500	1.3	4.51	5.6	19.13	23.64	72,212.72
08/13/89	System shut down to vent PCB-contaminated soil.					(62.66)	72,150.07
08/25/89	6,000	1.5	4.80	5.1	16.08	20.89	72,484.02
09/07/89	5,800	2.4	7.43	8.9	27.13	34.56	72,844.41
09/21/89	6,100	1.4	4.56	5.5	17.63	22.19	73,241.66
10/05/89	6,100	1.4	4.56	5.1	16.35	20.91	73,543.35

		TCA Mol. Wt. = 133.4		**TCE Mol. Wt. = 131.4**		**Total VOCs Removed**	
Date	**Flow Rate (ft^3/min)**	**Conc. (ppm)**	**Mass Removed (lb/d)**	**Conc. (ppm)**	**Mass Removed (lb/d)**	**Mass Rate (lb/d)**	**Cumulative (lb)**
10/19/89	6,600	1.1	3.87	4.0	13.88	17.75	73,813.96
10/31/89	6,100	1.3	4.23	4.6	14.75	18.98	74,034.34
11/17/89	6,500	1.2	4.16	4.7	16.06	20.22	74,367.53
12/01/89	6,100	1.0	3.25	3.7	11.86	15.12	74,614.89
12/15/89	6,200	1.3	4.30	4.8	15.64	19.94	74,860.31
12/29/89	5,600	1.2	3.59	4.4	12.95	16.54	75,115.66
01/11/90	5,900	1.2	3.78	4.4	13.64	17.42	75,336.40
01/25/90	5,800	1.4	4.33	5.0	15.24	19.58	75,595.38
02/08/90	5,200	1.9	5.27	7.0	19.13	24.40	75,903.23
02/22/90	5,100	1.8	4.90	6.7	17.96	22.86	76,234.07
03/09/90	5,200	2.3	6.38	8.4	22.96	29.34	76,625.56
03/22/90	5,400	1.9	5.47	6.9	19.58	25.06	76,979.15
04/05/90	5,700	1.6	4.87	6.0	17.98	22.84	77,314.45
04/22/90	5,700	1.7	5.17	5.8	17.38	22.55	77,700.26
05/03/90	5,700	1.8	3.53	6.4	12.37	15.90	77,851.29
05/17/90	5,700	3.7	7.26	13.0	25.12	32.38	78,092.68
05/31/90	5,700	4.5	8.83	15.0	28.99	37.81	78,443.64
06/14/90	5,900	5.1	10.36	18.0	36.00	46.36	78,864.51
06/28/90	5,500	4.9	9.28	18.0	33.56	42.84	79,310.49
07/12/90	5,700	4.3	8.44	18.0	34.78	43.22	79,740.77
07/26/90	5,400	4.5	8.36	20.0	36.61	44.98	80,181.75
08/09/90	5,500	3.4	6.44	17.0	31.70	38.13	80,597.30
08/23/90	5,000	3.3	5.68	17.0	28.82	34.49	80,960.44
09/06/90	5,000	3.0	5.16	16.0	27.12	32.28	81,294.33
09/20/90	5,100	3.0	5.27	16.0	27.66	32.93	81,620.40
10/05/90	5,100	2.8	4.91	15.0	25.93	30.85	81,962.07
10/18/90	5,400	2.7	5.02	14.0	25.63	30.65	82,247.59
11/01/90	5,200	2.7	4.83	15.0	26.44	31.28	82,557.20
11/15/90	5,200	2.8	5.01	15.0	26.44	31.45	82,870.84
11/28/90	5,100	2.6	4.56	13.0	22.48	27.04	83,142.42
12/14/90	5,100	2.2	3.86	11.0	19.02	22.88	83,427.68
12/28/90	5,000	2.2	3.79	11.0	18.65	22.43	83,654.24
01/10/91	5,800	1.9	3.79	9.7	19.07	22.87	83,864.55
01/24/91	6,200	1.7	3.63	8.4	17.66	21.28	84,085.30
02/07/91	5,400	1.8	3.35	8.7	15.93	19.27	84,288.07
02/21/91	5,200	1.9	3.40	8.9	15.69	19.09	84,479.88
03/07/91	5,400	2.1	3.90	9.0	16.48	20.38	84,677.23
03/21/91	5,100	2.1	3.69	8.9	15.39	19.07	84,874.49
04/04/91	5,400	1.8	3.35	7.5	13.73	17.08	85,055.24
04/18/91	5,600	1.7	3.28	6.9	13.10	16.38	85,222.49
05/02/91	5,400	1.7	3.16	7.4	13.55	16.71	85,387.90
05/23/91	5,400	2.3	4.27	9.6	17.57	21.85	85,677.07
05/31/91	5,600	2.2	4.24	9.3	17.66	21.90	85,802.06
06/13/91	5,600	1.7	3.28	7.4	14.05	17.33	85,984.15
07/03/91	5,300	1.9	3.47	7.7	13.84	17.30	86,231.48

		TCA Mol. Wt. = 133.4		TCE Mol. Wt. = 131.4		Total VOCs Removed	
Date	Flow Rate (ft^3/min)	Conc. (ppm)	Mass Removed (lb/d)	Conc. (ppm)	Mass Removed (lb/d)	Mass Rate (lb/d)	Cumulative (lb)
07/15/91	5,700	1.9	3.73	8.0	15.46	19.19	86,387.86
07/25/91	5,400	1.7	3.16	7.4	13.55	16.71	86,516.05
08/08/91	5,400	1.6	2.97	6.9	12.63	15.61	86,677.60
08/22/91	5,600	1.5	2.89	6.3	11.96	14.85	86,829.89
09/05/91	5,800	1.2	2.40	5.4	10.62	13.01	86,969.21
09/19/91	5,700	1.2	2.35	6.1	11.79	14.14	87,104.98
10/04/91	5,900	1.2	2.44	4.8	9.60	12.04	87,245.23
10/17/91	5,600	1.1	2.12	4.7	8.92	11.04	87,352.39
10/31/91	5,900	0.5	1.02	0.2	0.40	1.42	87,414.68
11/14/91	5,500	0.6	1.14	4.8	8.95	10.09	87,472.19
11/27/91	5,700	1.1	2.16	4.7	9.08	11.24	87,571.20
12/12/91	5,700	1.1	2.16	4.7	9.08	11.24	87,691.63
12/26/91	5,800	1.2	2.40	4.8	9.44	11.83	87,807.00
01/09/92	5,800	1.1	2.20	5.1	10.03	12.22	87,927.28
01/23/92	5,800	1.1	2.20	5.0	9.83	12.03	88,048.54
02/06/92	5,600	1.1	2.12	4.6	8.73	10.85	88,162.94
02/20/92	5,700	1.1	2.16	4.7	9.08	11.24	88,273.40
03/05/92	5,800	1.2	2.40	4.8	9.44	11.83	88,388.77
03/19/92	5,500	1.1	2.08	4.9	9.14	11.22	88,504.03
04/02/92	5,900	0.9	1.83	3.7	7.40	9.23	88,606.27
04/16/92	6,000	0.9	1.86	3.7	7.53	9.38	88,699.33
04/30/92	5,900	1.1	2.23	4.4	8.80	11.03	88,801.43
05/14/92	5,800	0.8	1.60	3.4	6.69	8.28	88,898.01
05/28/92	5,900	0.7	1.42	3.0	6.00	7.42	88,976.53
06/11/92	5,700	0.7	1.37	3.1	5.99	7.36	89,050.46
06/25/92	5,000	0.8	1.38	3.2	5.42	6.80	89,121.28
07/09/92	5,100	0.4	0.70	1.6	2.77	3.47	89,172.63
07/23/92	5,400	1.0	1.86	4.2	7.69	9.55	89,237.71
08/06/92	5,300	1.0	1.82	4.6	8.27	10.09	89,335.89
08/20/92	5,100	1.0	1.76	4.3	7.43	9.19	89,432.28
09/03/92	5,500	1.0	1.89	4.1	7.64	9.54	89,525.92
09/17/92	5,700	0.9	1.77	3.6	6.96	8.72	89,617.22
10/15/92	5,600	1.0	1.93	4.1	7.78	9.71	89,801.55
10/29/92	5,800	1.1	2.20	4.8	9.44	11.63	89,908.28
11/13/92	5,500	1.1	2.08	4.6	8.58	10.66	90,027.70
11/30/92	5,400	1.1	2.04	4.5	8.24	10.28	90,154.85
12/10/92	5,800	1.0	2.00	4.1	8.06	10.06	90,227.49
12/23/92	5,700	1.0	1.96	4.3	8.31	10.27	90,321.88
01/07/93	5,800	1.1	2.20	4.6	9.04	11.24	90,437.12
01/26/93	5,500	1.0	1.89	4.4	8.20	10.10	90,581.91
02/05/93	5,700	0.9	1.77	4.1	7.92	9.69	90,652.57
02/18/93	5,800	0.9	1.80	4.1	8.06	9.86	90,743.32
03/04/93	5,600	0.8	1.54	3.8	7.21	8.76	90,836.40
03/18/93	5,800	0.9	1.80	4.2	8.26	10.05	90,930.45
04/01/93	5,900	1.0	2.03	4.2	8.40	10.43	91,032.88

Date	Flow Rate (ft^3/min)	TCA Mol. Wt. = 133.4 Conc. (ppm)	TCA Mass Removed (lb/d)	TCE Mol. Wt. = 131.4 Conc. (ppm)	TCE Mass Removed (lb/d)	Total VOCs Removed Mass Rate (lb/d)	Total VOCs Removed Cumulative (lb)
04/08/93	5,800	1.0	2.00	4.1	8.06	10.06	91,084.10
04/23/93	5,700	0.8	1.57	3.6	6.96	8.53	91,183.66
05/20/93	5,800	0.9	1.80	4.2	8.26	10.05	91,362.83
06/17/93	5,700	1.0	1.96	4.9	9.47	11.43	91,577.69
07/15/93	5,600	0.9	1.66	4.2	7.97	9.63	91,788.30
08/20/93	5,400	0.7	1.30	3.6	6.59	7.89	92,013.59
09/29/93	5,500	0.5	0.95	2.7	5.03	5.98	92,211.76
10/28/93	5,800	0.5	1.00	2.3	4.52	5.52	92,330.89
11/30/93	5,700	0.5	0.98	2.7	5.22	6.20	92,469.00
01/04/94	5,900	0.6	1.22	2.8	5.60	6.82	92,631.71
02/22/94	5,200	0.7	1.25	3.1	5.46	6.72	92,868.60
03/07/94	5,000	0.7	1.20	3.9	6.61	7.82	92,936.08
04/06/94	5,700	0.8	1.57	2.5	4.81	6.38	93,088.18
05/05/94	5,800	0.6	1.12	4.1	8.02	9.14	93,320.49
06/02/94	6,200	0.6	1.17	2.5	5.17	6.34	93,475.33
07/07/94	6,000	0.5	1.07	2.6	5.37	6.44	93,635.18
08/04/94	6,300	0.3	0.69	1.7	3.65	4.35	93,743.08
09/06/94	6,300	0.5	1.04	2.7	5.68	6.72	93,873.52
10/13/94	6,200	0.6	1.26	3.0	6.33	7.59	94,062.59
11/03/94	6,200	0.6	1.26	2.4	5.00	6.26	94,166.44