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Hanford Soil Partitioning and Vapor Extraction Study

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Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Bechtel Hanford, Inc.
Richland, Washington

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Hanford Soil Partitioning and Vapor Extraction Study

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EXECUTIVE SUMMARY

Vapor-phase adsorption and desorption testing was performed using carbon tetrachloride and Hanford Site soils to estimate vapor-soil partitioning and reasonably achievable carbon tetrachloride soil concentrations during active vapor extraction efforts at the 200 West Area of the Hanford Site. Two experimental apparatus were used for data collection: an adsorption/desorption column apparatus to collect partitioning information, and a flow-through cell that simulated field conditions of a highly contaminated silty sand layer with little or no flow (no advective transport) with an overburden of sand containing the high-velocity field and thus affording the primary mechanism for carbon tetrachloride removal.

The major findings are summarized below.

- At 7% and 10% soil moisture for the Hanford silty sand, carbon tetrachloride adsorption was shown to be controlled by moisture content, as evidenced by higher adsorption affinities at the 10% moisture content. Linear partition coefficients for the 7% and 10% soil moisture contents were 3.1 L/kg and 6.7 L/kg, respectively. The Hanford sand at a 10% soil moisture exhibited a linear partition coefficient of 1.6 L/kg.

- Desorption experiments in the column apparatus (10% moisture, silty sand) indicated that only 9.4% of the initial mass of carbon tetrachloride was removed, leaving an approximate soil concentration of 12 mg/kg. It should be noted that this soil concentration is considered representative of that which is achievable under ideal conditions where flow is passing directly through the area of contamination.

- Impulse tracer testing using sulfur hexafluoride yielded a residence time of 145 minutes and 317 minutes in the respective 4-ft and 8-ft flow-through cells. Greater than 95% of the tracer mass was removed from the flow-through cells within two residence times. This correlated well with the observance of a rapid carbon tetrachloride concentration decrease during the first two pore volume flushes for both flow-through cells.

- Flow-through cell testing yielded higher percent removals (70% to 99%), but the removals are indicative of extraction of free product. The final silty sand concentration ranged between 302 mg/kg and 42,160 mg/kg, indicating the controlling effect of molecular diffusion through the low-velocity field (silty sand layer) into the high-velocity field (silica sand layer). These "final" silty sand concentrations were achieved while the discharge concentration from the flow-through cells was less than 1 part per million by volume (ppmv).

- Calculation of carbon tetrachloride soil concentrations using measured gas-phase concentrations and empirical relationships can lead to significant error. The empirical calculations using vapor-phase concentrations, measured following a recovery period,

yielded a final silty sand concentration of 0.22 to 0.37 mg/kg, whereas the silty sand concentration from mass balance calculations ranged from 302 to 42,160 mg/kg.

- Applying the value of Kd resulting from the adsorption isotherm for the 10% moisture silty sand resulted in solid-phase concentrations of 2.8 to 4.5 mg/kg. These values remain significantly different than the known solid-phase concentrations. It can be concluded that Kd values developed from adsorption isotherms will not necessarily afford accurate solid-phase predictions during vapor extraction operations. Inaccuracies will occur in systems that exhibit irreversible adsorption. Although true irreversible adsorption may not occur, sufficiently slow desorption kinetics will result in what amounts to irreversibility from a practical standpoint.

- Both the flow-through cell and column testing indicated significant levels of "apparent" irreversible adsorption, where the effects of slow diffusion kinetics resulted in vapor-phase concentrations that were less than detection limits during intraparticle diffusion-dominated mass transfer.

- It is recommended that field extraction operations include vapor concentration monitoring during *and after* an extraction event. Collection frequency should be sufficient to adequately define the concentration time profile and should be more frequent at the early stages of an extraction event. Ideally, the concentration-time profile would allow the regions of extraction to be defined, which would assist in defining when desorption-limited mass transfer occurs.

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1.0 INTRODUCTION

This report describes the testing and results of laboratory experiments conducted to assist the carbon tetrachloride soil vapor extraction (SVE) project operating in the 200 West Area of the Hanford Site. This study was conducted by faculty and students of Washington State University (WSU) for Bechtel Hanford, Inc.

1.1 BACKGROUND

In the 200 West Area, carbon tetrachloride was used at Z Plant (currently called the Plutonium Finishing Plant) in mixtures with other organics to recover plutonium from aqueous streams. The chemical processes used to recover plutonium resulted in the production of actinide-bearing organic and aqueous waste liquids, which were discharged to the soil column at subsurface disposal facilities near Z Plant. The organic liquids consisted of 50% to 80% by volume carbon tetrachloride mixed with either tributyl phosphate, dibutyl butyl phosphonate, or lard oil. These organic wastes made up approximately 4% to 8% of the total volume of liquid wastes discharged to the soil column disposal facilities. Carbon tetrachloride was discharged to the unsaturated zone as an aqueous-phase liquid and also as a dense, non-aqueous phase liquid (DNAPL). From 1955 to 1973, approximately 36,000 to 580,000 L (1,300,000 to 2,000,000 lb) of carbon tetrachloride was discharged to the unsaturated zone (Rohay et al. 1994).

On December 20, 1990, the U.S. Environmental Protection Agency and the Washington State Department of Ecology requested the U.S. Department of Energy, Richland Operations Office to proceed with the detailed planning required to implement an Expedited Response Action (ERA) for removing carbon tetrachloride from the unsaturated soils in the 200 West Area of the Hanford Site. The request was based on concerns that the carbon tetrachloride residing in the soils was continuing to spread to the groundwater and, if left unchecked, would significantly increase the extent of groundwater contamination. The purpose of this ERA was to minimize carbon tetrachloride migration within the unsaturated zone beneath and away from the carbon tetrachloride disposal sites in the 200 West Area.

The first SVE system began operating at the site in February 1992. This original system was later supplemented with two other systems for a present total extraction capacity of 3,000 ft^3/min. To date, approximately 150,000 lb of carbon tetrachloride has been removed from the unsaturated zone by the SVE operations. During this time, the concentration of carbon tetrachloride in the extracted soil gas has fallen from initial levels of several hundred to several thousand parts per million by volume (ppmv) down to concentrations in the 100-ppmv range.

1.2 STUDY OBJECTIVES

The four stated objectives of this study were as follows:

Objective 1. Determine the vapor-phase soil partitioning coefficients for carbon tetrachloride as a function of general soil type and moisture content.

Objective 2. Determine the carbon tetrachloride extraction efficiency as a function of interstitial air flow, soil type, and moisture content.

Objective 3. Evaluate the influence of a low-permeability layer containing carbon tetrachloride on vapor extraction efficiency.

Objective 4. Estimate a reasonably achievable carbon tetrachloride soil concentration.

1.3 STUDY OVERVIEW

To meet the stated objectives, the study was divided into two general experimental components, which are briefly described as follows:

1. Closed-loop and flow-through column experiments, which addressed Objectives 1, 2, and 4. The results of these tests provide adsorption and desorption isotherms for carbon tetrachloride on sand and silty sand. These experiments were performed at the WSU Tri-Cities campus.

2. Flow-through cell (box) experiments using a low-permeability lens, which addressed Objectives 2, 3, and 4. The results of these tests provide the rate of desorption of carbon tetrachloride from silty sand. These experiments were performed at the WSU Pullman campus.

Soils obtained from the 200 West Area were used in the testing conducted for this study. Flow rates through the columns and boxes were performed at the average rate of soil gas movement induced at the site by the SVE operations. This rate was derived by previous tracer gas testing performed at the site (Barna 1995). The measurement of carbon tetrachloride in the vapor phase was performed using gas chromatography. Experimental work began in Spring 1995 and will be completed in Spring 1996. The testing methodology and results are described in more detail in later sections of this report.

2.0 SOIL CHARACTERISTICS AND PARTITIONING

The influence of soil characteristics on organic contaminant partitioning is well known. It is important, therefore, to use representative soils when collecting information necessary for field application. Field representative data were generated herein by using soils collected from the 200 West Area. It should be noted, however, that soil heterogeneity in the 200 West Area is significant, and the data generated in this study are best described as yielding information within a range of what could be expected regarding the adsorption and desorption kinetics of carbon tetrachloride for the soils at the site.

Basic soil characterization data were collected on a 200 West Area silty sand[1] and sand[2]. These data are used to draw inferences regarding observed gas-phase carbon tetrachloride soil adsorption and desorption phenomena.

2.1 DESCRIPTION OF THE SOILS USED

For this study, two types of soils were primarily used: sand and silty sand. Both the sand and silty sand were obtained from the Hanford Site and were stored in plastic containers. The silty sand was obtained from well 299-W15-31 at a depth of 130 to 140 ft, and the Hanford sand from well 699-35-69A. These soils were considered to be representative of the soils located in the SVE operational area. Additionally, for the box tests, clean Ottawa sand was used above the Hanford silty sand as a homogenous porous medium. The properties of all the soils are provided in Table 1.

In addition to the Hanford sand and silty sand, Hanford caliche was used in some limited testing. Properties of the caliche were not developed because of the limited role for which it was used.

2.2 PHASE DISTRIBUTION AND CONTAMINANT TRANSPORT

The fate of a nonaqueous-phase liquid (NAPL) in the subsurface is defined by a series of complex, interconnected processes. Transport of a NAPL can occur through percolation of free product, vapor-phase transport by advection and/or diffusion, and partitioning into an aqueous phase and transport as an aqueous-phase contaminant (Gierke et al. 1992). These processes result in a contaminant plume or plumes that gradually migrates away from the source (Hughes et al. 1992). During plume migration the contaminant will partition into the vapor, aqueous, and solid (soil) phases with an observed rise in concentration in each phase until local equilibrium is achieved. If a sufficient mass of NAPL is discharged, free product can remain as an additional

[1]Texture classification USDA - sandy loam

[2]Texture classification USDA - loamy sand

Table 1. Soil Properties for Those Soils Used in the Experimental Program.

Parameter	Coarse Silica Sand	Hanford Sand	Hanford Silty Sand
Organic carbon (%)	<0.06	0.07	0.11
Cation exchange capacity (cmol(+)/kg)	<0.3	4.6	12.2
Surface area (m^2/g)		5.2	26.8
Density (g/cm^3)	1.65		1.5

Elemental Analysis (weight %)	Hanford Sand	Hanford Silty Sand
SiO_2	72.27	62.32
Al_2O_3	12.98	11.48
TiO_2	0.55	1.67
FeO	3.09	7.06
MnO	0.07	0.13
CaO	3.41	15.26
MgO	1.64	3.28
K_2O	2.53	1.35
Na_2O	2.67	2.00
P_2O_5	0.13	0.25
Trace Elements (ppm)	**Hanford Sand**	**Hanford Silty Sand**
Ni	21	19
Cr	40	56
Sc	14	26
V	79	224
Ba	848	601
Rb	82	42
Sr	383	401
Zr	192	203
Y	23	29
Nb	13.5	15.3
Ga	15	19
Cu	19	15
Zn	52	79
Pb	10	9
Th	9	9

phase in the subsurface. The mass of free product remaining and the contaminant concentration in each phase is dependent upon the NAPL chemical characteristics and site-specific conditions that include aqueous-phase solubility, vapor pressure, temperature, pressure, soil moisture content, soil organic carbon content, and soil cation exchange capacity.

Volatilization of the residual liquid in the source will result in a vapor-phase plume that spreads throughout the unsaturated zone. Based on equilibrium partitioning previously discussed, the vapor phase will partition to the dissolved phase when it comes in contact with uncontaminated soil moisture. Liquid-solid mass transfer will also occur when some of the dissolved contaminant sorbs to the soil. As equilibrium is maintained between the three phases, the plume will spread farther away from the source. Some of the vapor may eventually reach the ground surface and escape to the atmosphere, while some of it may reach the groundwater. Groundwater may also become contaminated when rainwater or runoff infiltrating the subsurface carries some of the dissolved contaminant down through the soil column with it.

In most studies, vapor transport, in the absence of artificially imposed velocities from vapor extraction, has been treated only as a diffusive process; but in studies conducted by Falta et al. (1993) and Mendoza and Frind (1990a, 1990b), density-driven vapor migration (migration resulting from density gradients) was considered. If a contaminant consists of high molecular weight chemicals, such as carbon tetrachloride, the contaminated vapor phase would have a higher density than the uncontaminated soil gas. This causes a significant density gradient between the uncontaminated soil gas and the contaminated vapor plume, which induces advective vapor transport in the vertical direction. The degree of advective transport is also significantly affected by temperature, moisture content, and organic carbon content. It was found that higher temperatures increased advective transport because of increases in the vapor-phase concentration and the density gradient. Higher temperatures also resulted in a lower value for Henry's Law constant, which decreased the retardation coefficient. In contrast, higher moisture and organic carbon contents acted to increase the retardation coefficient, or decrease advective transport (Hughes et al. 1992).

Mendoza and Frind (1990b) concluded that density-driven advection can be a dominant transport mechanism that results in longer travel distances, more rapid vapor transport, and larger contaminated areas. One consequence of density-driven advection is that it can greatly reduce the time it takes for contaminants to reach the groundwater.

Sleep and Sykes (1989) also conducted a study in which they coupled density-driven flow with externally induced pressure gradients, such as those created by a vacuum pump or blower. It was found that externally induced pressure gradients negated the impacts of density-driven flow even when a vacuum as low as 0.05 cm of water was applied. One significance of this finding is that when conducting experiments on SVE or some other remediation technique requiring pumps and/or blowers, density effects can be ignored.

The equilibrium form of the advective-dispersive equation is valid only in systems that are diffusion dominated or weakly advective. In studies done on SVE, it has been found that there is

usually long tailing of the effluent curve that is not observed when applying the equilibrium model. Therefore, in cases where advection would dominate, such as with SVE systems, the equilibrium model does not prove adequate (Armstrong et al. 1994).

Many authors including Rathfelder et al. (1991), McClellan and Gillham (1992), Armstrong et al. (1994), and Wilkins et al. (1995) reported evidence of nonequilibrium behavior during vapor extraction experiments following the removal of the pure phase contaminant. It is believed that the processes of volatilization from the dissolved phase (contaminant associated with water associated with the soil) to the vapor phase and contaminant desorption from the sorbed phase to the dissolved phase are rate limiting. These rate-limiting transport mechanisms cause the long effluent tailing observed in many studies and result in reduced extraction efficiencies and excessive cleanup times (Rathfelder et al. 1991; Armstrong et al. 1994). To account for the rate-limiting processes that are often observed, a nonequilibrium model has become necessary. Several conceptual models dealing with physical and/or chemical nonequilibrium processes of volatilization and sorption have been developed by authors including Cho and Jaffe (1990), Brusseau (1991), and Armstrong et al. (1994).

2.3 FACTORS AFFECTING PARTITIONING

In addition to those factors noted in the previous section, three primary factors affecting partitioning have been identified. These three factors are moisture content, naturally occurring organic carbon, mineralogy, and porosity.

2.3.1 Moisture Content

The moisture content of the soil plays a significant role in the partitioning of a contaminant. Armstrong et al. (1994) provided a conceptual model based upon the assumption that diffusion between the vapor and aqueous phases takes place through a water boundary layer. The concentration gradient between the average aqueous phase concentration and the equilibrium concentration at the liquid/vapor interface provides the driving force for volatilization from the aqueous phase. Pedersen and Curtis note that vapor diffusion rate decreases significantly with increasing soil moisture content.

2.3.2 Adsorption to Soil Organic Carbon and Mineral Grains

The amount of naturally occurring organic carbon can contribute significantly to the adsorptive capacity of soil for volatile organic compounds and has been shown to be the dominant factor for soils with a relatively high f_{oc} (fraction of organic carbon) content. However, when f_{oc} is less than 0.1%, sorption to mineral grains may become more dominant (Armstrong et al. 1994, Hughes et al. 1992).

2.3.3 Intraparticle Porosity

Intraparticle porosity refers to the very small pores and associated surfaces within a particle of soil. IUPAC classifies these intraparticle pores based on size as follows:

- Micropores - Cylindrical or split-shaped pores with diameters less than 20 Å
- Mesopores - Pores with diameters between 20 to 500 Å
- Macropores - Pores greater than 500 Å.

Ferrell and Reinhard (1994) have demonstrated that adsorption in micropores contributes significantly to sorbate uptake and contributes to isotherm non-linearity on solids with low natural organic matter. They further note that hysteresis between adsorption and desorption may result from the fact that the nature of the micro-environment has been changed due to the initial adsorption. They state that the rate of desorption from soils with a high amount of intraparticle porosity is controlled by desorption from the intraparticle spaces and once external contaminant is removed, the internal contaminant can require months or even years to completely desorb. The factors affecting hysteresis would be most significant for molecules that can access the micropores. It can be seen that carbon tetrachloride, having an approximate molecular diameter of 5 Å, would have access to micropores.

This slow desorption phenomena must be adequately defined in order to make rational vapor extraction design and operation decisions and to estimate reasonably achievable treatment levels.

2.4 PREDICTION OF THE EQUILIBRIUM CONDITION

One of the most important aspects of full-scale vadose zone cleanup activities is the estimation of soil contaminant concentration from measured gas-phase concentrations. Generally, equilibrium is assumed and predictive equations are employed to determine residual soil concentration. This approach assumes that the soil particles are surrounded by a layer of sorbed water and that equilibrium is defined by the partitioning between vapor, aqueous, and solid phases. A sequential solution procedure is as follows:

1. Measurement of soil gas concentration

2. Estimation of liquid-phase contaminant equilibrium concentration in the water layer using Henry's Law

3. Estimation of soil-contaminant partition coefficient (K_d) using the following relationship:

$$K_d = f_{oc} K_{oc} \qquad (1)$$

where

f_{oc} = soil organic carbon content
K_{oc} = organic carbon (contaminant) partition coefficient.

4. The soil organic carbon content is typically a measured value while K_{oc} is calculated using an empirical formula of the form

$$\log(K_{oc}) = a \quad \log(K_{ow}) + b \tag{2}$$

where

K_{ow} = octanol water partition coefficient
a and b = empirical curve-fitting constants, the values of which are dependent on contaminant chemical class.

5. Finally, the contaminant concentration on the soil (C_s) is calculated using equation 3.

$$C_s = K_d C_w \tag{3}$$

where

C_w = contaminant concentration in the adsorbed water.

Three points of concern are immediately apparent when applying this approach to defining vadose zone equilibrium conditions. First, the basic calculations (equations 1 and 2) rely on empirical relationships that were originally developed for saturated soil conditions. At best, only order of magnitude estimates should be expected from this approach in the vadose zone. Second, equation 3 (a linear Freundlich equation) assumes linear adsorption characteristics. This may be valid at low contaminant concentrations or over narrow concentration ranges, but should not be assumed to apply for the broad range of system conditions commonly experienced in field conditions. Finally, equation 3 is based on the assumption of complete reversibility of adsorption, an assumption that may not be valid if significant intraparticle adsorption occurs.

3.0 EXPERIMENTAL METHODS

Laboratory testing was performed to develop the information necessary to realize the objectives of this study. These tests included laboratory-scale closed-loop and flow-through column tests and flow-through box tests. In addition, soil pneumatic conductivity was determined for the soils used in this experimentation, and preliminary adsorption/desorption testing was performed on a caliche sample.

3.1 COLUMN TESTS

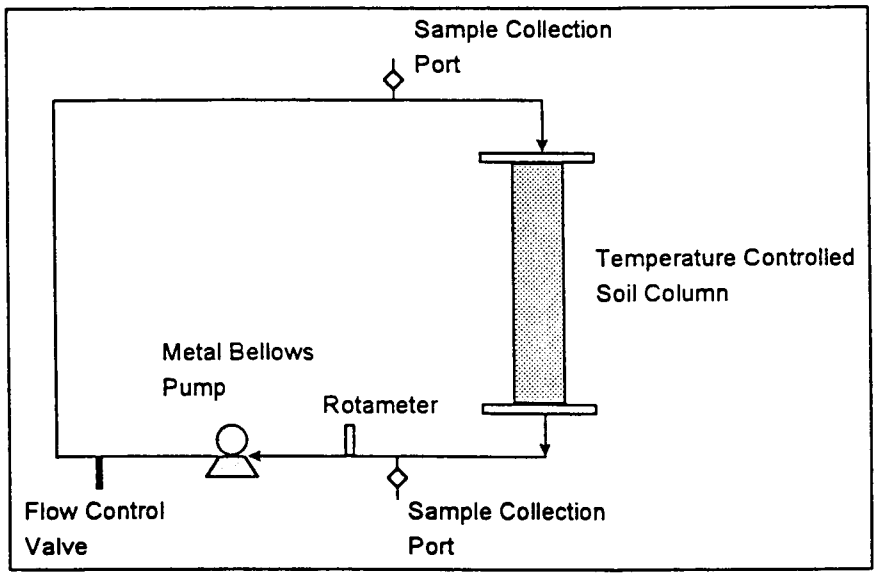
The column tests were performed to develop carbon tetrachloride adsorption isotherms and to perform desorption testing to assess a "best case" scenario for carbon tetrachloride removal from Hanford silty sand and sand at 7% and 10% moisture. A schematic representation of the column testing apparatus is shown in Figure 1. The adsorption isotherms were developed with the apparatus in a closed-loop mode, whereas desorption information was collected in a flow-through mode.

The all-stainless steel apparatus consisted of a 2.5-in.-inner-diameter column, housed in a temperature control bath that was maintained at 14°C, connected to a metal bellows pump with 1/8-in. tubing. Sampling ports were placed at the inlet and outlet of the column. Flow was monitored continuously with a rotameter and checked daily with a bubble meter. Gas-phase samples were collected at predetermined time intervals and carbon tetrachloride concentration measured by gas chromatography.

3.1.1 Adsorption Kinetics and Isotherm Development

Adsorption kinetic and isotherm information was developed for two Hanford soils (sand collected at a depth of about 20 m and silty sand from the just above the caliche layer) at two moisture contents (7% and 10%). These soil moistures were selected as being within the range of "typical" values at the Hanford Site. Although soil moistures greater than 10% have been recorded in the silty sand at Hanford, preliminary experimentation indicated that air flow was significantly restricted at values greater than 10% and, as a result, soil moistures above 10% were not evaluated. Adsorption testing involved loading a column with a predetermined mass (dry weight) of soil in an uncompacted state, sealing the system and adding a known mass of carbon tetrachloride using a microliter syringe. Flow was initiated and samples collected for analysis. Initial concentration-time profiles were used to define adsorption kinetics and estimate time to equilibrium. Conflicting studies by others indicated that it would take anywhere from several minutes to a couple of months to reach equilibrium during the sorption process (Ball and Roberts 1992, Kearl et al. 1991). By experimenting, it was found that these soils required at least 20 days of closed-loop operating to generate a single equilibrium concentration point.

Figure 1. Schematic Diagram of the Soil Column Test Apparatus.



The general methodology to develop an adsorption isotherm included the following steps:

1. Weigh a soil sample and then bake it at 105°C for 24 hr and weigh again. Then add the necessary amount of water to result in a 7% or 10% (w/w) moisture content.

2. Place the soil in one of the 2.5-in.-diameter stainless steel columns. (Each end of the cylindrical column has a removable sintered stainless steel filter to allow airflow and to hold the soil in the column.) Leave the soil uncompacted to facilitate adsorption of the carbon tetrachloride.

3. Place the column in a water bath maintained at approximately 14°C (which is the approximate temperature of the unsaturated zone in the Z-crib area). Hook up the stainless steel tubing to the top and the bottom of the column. The tubing is connected to a rotameter and steel bellows pump. Part of the tubing is also placed within the water bath to bring the column inlet air temperature to 14°C. Measure system gas-phase volume with a low-pressure manometer.

4. Start the pump so that air begins flowing in closed-loop through the system.

5. Inject a known quantity of carbon tetrachloride into the system using a microliter syringe through the sampling port.

6. Withdraw 50-μL gas samples from both sampling ports at predetermined time intervals and measure carbon tetrachloride concentration using the gas chromotograph.

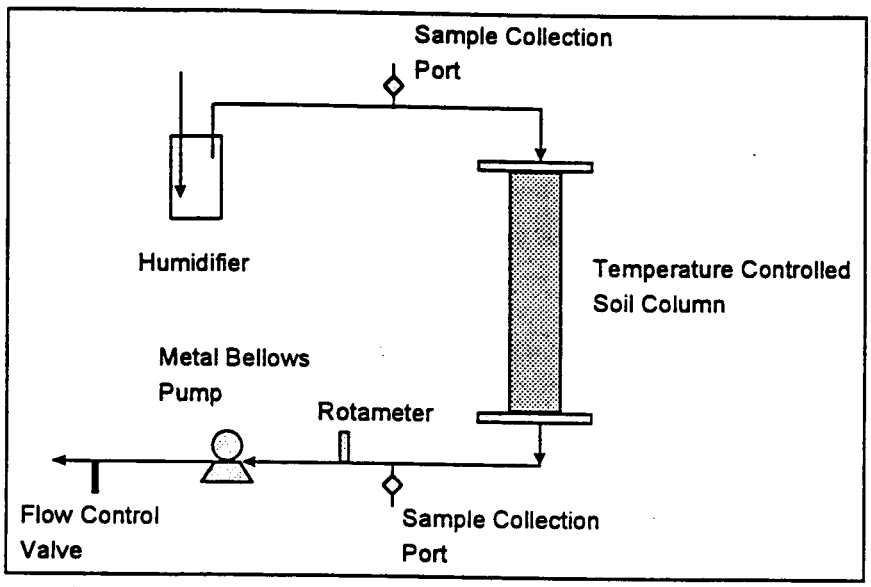
7. Evaluate the resulting concentration-time profiles to determine when "equilibrium" is achieved. Calculate mass adsorbed by mass balance. This establishes a point on the isotherm curve.

8. Inject additional carbon tetrachloride into the system and repeat steps 6-7 to establish another isotherm point.

3.1.2 Desorption Data Collection

Desorption data were collected using the soils which had been previously equilibrated using adsorption protocol. The apparatus depicted in Figure 1 was used for desorption testing in a flow-through mode of operation (Figure 2). Humidified air was drawn through the soil at a predetermined rate and gas-phase samples were collected at the column outlet.

Figure 2. Schematic Representation of Desorption Column Testing Configuration.



The general methodology applied to desorption testing included the following.

1. Use a column that has reached equilibrium between the vapor phase and the sorbed phase during the adsorption isotherm development. Cool it in a freezer and then compact the soil within the column to more closely simulate flow conditions through the soil in the field. (The column is cooled prior to compaction to minimize loss of carbon tetrachloride during the compaction process.)

2. Place the column in a water bath maintained at approximately 14°C. Hook up the stainless steel tubing to the top and the bottom of the column. The tubing is connected to a bubble flow meter and vacuum pump on the discharge side of the column. This is a flow-through system. The room air is pulled into the system through a flask that humidifies the air to approximately 100% relative humidity. This is done to simulate the subsurface soil gas conditions.

3. Start the pump so that air begins flowing through the column. Adjust the flow using the bubble flow meter and a valve to limit the superficial flow-through the column to 0.5 ft/hr, which is the average rate of flow in the subsurface as determined by previous field tracer gas testing (Barna 1995).

4. Monitor the concentration of carbon tetrachloride in the effluent of the column.

5. Calculate the carbon tetrachloride removed based on flow and concentration over time. Based on the amount removed and the initial mass of carbon tetrachloride on the soil, calculate the carbon tetrachloride remaining on the soil.

6. Continue operating and monitoring the desorption system until the concentrations are at detection limits. Stop flow from the column and monitor the rate and extent of the rebound of carbon tetrachloride vapor in the head space of the column by collecting column head space samples as a function of time. This provides an indication of the rate at which carbon tetrachloride concentrations in the soils at the site will rebound following the cessation of extraction operations.

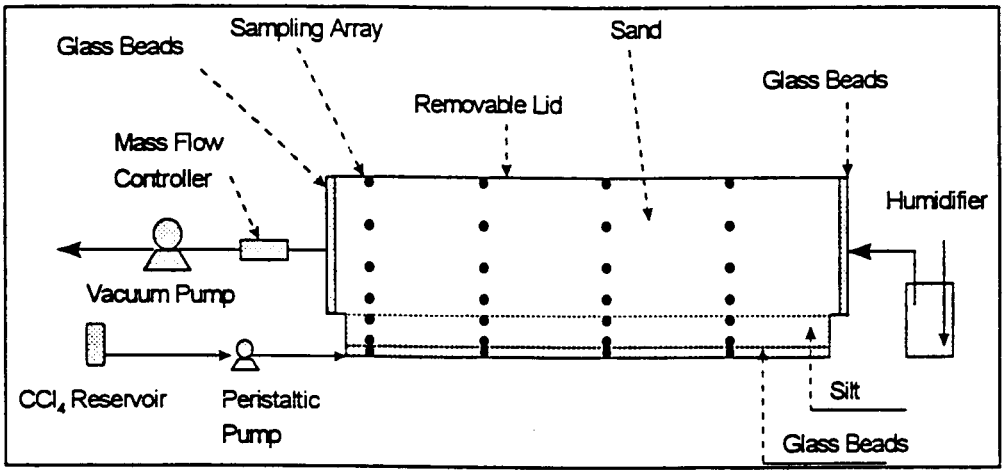
3.2 FLOW-THROUGH CELL TESTS

The box tests were performed to develop an understanding of the limitations to site remediation caused by a low-permeability lens. The low-permeability lens used in the test was silty sand from the site, which is the same soil that overlies the caliche layer. All the box desorption tests were performed similarly, using silty sand at 9% moisture content.

The apparatus used to perform the box tests shown in Figure 3. Two boxes, with the dimensions 4 ft by 2 ft by 6 in. and 8 ft by 2 ft by 6 in. (L x H x W), were constructed of stainless steel. There was a shallow channel around the perimeter of each box in which to place a viton o-ring to create an airtight seal between the cell and the removable lid.

At both ends of the cells, holes were tapped 9 in. from the top to serve as the air inlet and outlet ports. On one side there was another tapped hole 1 in. from the bottom of the cell to serve as the inlet port for the liquid carbon tetrachloride. Along one side of each cell, 28 smaller holes were tapped for soil gas sampling ports. Four vertical sets of holes were drilled approximately 1 ft or

Figure 3. Schematic Representation of Flow-Through Cell.



2 ft apart for the 4-ft and 8-ft cells, respectively. For each set, seven ports were at heights of 1, 3, 6, 8, 10, 16, and 22 in. from the bottom of the cells. These ports allowed soil gas sampling that delineated the vertical and horizontal extent of the carbon tetrachloride vapor within the box.

At each end of the boxes, a 1-in. layer of 0.2-mm-diameter glass beads was placed to disperse the air uniformly across the sand layer. Between the sand and the glass beads there was a piece of sintered stainless steel plate to keep the beads separated from the sand and to again aid in evenly distributing the air. The glass beads and the sintered steel plate were supported by a 2-in.-wide shelf that was constructed at both ends of the cells. This shelf, which was raised 6 in. from the bottom of each cell, prevented the migration of liquid carbon tetrachloride up through the inlet and outlet glass bead layer and resulted in a physical separation between the air inlet and the silty sand layer.

The general methodology for performing a flow-through cell run was as follows:

1. Fill the bottom 1 in. of the box with glass beads. These glass beads serve to distribute the liquid carbon tetrachloride across the bottom of the box. Cover the glass beads with a 5-in. layer of silty sand and compact with a standard compactor in 2-in. lifts to a depth of 6 in. (silty sand + glass beads). The silty sand is the low-permeability lens that is tested by this setup. Fill the remaining 18 in. of the box with clean Ottawa sand. The sand is a homogenous medium through which room temperature air flow will pass, sweeping across the top of the silty sand.

2. Fill the glass beads layer with a known quantity of liquid carbon tetrachloride. This rises into the silty sand through capillary action.

3. Let the box sit until the carbon tetrachloride concentrations in the air throughout the box are at equilibrium with the liquid carbon tetrachloride (approximately 120,000 ppmv).

4. Begin pulling air through the box to desorb the carbon tetrachloride. Use a bubble meter and a valve to control air flow at a predetermined rate of 0.5 to 1.5 ft/hr (Barna 1995). Monitor the carbon tetrachloride in the effluent stream, within the sand and silty sand at predetermined time intervals.

5. Calculate the carbon tetrachloride removed based on flow and concentration over time. By mass balance, calculate the carbon tetrachloride remaining in the box.

6. Stop flow from the box and monitor the rate and extent of the rebound of carbon tetrachloride vapors throughout the box. This provides an indication of the rate at which carbon tetrachloride concentrations in the soils at the site will rebound following the cessation of extraction operations.

Four box tests were performed. The first test (Run 1) was performed using only sand and a tracer gas to establish baseline extraction levels and to check out system functionality. The final three tests used the general methodology described above.

Following silty sand and sand construction, a tracer gas test was performed using SF_6. These tests were used to define the dispersion characteristics of the cell and to check for short circuiting prior to the initiation of carbon tetrachloride testing.

3.3 ADDITIONAL TESTS

In addition to the column tests and the box tests, testing was performed to provide background information to support the study. This testing included a qualitative study of caliche adsorption/desorption characteristics and the development of pneumatic conductivities for the Hanford sand and silty sand.

3.3.1 Caliche Adsorption and Desorption

The caliche layer at the site is suspected of retarding the downward movement of carbon tetrachloride and perhaps diverting flow to the southwest (due to the slope of the caliche layer in that direction). The caliche layer is also believed to act as a very low-permeability zone that could hold a substantial mass of the carbon tetrachloride (as both a DNAPL and as a sorbed phase with a very slow release mechanism).

Even though the caliche layer appears to be very important in regards to the remediation of the site, the column and box testing could not use the caliche because of its inherent qualities of being a cemented and easily fractured unit and it was felt that achieving a uniform layer of

caliche in the box or column would not be possible. Attempts were made to use it within a column by slowly removing material from a chunk of caliche, but this proved fruitless because of the need to ensure a tight fit along the entire length of the soil/column wall interface. However, some qualitative and semi-quantitative tests were performed using caliche collected from the Hanford Site. These tests provided indications of the rates of water and liquid carbon tetrachloride transport through the caliche and the rate of carbon tetrachloride desorption in the vapor phase.

The rates of water and carbon tetrachloride transport through the caliche were determined with an experimental set-up somewhat analogous to the "falling head test" performed to determine the hydraulic conductivity of a soil. Because of the previously noted difficulty in placing the caliche in a column, it was decided that a glass tube would be used to "bore" a "plug" of caliche into the glass tube. Although there is high uncertainty regarding the effect of this "boring" process on the integrity of the caliche, there was no visual appearance of fracturing and the method seemed to work for providing a snug fit of the plug in the glass tube. With the caliche plug in place, the glass tube was held vertical and water or carbon tetrachloride was poured into the top of the tube to create a head of liquid over the caliche plug. The rate of liquid transport was then visually monitored and timed. At the conclusion of each test, the plug was pushed out and broken apart to verify that depth of liquid transport within the center of the caliche plug.

The rate of carbon tetrachloride desorption from the caliche used a chunk of caliche that was weighed and then left to saturate in liquid carbon tetrachloride. The chunk was then allowed to sit in the laboratory hood with the inflow of room air flowing across it. Visual observation of the color changes were noted and weights were recorded to document the amount of residual carbon tetrachloride remaining on the caliche.

3.3.2 Pneumatic Conductivity of Soils

Tests were performed to determine an order-of-magnitude estimate of the pneumatic conductivity for the Hanford silty sand and sand. The pneumatic conductivity is a measure of the ability of air to flow-through soil and is analogous to hydraulic conductivity for water flow-through soil. Although there is an American Society for Testing and Materials standard for determining the hydraulic conductivity of a soil, no such standard exists for determining pneumatic conductivity.

The pneumatic conductivity testing was performed using a column packed with soil and a measured induced air flow rate and a measured pressure drop across the soil column. A deviation of Darcy's law was then used to calculate the pneumatic conductivity. This pneumatic conductivity information is useful for many purposes, including input for modeling the site SVE extraction operations.

3.4 CARBON TETRACHLORIDE QUANTIFICATION

The carbon tetrachloride concentrations were measured using an SRI 8610 or Varian gas chromatograph with an electron capture and thermal conductivity detectors calibrated from approximately 0.01 to 2.2 ppmv and 200 to 1,000 ppmv, respectively. Calibration of the gas chromatograph was performed every day before sampling with an end of day check after the sampling to measure the change in the response. Quality assurance was afforded by Scott gas standards that were used to check calibration curves on a daily basis.

4.0 RESULTS AND DISCUSSION

4.1 COLUMN TESTS

4.1.1 Adsorption Kinetics and Isotherm Development

A representative carbon tetrachloride adsorption concentration time profile is presented in Figure 4. It can be seen that detectable concentration decrease ceased after approximately 20 days and based on these and similar data, equilibration time was selected as 20 days. It should be noted that "full" equilibration may in fact take significantly longer, but to facilitate the collection of data within a reasonable time frame, equilibrium was assumed.

Adsorption isotherms for the silty sand at 7% and 10% moisture Hanford sand at 7% moisture are shown in Figure 5. Each data set has been fit with a linear line of best fit for descriptive purposes. The shape of the adsorption data (especially at 7% soil moisture) describes an "unfavorable"[3] isotherm that can indicate that the soil has a relatively low adsorption affinity for carbon tetrachloride. This cannot be stated conclusively here, however, because the system is actually tri-phase (gas, soil, and water) and the water associated with the soil is contributing to the "appearance" of adsorption due to carbon tetrachloride solubility. This could be affecting the shape of the isotherm as a function of vapor concentration. Regardless of the physical or chemical system conditions controlling adsorption, these isotherms are a representation of the *adsorption* characteristics of the silty sand above the caliche layer in 200 West Area.

It can be seen that soil moisture increases the adsorption capacity of the silty sand and that the silty sand has a higher adsorptive capacity than the Hanford sand. This is not unexpected when consideration is given to the higher intraparticle surface area, organic carbon content, and cation exchange capacity associated with the silty sand as both are known to increase adsorption

[3]Unfavorable isotherms have a concave appearance, while favorable isotherms have the classical "Langmuirian" shape.

Figure 4. Representative Adsorption Kinetic Data for Silty Sand at 10% Moisture.

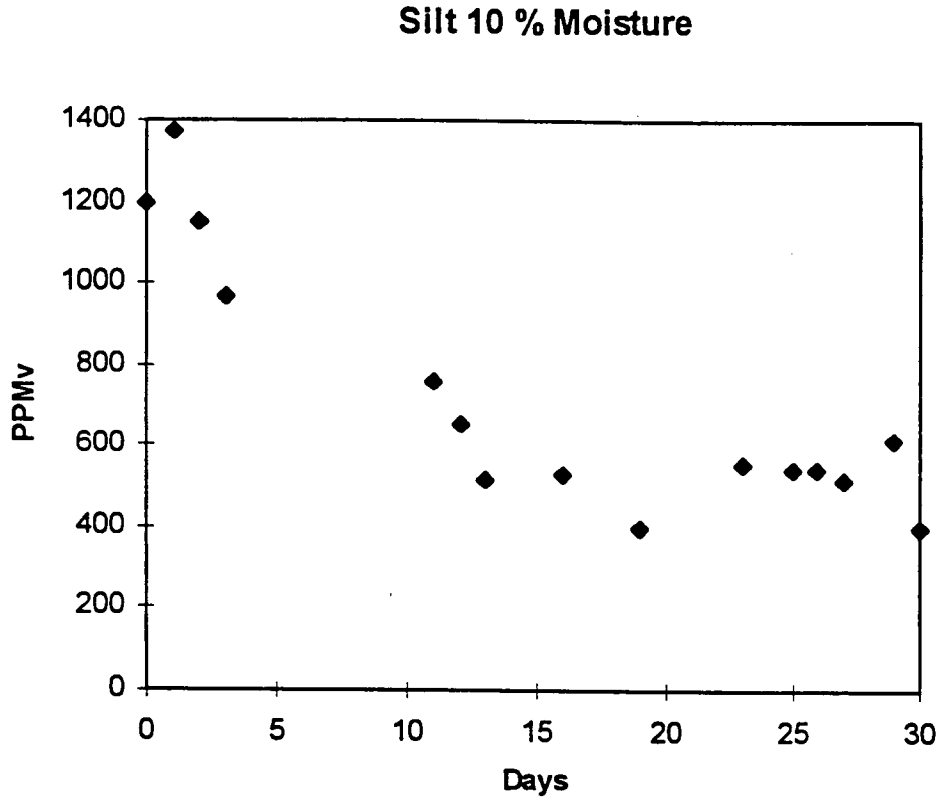
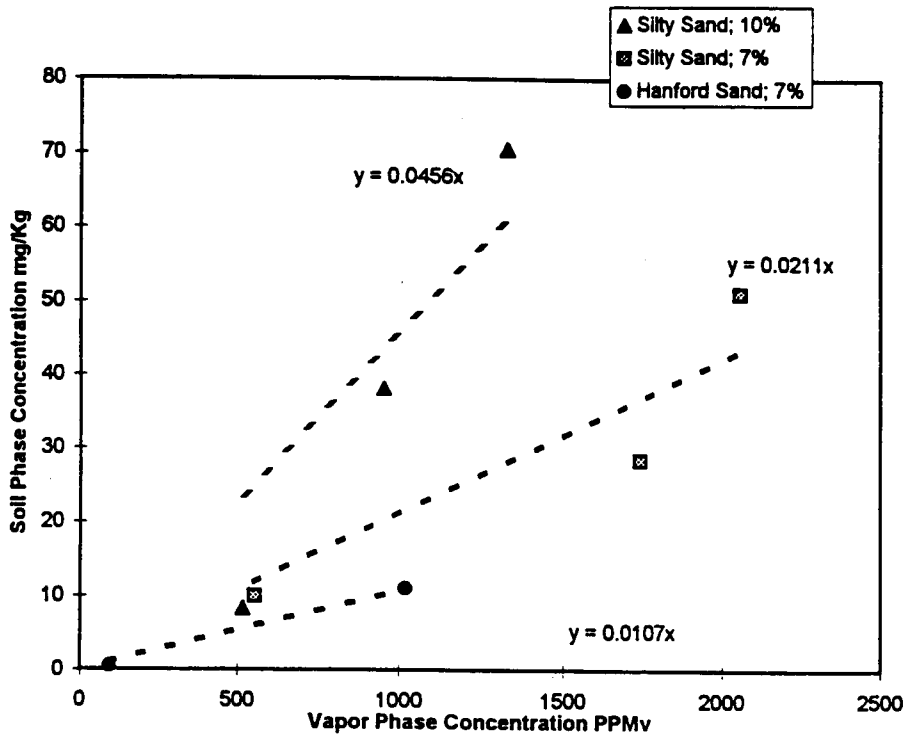


Figure 5. Carbon Tetrachloride Adsorption Isotherms for Silty Sand at 7% and 10% Soil Moisture and Hanford Sand at 7% Moisture.



affinity. It will be pointed out later, however, that the adsorption data do not necessarily allow for accurate predictions under desorption conditions, as would be experienced during vapor extraction operations.

4.1.2 Desorption Column Data

The desorption column testing yielded interesting results. Desorption data were collected following a series of adsorption tests by compacting the soil and passing conditioned air through the column in a flow-through mode of operation. Column discharge samples were collected as a function of time and quantified for carbon tetrachloride concentration. Representative concentration time profiles for 10% moisture silty sand are shown in Figures 6 and 7.

These data indicate that gas-phase concentrations in the low-ppbv range are achieved initially within 150 minutes, after which ppbv concentrations are reached within only a few minutes. Of significance is the observance of the relatively low total percent removal that was achieved during the first two desorption runs (approximately 8.4%) and that this value increased to only 8.7% over the next three desorption runs. Four additional desorption runs (nine total) were performed yielding an overall removal of 9.7% of the original 3,740 μg carbon tetrachloride initially present and a "final" carbon tetrachloride soil concentration of approximately 12 mg/kg.

The observed low level of carbon tetrachloride removal is made evident in Figure 8. It can be seen that cumulative mass removal approaches its maximum at about 200 minutes, and only minor increases in mass removal are realized beyond this time.

4.2 BOX TESTS

4.2.1 Run 1 - Tracer Gas Testing

Impulse tracer gas tests using SF_6 were performed on each extraction cell to determine the hydraulic characteristics of the airflow. The results of the 4-ft cell test are presented in Figure 9. The airflow through the cell was 0.218 L/min, which corresponded to an estimated interstitial flow velocity of 1.54 ft/hr based on a porosity of 40% for the coarse sand. The porosity was estimated using a simple water displacement test.

Figure 6. Carbon Tetrachloride Desorption Concentration-Time Profile for the First Two Desorption Runs and Cumulative Mass Removed for 10% Soil Moisture Silty Sand.

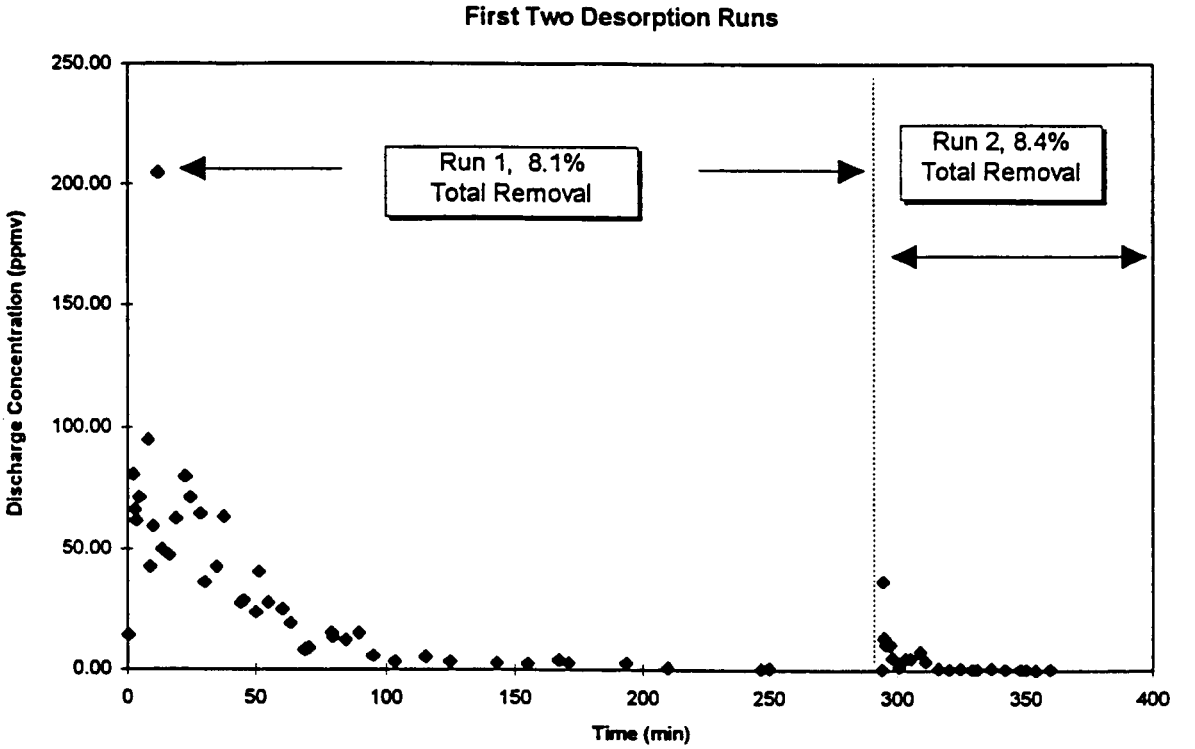


Figure 7. Carbon Tetrachloride Desorption Concentration-Time Profile for Desorption Runs 2-5 and Cumulative Mass Removed for 10% Soil Moisture Silty Sand. Percent Removals are Expressed as Total Cumulative Values.

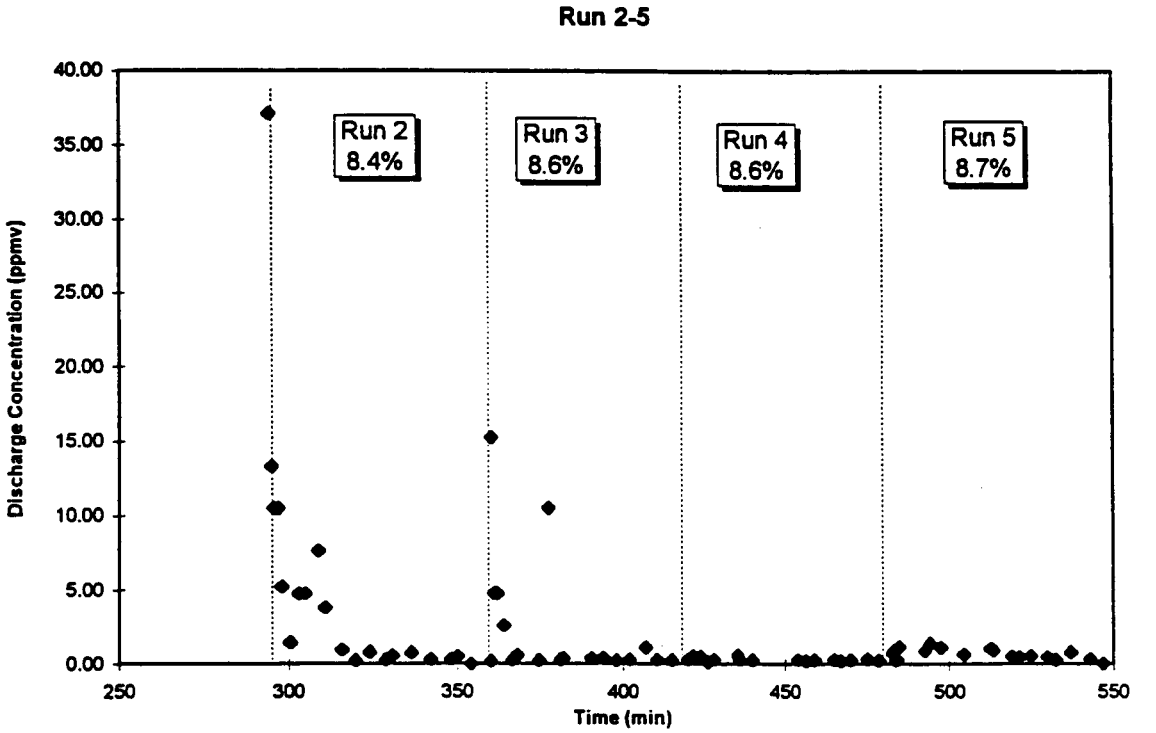


Figure 8. Column Carbon Tetrachloride Effluent Concentration and Cumulative Mass Removal for the Silty Sand at 10% Moisture.

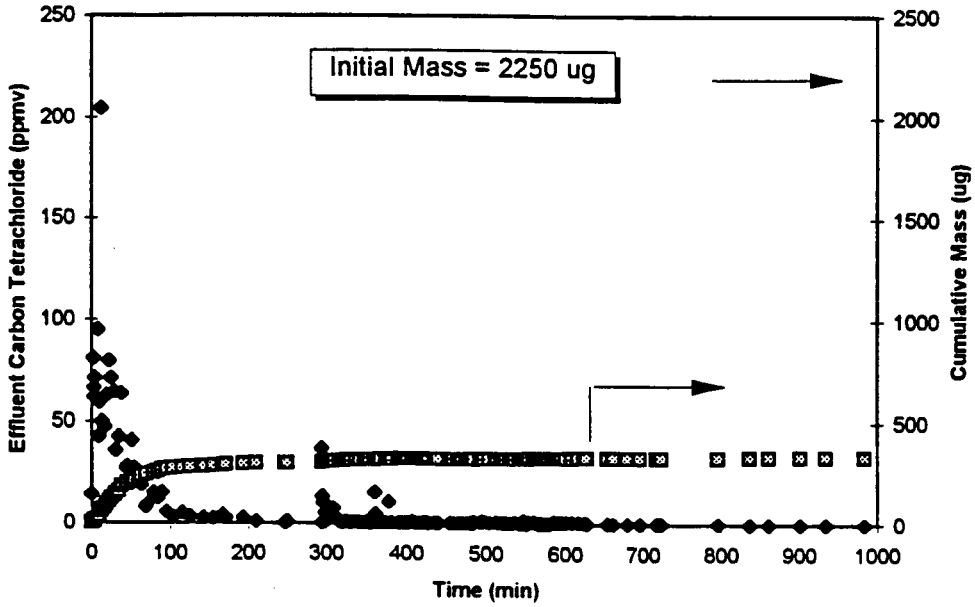
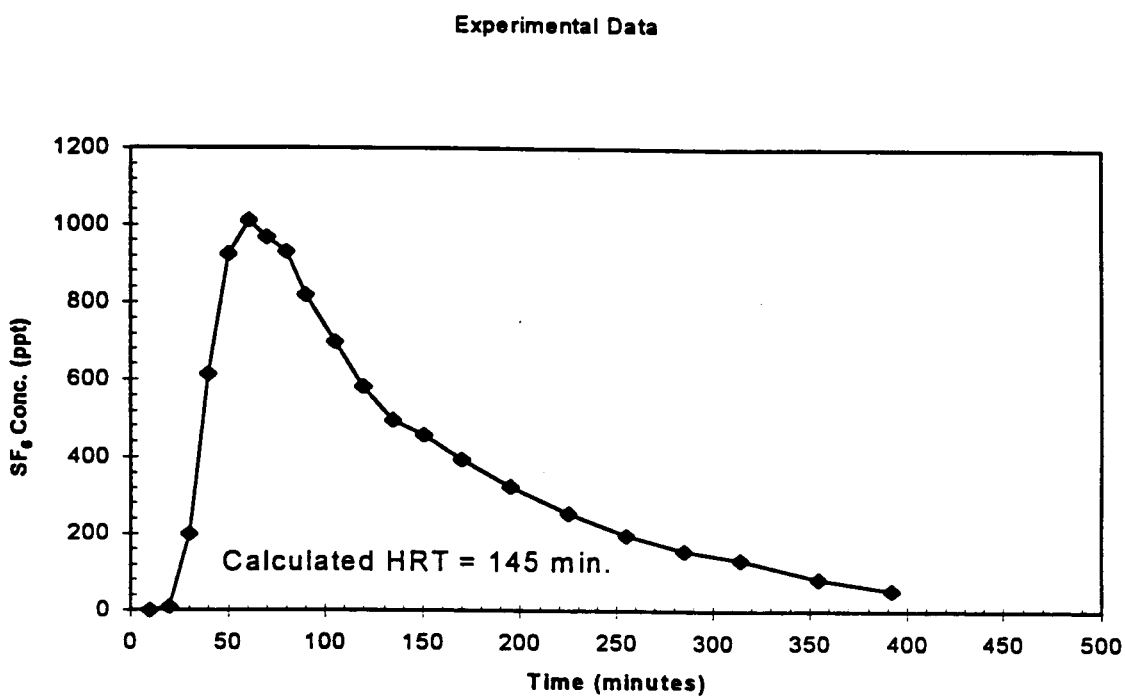


Figure 9. Inert SF_6 Tracer Response Curve for the 4-ft Extraction Cell at an Interstitial Velocity of 1.54 ft/hr.



Based on the flow and an estimated pore volume of 32.6 L, the theoretical residence time was determined to be 149 minutes. The actual residence time was calculated using the following equation:

$$\bar{t} = \frac{\Sigma\ t_i C_i}{\Sigma\ C_i} \tag{4}$$

where

$\bar{t}$	=	mean residence time (minutes)
t_i	=	time (minutes)
C_i	=	SF_6 concentration (parts per trillion by volume).

The hydraulic residence time calculated from equation 4 was 145 minutes, which corresponded to an actual pore volume of 31.6 L and a porosity of 38.8%. These data suggest that the 4-ft flow-through cell configuration resulted in flow characteristics indicative of dispersed plug flow and exhibited minimal short circuiting or dead volume.

A tracer test was also performed on the 8-ft cell (Figure 10). Excellent results were again achieved from these tests. The flow during the test was 0.204 L/min, yielding an interstitial velocity of 1.48 ft/hr. The data in Figure 10 show the experimental tracer response curve. With an estimated pore volume of 66.6 L, the theoretical hydraulic residence time was 318 minutes. The actual hydraulic residence time, as calculated from equation 4, was very close to the theoretical at 317 minutes. The corresponding pore volume and porosity were 64.7 L and 38.9%, respectively.

4.2.2 Run 2 - Flow-Through Cell Testing: 4- and 8- ft Apparatus

The data in Figure 11 indicate four distinct zones of extraction based on the different slopes that can be observed within the vertical dashed lines. The first zone is the removal of carbon tetrachloride by purging of the pore spaces in the high-velocity field contained within the silica sand overlying the silty sand. This hypothesis is supported by the results of the SF_6 tracer testing that indicated greater than 95% tracer removal within two pore volumes. The carbon tetrachloride concentration is shown to decrease from 100,000 ppmv to 42,000 ppmv in 5 hr (300 minutes) and then fluctuate from 42,000 ppmv to 45,000 ppmv for the next 265 hr. The initial rapid concentration decrease that was observed to occur during the first 5 hr corresponds almost exactly to two residence times or pore volumes. The second phase of carbon tetrachloride removal is controlled by capillary action carrying free product to the silty sand-sand interface. The third phase of removal is controlled by carbon tetrachloride diffusion out of the silty sand layer, and the final phase of the removal is controlled by intraparticle diffusion of carbon tetrachloride. The vapor-phase discharge concentration during the final phase of extraction ranged from approximately 7 ppmv to 1 ppmv over the final 150 hr of operation.

The data in Figures 12 and 13 represent the cumulative mass removed for the 4-ft flow-through cell. The individual experiments are identical except that the air during the second extraction

Figure 10. Inert SF_6 Tracer Response Curve for the 8-ft Extraction Cell at an Interstitial Velocity of 1.48 ft/hr.

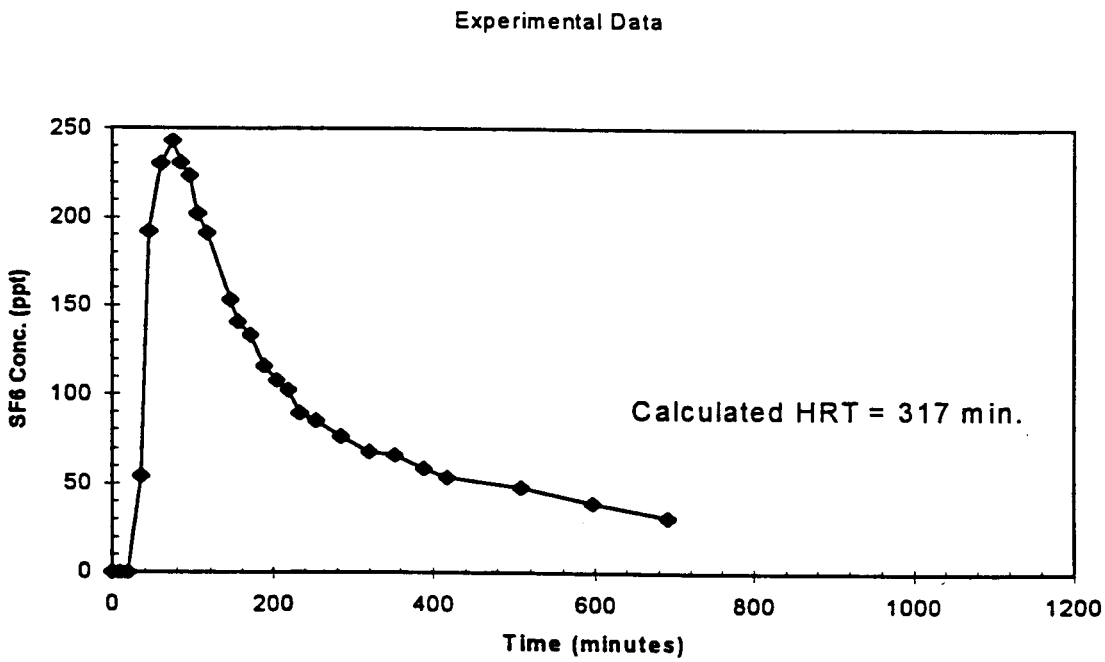


Figure 11. Discharge Concentration Profile for the 4-ft Cell, Flow Velocity 1.5 ft/hr, Relative Humidity 35%.

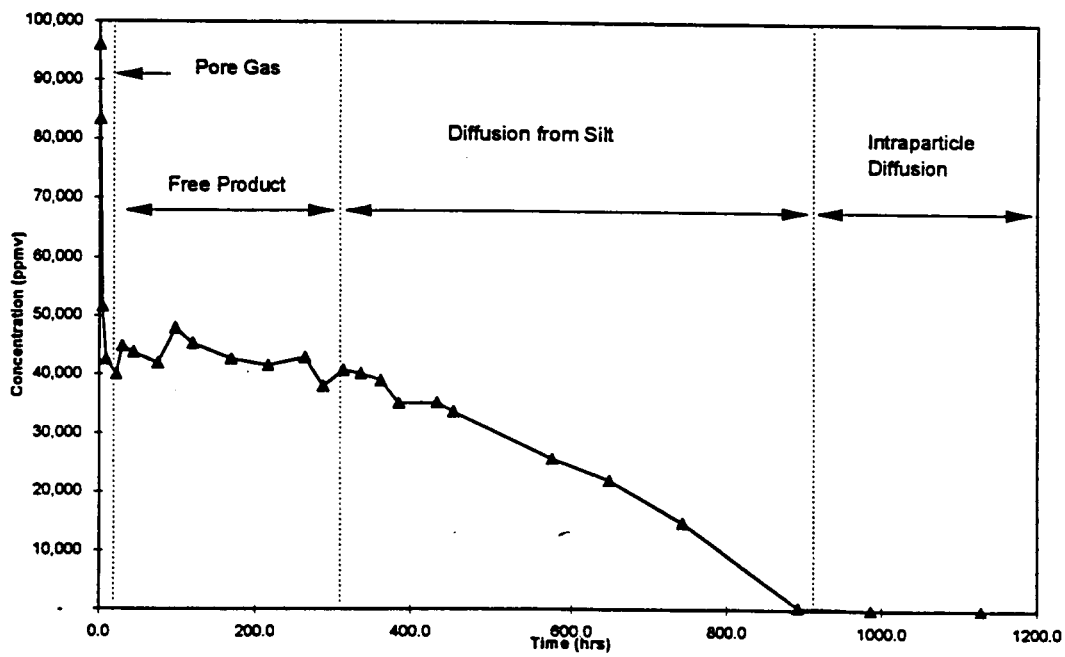


Figure 12. Cumulative Mass Removal for the 4-ft Cell, Flow-Through Velocity 1.5 ft/hr, Inlet Air Relative Humidity 35%.

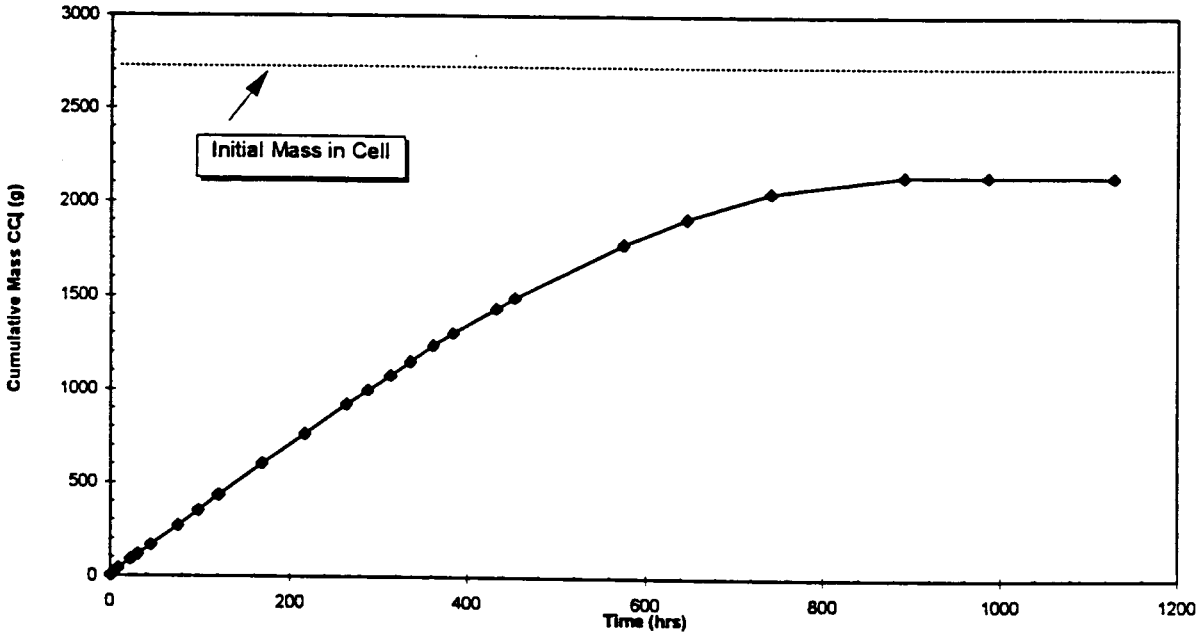
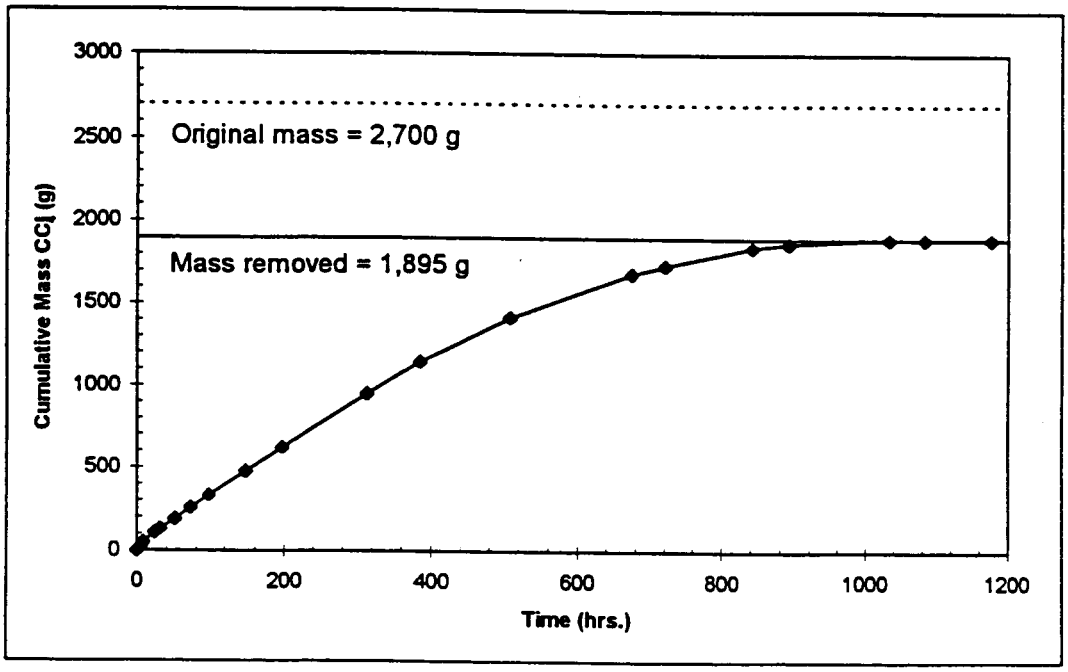


Figure 13. Cumulative Mass Removal for the 4-ft Cell, Flow-Through Velocity 1.5 ft/hr, Inlet Air Relative Humidity 100%.



event was maintained at 100% relative humidity, while during the first event (Figure 12) the inlet air humidity was approximately 35%.

Both 4-ft cell experiments yielded in similar results. Significant carbon tetrachloride remained in the silty sand layer following the termination of each experiment. At the completion of the 4-ft cell experiments, approximately 551 g and 1,366 g carbon tetrachloride remained in the silty sand for the respective 35% and 100% relative humidity runs, yielding 80% and 70% removal. Estimated solid-phase (silty sand) carbon tetrachloride concentrations are 17,006 mg/kg and 42,160 mg/kg. This is in sharp contrast to the results of the column desorption testing that indicated a final soil concentration of 12 mg/kg with an overall removal of 8.7%.

The data collected during 8-ft flow cell testing are presented in Figure 14. It can be seen that the general shape of the curve is similar to Figures 12 and 13; the total mass removed is significantly greater, however. The data indicate that approximately 20 g of carbon tetrachloride remains in the silty sand yielding a soil concentration of approximately 302 mg/kg. The difference in results between the 4- and 8-ft cells is unknown at this time.

At the completion of each flow-through cell extraction test, the soil gas was tested over a period of several weeks to monitor carbon tetrachloride rebound. The final vapor-phase "equilibrium" concentrations were then used with equations 1 through 3 (Section 2.4) to estimate the mass of carbon tetrachloride remaining in the cell in a fashion identical to the method used in field applications. The results of these calculations compared to mass balance estimates of residual carbon tetrachloride are presented in Table 2.

The data in Table 2 are significant with regard to the apparent error incurred when applying the standard equilibrium equations (equations 1 through 3) as a means of estimating soil concentration during remediation operations. It can be seen that calculations can underestimate soil concentrations by as much as four orders of magnitude. Furthermore, application of Kd determined for the silty sand at 10% moisture and the linear Freundlich equation did not result in a significant improvement in prediction. This is a result of the observed level of irreversible adsorption experienced during experimentation and the inability of *adsorption* data to account for irreversible adsorption.

4.3 COLUMN DESORPTION AND FLOW-THROUGH CELL COMPARISON

The observed difference in "final" soil concentration between the desorption column and flow-through cell is important. This difference can be used to set a range of anticipated soil concentrations that brackets ideal removal conditions (12 mg/kg) when flow is possible through a contaminated layer of silty sand to non-ideal conditions when carbon tetrachloride removal is dictated by diffusion from a zero velocity field to areas where flow is occurring (302 to 42,160 mg/kg). Both the column and flow-through cell data indicated that rebound vapor concentrations cannot be used to estimate carbon tetrachloride soil concentrations through application of empirical equilibrium equations (equations 1 through 3) or through application of

Figure 14. Cumulative Mass Removal for the 8-ft Cell, Inlet Air Relative Humidity 100%.

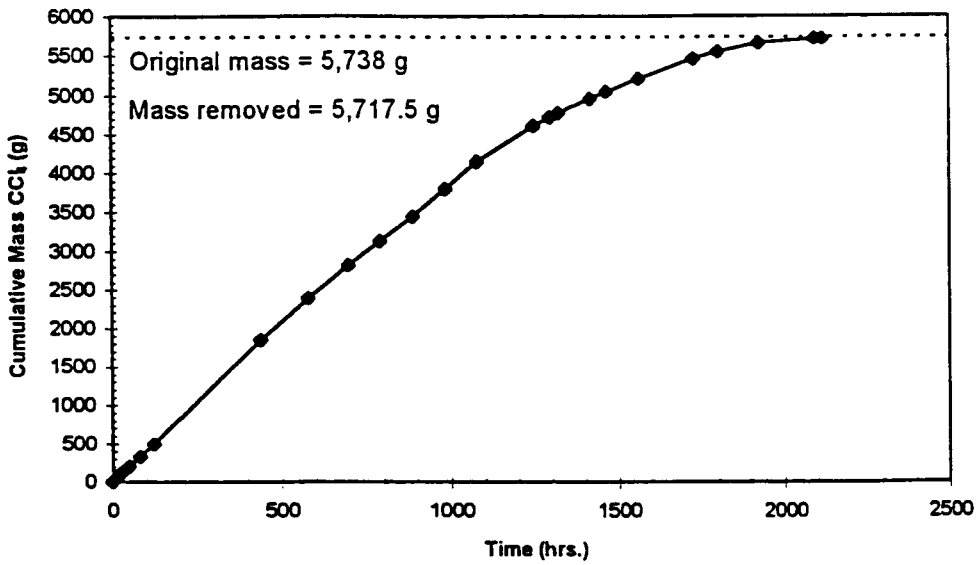


Table 2. Residual Carbon Tetrachloride Estimated Using Equilibrium Calculations and Mass Balance Analysis.

Experiment	Vc (ppmv)	MB[a] (g)	MS[b] (g)	q_a (mg/kg)	q_b (mg/kg)	q_c (mg/kg)
4-ft cell, 35% relative humidity	93[c]	551	0.011	17,006	0.34	4.2
4-ft cell, 100% relative humidity	99[d]	1,366	0.012	42,160	0.37	4.5
8-ft cell, 100% relative humidity	61[e]	20.5	0.015	302	0.22	2.8

[a]Mass remaining based on mass balance calculations.
[b]Mass remaining in silty sand based on equilibrium calculations.
[c]Measured at 36 days.
[d]Measured at 19 days.
[e]Measured at 40 days.
q_a = silty sand concentration based on mass balance.
q_b = silty sand concentration based on equilibrium calculations.
q_c = silty sand concentration based on Kd calculated from adsorption isotherm.

Kd from derived adsorption isotherms on the soil under investigation. This is a result of slow desorption kinetics, likely caused by intraparticle adsorption in the silty sand. Farrell and Reinhard (1994) concluded that trichloroethylene is resistant to desorption from a sand with low organic carbon (0.15%) and a surface area of 12 m^2/g, supporting the results of this investigation.

4.4 RESULTS OF ADDITIONAL TESTS

Preliminary tests were performed to evaluate the effect of increasing temperature on carbon tetrachloride removal. Limited column testing did show that enhanced removal does occur, but this removal could not be quantified at this time. Hot air was drawn into the 8-ft flow-through cell, but the relatively low flow did not afford a mechanism to warm the soil in a reasonable time frame.

4.5 APPLICATION

Several points can be made based on the results of this study regarding field application. It is significant to know that adsorption isotherm information (Kd) developed on native soil may not allow for contaminant concentrations to be estimated from measured vapor concentrations during vapor extraction remediation activities. Soil contaminant concentration predictions were shown to underestimate actual values by up to four orders of magnitude in systems where air is not drawn directly through a contaminant-laden layer. If air is drawn through the contaminant layer, predictions would more closely represent actual soil concentrations because significantly lower soil contaminant concentrations are possible.

One of the most informative data sets with regard to field vapor extraction activities was developed during the flow-through cell testing. The four distinct zones of removal gave valuable information regarding field activities. First, it is imperative to monitor vapor concentration during *and after* an extraction event. Collection frequency should be sufficient to adequately define the concentration time profile and should be more frequent at the early stages of an extraction event. Ideally, the concentration-time profile would allow the regions of extraction to be defined as in Figure 11.

- Pore gas evacuation
- Free product removal
- Diffusion from low-velocity fields
- Desorption-controlled removal.

Although the "breaks" in rate of concentration decrease may not be as apparent in field situations due to the complex heterogeneous nature of the subsurface, relatively rapid concentration decrease followed by at least one slower rate of concentration decrease should be observed. During the rapid rate of concentration decrease, maximum flows would result in efficient removal. When the rate of decrease reaches an asymptotic level and the contaminant collection

yield reaches a perceived minimum, higher flows will probably not enhance removal. This is the region of removal controlled by desorption kinetics, and the data collected in this study indicate that even though a relatively high-concentration gradient exists with regard to known *adsorption* characteristics, mass transfer is extremely slow. At this point in the field extraction operation, efficiency of removal would be enhanced by turning the pump(s) off and allowing for a period of recovery. During this period, contaminant concentrations should be monitored to determine the new "equilibrium" condition. When a steady vapor concentration is achieved, extraction operations should resume and another concentration time profile developed. This profile would then be compared to previous profiles and, when the concentration again reached the asymptotic level, the pumps would be turned off.

The adsorption and desorption data collected herein indicate that accurate estimation of residual contaminant soil concentrations from vapor concentrations during extraction (desorption) operations is very difficult. Current predictive models do not account for the non-equilibrium or hysteresis conditions that have been shown to occur. Predictive error was shown to be greatest when the contaminant was contained in a low velocity field (flow-through cell). The flow-through cell data indicated that even though significant carbon tetrachloride remained in the silty sand layer (302 to 42,160 mg/kg), the vapor concentration following up to 40 days of recovery ranged from 61 to 99 ppmv. This suggests that once free product has been removed and further removal is controlled by desorption kinetics, the threat to the environment is significantly reduced.

If it can be safely assumed that the air flow paths run through the contaminant-laden soil, vapor-phase concentration estimation from adsorption data may yield predictions to within an order of magnitude or better. If accurate, ultimately achievable soil concentration information is desired, soil should be collected from the site during installation of extraction wells and the contaminant or contaminants added at levels representative of field values in a sealed stainless steel column. The soil should then be allowed to equilibrate for at least 1 month. Extraction operations could then be performed similar to the procedure employed in this work to define attainable soil concentration levels. Care should be taken for volatile compounds that are known to be amenable to aerobic biodegradation as bacterial cultures may be introduced during the laboratory-scale operation that could lead to erroneous results for long-term extraction operations.

5.0 RECOMMENDED ADDITIONAL TESTING

5.1 REFINEMENT OF THE LABORATORY DATA

The development of the testing methods and the performance of the tests to complete this scope of work has revealed some areas where the data could be refined and other useful data could be gathered. Two of these areas are described below.

5.1.1 Radiolabeled Carbon Tetrachloride for Mass Balance

Accurate and precise measurement of carbon tetrachloride is difficult at the very low vapor-phase concentrations that were required by these tests. It is suggested that a limited number of the tests be repeated using radiolabeled carbon tetrachloride, which would provide much better accuracy and precision in the measurement of the carbon tetrachloride. This would result in a significant improvement in the mass balance calculations, which is particularly useful for quantifying the "tailing" during the desorption testing.

5.1.2 Aqueous-Phase Carbon Tetrachloride Sorption/Desorption

The majority of the laboratory testing completed in this project used vapor-phase or separate liquid-phase adsorption to the soils. However, much of the site soils were exposed to carbon tetrachloride in an aqueous phase along with other organic compounds, which may have resulted in different adsorption and desorption characteristics than those which were studied in this project. It is suggested that some adsorption tests be performed using aqueous-phase carbon tetrachloride and a mixture of selected organics and carbon tetrachloride. Vapor-phase competitive adsorption and desorption is almost completely absent in the literature. These data would provide a more complete understanding of the soil partitioning at the site.

5.2 QUANTIFYING THE RATE OF CARBON TETRACHLORIDE RELEASE

An important result of this laboratory testing is the indication that much of the carbon tetrachloride remaining in the unsaturated zone at the site is influenced by slow desorption kinetics. This has important ramifications regarding planned additional remedial efforts at the site and the development of the Record of Decision. The testing described below is intended to more clearly quantify the impact of desorption/diffusion controlled release and to measure the effects that enhanced extraction technologies would afford.

5.2.1 Water Flush to Estimate Carbon Tetrachloride Release

An important element in understanding the ability to transport the carbon tetrachloride remaining in the site soils is the ability of the carbon tetrachloride to be flushed out by water moving through the soil. Although water percolation from precipitation events does not occur at the Hanford Site, this flush test would give one conservative estimate regarding the release potential. This testing would quantify the rate of carbon tetrachloride removal by water movement. The results of this testing may be useful for both the SVE operations and the groundwater pump-and-treat project.

5.2.2 Long-Term Carbon Tetrachloride Rebound Testing

The rate at which the carbon tetrachloride enters the vapor-phase by desorption from the soils following cessation of SVE operations is important for determining the frequency of required intermittent SVE extraction operations. The testing performed to date has provided an indication of this rate, but it is recommended that additional testing be performed over a wider variety of conditions to provide a better basis for assessing the immobility of the carbon tetrachloride and the impact on SVE operations.

5.3 SVE ENHANCEMENT TESTING

It is thought that the desorption of much of the carbon tetrachloride remaining in the unsaturated zone soils at the site is diffusion rate limited. The following recommended tests are proposed as ways of studying potential SVE enhancements that might be used to increase the rate of carbon tetrachloride desorption.

5.3.1 Hot Air Injection

Heat can be used to increase the rate of carbon tetrachloride from the site soils. Hot air injection is one potential SVE enhancement that could be tested to quantify its applicability for the site soils and to provide a basis for an economic assessment of heating the subsurface soils. Limited laboratory testing is now being performed as part of this study to provide an indication of the value of heating the soils to increase the rate of carbon tetrachloride removal from soil.

5.3.2 Dry Air Injection

Previous testing by others indicated that dry air is more effective than high humidity air for removing carbon tetrachloride from soil. Most of the desorption testing performed as a part of the study described in this report used high humidity air, which simulates field conditions. A potential SVE enhancement is the injection of dry air into the subsurface. The effectiveness of this application could be tested in the laboratory, again providing a basis for comparison and for economic analysis. Additionally, testing could be performed using hot, dry air to measure its effectiveness.

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APPENDIX A

CARBON TETRACHLORIDE FATE EMPIRICAL CALCULATIONS

Mass of CCl_4 Remaining in the Sand Layer at the End of Run 2

Vapor Phase:

$M_v = C_v \times (10^{-3}) \times P \times V_v \times MW/RT$

M_v	=	mass in vapor phase (mg)	unknown
C_v	=	vapor phase conc. (ppm)	93
P	=	atmospheric pressure (atm)	0.91 (690 mmHg/760 mmHg)
V_v	=	vapor pore volume (L)	31.75 ($V_v = .39V_T$)
MW	=	molecular weight of chemical (g/mol)	153.81
R	=	ideal gas constant (.08206 atm-m3/mol-K)	0.08206
T	=	temperature (K)	293

M_v = 17.19 mg

Dissolved Phase:

$M_w = C_v \times P \times MW/(10^6 \times H) \times V_w$

M_w	=	mass in dissolved phase (mg)	unknown
H	=	Henry's Law constant (atm-m^3/mol)	0.023
V_w	=	water pore volume (L)	0.00 (Assuming dry sand)

M_w = 0.000 mg

Sorbed Phase:

$K_d = f_{oc}K_{oc}$ (liquid/solid partitioning coefficient)

f_{oc}	=	organic carbon content (-)	<0.0006 (below detection for analysis procedure)
K_{oc}	=	liquid/organic partitioning coefficient (mL/g)	439

K_d = 0 (ug/g)/(ug/mL) (assumed to be negligible)

$M_s = K_d \times C_w \times p_b \times V_T$

C_w	=	dissolved conc. (mg/L) = $C_v \times P \times MW/(10^6 \times H)$ =	0.000
p_b	=	bulk density (g/cm^3)	1.65
V_T	=	total volume (L)	81.42

M_s = 0.00 mg

Total Mass:

$M_T = M_v + M_w + M_s$ = 17.19 mg

Mass of CCl_4 Remaining in the Silt Layer at the End of Run 2

Vapor Phase:

$M_v = C_v \times (10^{-3}) \times P \times V_v \times MW/RT$

M_v	=	mass in vapor phase (mg)	unknown
C_v	=	vapor phase conc. (ppm)	93
P	=	atmospheric pressure (atm)	0.91 (690 mmHg/760 mmHg)
V_v	=	vapor pore volume (L)	3.14 ($V_v = 0.29V_T$-V_w = 6.27-3.13)
MW	=	molecular weight of chemical (g/mol)	153.81
R	=	ideal gas constant (.08206 atm-m3/mol-K)	0.08206
T	=	temperature (K)	293

M_v = 1.700 mg

Dissolved Phase:

$M_w = C_v \times P \times MW/(10^6 \times H) \times V_w$

M_w	=	mass in dissolved phase (mg)	unknown
H	=	Henry's Law constant (atm-m^3/mol)	0.023
V_w	=	water pore volume (L)	3.13 (at 8.8% moisture, 3130 g of water were present - 3.13 L)

M_w = 1.771 mg

Sorbed Phase:

$K_d = f_{oc}K_{oc}$ (liquid/solid partitioning coefficient)

f_{oc}	=	organic carbon content (-)	0.0011
K_{oc}	=	liquid/organic partitioning coefficient (mL/g)	439

K_d = 0.4829 (ug/g)/(ug/mL)

$M_s = K_d \times C_w \times p_b \times V_T$

C_w	=	dissolved conc. (mg/l) = $C_v \times P \times MW/(10^6 \times H)$ =	0.566
p_b	=	bulk density (g/cm^3)	1.6
V_T	=	total volume (l)	21.63

M_s = 9.46 mg

Total Mass:

$M_T = M_v + M_w + M_s$ = 12.93 mg

Mass of CCl_4 Remaining in the Sand Layer at the End of Run 3

Vapor Phase:

$M_v = C_v \times (10^{-3}) \times P \times V_v \times MW/RT$

M_v	=	mass in vapor phase (mg)	unknown
C_v	=	vapor phase conc. (ppm)	61
P	=	atmospheric pressure (atm)	0.91 (690 mmHg/760 mmHg)
V_v	=	vapor pore volume (L)	50.45 ($V_v = .39V_T - V_w$)
MW	=	molecular weight of chemical (g/mol)	153.81
R	=	ideal gas constant (.08206 atm-m3/mol-K)	0.08206
T	=	temperature (K)	293

M_v = 17.91 mg

Dissolved Phase:

$M_w = C_v \times P \times MW/(10^6 \times H) \times V_w$

M_w	=	mass in dissolved phase (mg)	unknown
H	=	Henry's Law constant (atm-m^3/mol)	0.023
V_w	=	water pore volume (L)	14.45 at 5% moisture

M_w = 5.36 mg

Sorbed Phase:

$K_d = f_{oc}K_{oc}$ (liquid/solid partitioning coefficient)

f_{oc}	=	organic carbon content (-)	< 0.0006 (below detection of analysis procedure)
K_{oc}	=	liquid/organic partitioning coefficient (mL/g)	439

K_d = 0 (ug/g)/(ug/mL) (assumed to be negligible)

$M_s = K_d \times C_w \times p_b \times V_T$

C_w	=	dissolved conc. (mg/L) = $C_v \times P \times MW/(10^6 \times H)$ =	0.371
p_b	=	bulk density (g/cm^3)	1.65
V_T	=	total volume (L)	81.42

M_s = 0.00 mg

Total Mass:

$M_T = M_v + M_w + M_s$ = 23.28 mg

Mass of CCl_4 Remaining in the Silt Layer at the End of Run 3

Vapor Phase:

$M_v = C_v \times (10^{-3}) \times P \times V_v \times MW/RT$

M_v	=	mass in vapor phase (mg)	unknown
C_v	=	vapor phase conc. (ppm)	61
P	=	atmospheric pressure (atm)	0.91 (690 mmHg/760 mmHg)
V_v	=	vapor pore volume (L)	6.31 ($V_v = 0.29V_T$-V_w = 13.1 - 6.79)
MW	=	molecular weight of chemical (g/mol)	153.81
R	=	ideal gas constant (.08206 atm-m3/mol-K)	0.08206
T	=	temperature (K)	293

M_v = 2.24 mg

Dissolved Phase:

$M_w = C_v \times P \times MW/(10^6 \times H) \times V_w$

M_w	=	mass in dissolved phase (mg)	unknown
H	=	Henry's Law constant (atm-m^3/mol)	0.023
V_w	=	water pore volume (l)	6.79 (at 9.1% moisture, 6792 g of water were present - 6.79 L)

M_w = 2.52 mg

Sorbed Phase:

$K_d = f_{oc}K_{oc}$ (liquid/solid partitioning coefficient)

f_{oc}	=	organic carbon content (-)	0.0011
K_{oc}	=	liquid/organic partitioning coefficient (mL/g)	439

K_d = 0.4829 (ug/g)/(ug/mL)

$M_s = K_d \times C_w \times p_b \times V_T$

C_w	=	dissolved conc. (mg/L) = $C_v \times P \times MW/(10^6 \times H)$ =	0.371
p_b	=	bulk density (g/cm^3)	1.6
V_T	=	total volume (L)	45.23

M_s = 12.97 mg

Total Mass:

$M_T = M_v + M_w + M_s$ = 17.73 mg

Mass of CCl_4 Remaining in the Sand Layer at the End of Run 4

Vapor Phase:

$M_v = C_v \times (10^{-3}) \times P \times V_v \times MW/RT$

M_v	=	mass in vapor phase (mg)	unknown
C_v	=	vapor phase conc. (ppm)	99
P	=	atmospheric pressure (atm)	0.91 (690 mmHg/760 mmHg)
V_v	=	vapor pore volume (L)	29.00 ($V_v = .39V_T - V_w$)
MW	=	molecular weight of chemical (g/mol)	153.81
R	=	ideal gas constant (.08206 atm-m3/mol-K)	0.08206
T	=	temperature (K)	293

M_v = 16.71 mg

Dissolved Phase:

$M_w = C_v \times P \times MW/(10^6 \times H) \times V_w$

M_w	=	mass in dissolved phase (mg)	unknown
H	=	Henry's Law constant (atm-m^3/mol)	0.023
V_w	=	water pore volume (L)	2.76 at 5% moisture

M_w = 1.66 mg

Sorbed Phase:

$K_d = f_{oc}K_{oc}$ (liquid/solid partitioning coefficient)

f_{oc}	=	organic carbon content (-)	< 0.0006 (below detection for analysis procedure)
K_{oc}	=	liquid/organic partitioning coefficient (mL/g)	439

K_d = 0 (ug/g)/(ug/mL) (assumed to be negligible)

$M_s = K_d \times C_w \times p_b \times V_T$

C_w	=	dissolved conc. (mg/L) = $C_v \times P \times MW/(10^6 \times H)$ =	0.602
p_b	=	bulk density (g/cm^3)	1.65
V_T	=	total volume (L)	81.42

M_s = 0.00 mg

Total Mass:

$M_T = M_v + M_w + M_s$ = 18.37 mg

Mass of CCl_4 Remaining in the Silt Layer at the End of Run 4

Vapor Phase:

$M_v = C_v \times (10^{-3}) \times P \times V_v \times MW/RT$

M_v	=	mass in vapor phase (mg)	unknown
C_v	=	vapor phase conc. (ppm)	99
P	=	atmospheric pressure (atm)	0.91 (690 mmHg/760 mmHg)
V_v	=	vapor pore volume (L)	3.14 ($V_v = 0.29V_T$-V_w = 6.27 - 3.13)
MW	=	molecular weight of chemical (g/mol)	153.81
R	=	ideal gas constant (.08206 atm-m3/mol-K)	0.08206
T	=	temperature (K)	293

M_v = 1.81 mg

Dissolved Phase:

$M_w = C_v \times P \times MW/(10^6 \times H) \times V_w$

M_w	=	mass in dissolved phase (mg)	unknown
H	=	Henry's Law constant (atm-m^3/mol)	0.023
V_w	=	water pore volume (L)	3.13 (at 8.8% moisture, 3130 g of water were present - 3.13 L)

M_w = 1.89 mg

Sorbed Phase:

$K_d = f_{oc}K_{oc}$ (liquid/solid partitioning coefficient)

f_{oc}	=	organic carbon content (-)	0.0011
K_{oc}	=	liquid/organic partitioning coefficient (mL/g)	439

K_d = 0.4829 (ug/g)/(ug/mL)

$M_s = K_d \times C_w \times p_b \times V_T$

C_w	=	dissolved conc. (mg/L) = $C_v \times P \times MW/(10^6 \times H)$ =	0.602
p_b	=	bulk density (g/cm^3)	1.6
V_T	=	total volume (L)	21.63

M_s = 10.07 mg

Total Mass:

$M_T = M_v + M_w + M_s$ = 13.76 mg

APPENDIX B

COLUMN DESORPTION DATA FOR SILTY SAND AT 10% MOISTURE

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
0.25	14.27	0.7
2.5	80.89	4.9
3	66.61	6.1
3.5	61.85	7.9
4.5	71.37	16.2
8	95.16	27.2
9	42.82	29.0
10	59.48	36.3
12	204.60	60.9
13.5	49.96	68.6
16.5	47.58	79.4
19	62.81	95.0
22.5	79.93	110.1
24.5	71.37	124.8
28.5	64.71	137.0
30	36.16	145.9
34.5	42.82	159.2
37.5	63.76	184.2
44	27.60	192.7
45	28.55	199.7
50	23.79	205.6
51	40.92	213.2
54.5	27.60	223.5
60	24.74	232.1
63	19.03	238.8

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
68.5	8.09	241.1
70	9.04	245.0
79	15.23	251.0
79.5	13.32	254.0
84.5	12.37	260.4
89.5	15.23	268.6
95	5.71	271.9
103.5	3.09	274.6
115.5	5.23	279.2
125	3.38	283.0
143	2.75	285.1
155	2.62	287.7
167	4.23	290.5
171	2.85	293.6
193.5	2.70	298.0
210	0.99	299.8
247	0.46	300.4
250	0.91	301.9
294	0.41	302.5
294.5	37.11	304.4
295	13.32	305.1
295.5	10.47	306.2
297	10.47	307.6
298	5.23	308.5
300.5	1.43	308.9

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
303	4.76	309.8
305	4.76	310.9
309	7.61	312.8
311	381	313.9
316	0.95	314.3
320	0.23	314.3
324.3	0.81	314.6
329	0.29	314.7
331	0.57	314.9
336.5	0.76	315.2
342	0.33	315.4
348	0.32	315.5
350	0.50	315.6
354	0.01	315.6
360	0.22	315.7
360.25	15.23	316.0
361	4.76	316.5
362	4.76	317.2
364	2.59	317.8
366.5	0.29	317.9
368	0.62	318.0
374.5	0.23	318.1
377.5	10.49	320.4
381	0.27	320.5
382	0.40	320.6

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
390.5	0.40	320.8
394	0.46	321.0
398	0.25	321.1
402	0.32	321.2
407	1.12	321.6
410.5	0.32	321.7
415	0.29	321.8
420	0.31	321.9
421.5	3.92	322.0
424	3.60	322.1
426	0.92	322.2
428	2.29	322.3
435.5	4.18	322.5
436	2.16	322.6
440	1.96	322.7
454	2.22	322.9
456.5	1.44	323.0
459	1.83	323.0
465	2.29	323.1
467	1.31	323.2
470	1.90	323.2
475	248	323.3
478.5	1.57	323.4
482.5	5.10	323.5
483	6.02	323.6

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
483.5	1.96	323.6
484	2.09	323.6
484.5	7.98	324.3
492.5	6.02	324.6
494	9.48	324.8
497.5	7.58	325.1
504.5	4.51	325.3
512.5	7.19	325.6
513.5	6.41	325.8
519	3.53	325.9
521.5	3.20	326.0
525	3.73	326.1
530	3.20	326.3
532.5	2.03	326.3
537	5.49	326.5
543	2.35	326.6
547	0.26	326.6
547.5	13.08	326.7
548	1.44	326.8
550	6.15	326.9
552	0.52	326.9
555	6.93	327.3
561	8.30	327.8
564	3.33	327.9
567	0.65	327.9

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
570	3.40	328.0
573	0.59	328.0
576	0.07	328.0
579.5	0.39	328.1
584.5	5.56	328.3
587.5	6.21	328.6
591.5	7.13	328.9
595	5.95	329.1
601	6.02	329.4
608.5	6.87	329.8
616.5	6.21	330.1
624	5.03	330.3
627	1.96	330.5
653.5	2.94	330.9
660.5	2.94	331.1
679.5	2.48	331.4
696	2.09	331.7
717.5	1.90	331.9
719.5	2.42	331.9
723.5	2.09	332.5
795.5	1.57	333.1
836	0.85	333.3
860.5	0.72	333.5
900.5	0.20	333.5
933.5	0.07	333.5

Time (min)	Effluent Conc. (ppmv)	Cumulative Mass Removed (μg)
984	0.07	334.1
3862.5	2.48	359.1
3863.5	4.32	359.4
3866.5	10.46	360.3
3877.5	2.55	361.0
3904.5	2.48	361.4
3921.5	2.62	361.7
3940.5	2.22	361.9
3949.5	1.83	362.0

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