

Subsurface Venting of Hydrocarbon Vapors from an Underground Aquifer

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SUBSURFACE VENTING OF
HYDROCARBON VAPORS FROM
AN UNDERGROUND AQUIFER

FINAL REPORT

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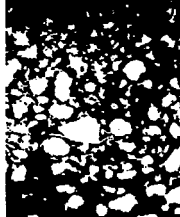
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1.0 EXECUTIVE SUMMARY

This report describes the results of a series of subsurface hydrocarbon venting experiments which were conducted at a petroleum fuels marketing terminal. This particular site was the location of a gasoline spill which had migrated to a shallow aquifer. The objectives of these experiments were to:

- o Quantitatively evaluate the effectiveness of soil venting techniques in controlling and eliminating hydrocarbon vapors from the unsaturated sand formation above the gasoline saturated soil;
- o Perform qualitative and quantitative analyses on the vapors extracted from the soil;
- o Determine the product vapor recovery rates and equivalent liquid product recovery rates at varying test cell evacuation rates; and
- o Evaluate the potential of soil venting as a means of controlling hydrocarbon vapor concentrations in the soil and removing spilled hydrocarbons from shallow aquifers.

Two test cells of identical configuration were installed. Each cell contained 16 vapor monitoring probes spaced at distances from 4 to 44 ft from a vapor extraction (vacuum) well. Each cell was configured with two air inlet wells to allow atmospheric air to enter into the formation. The vapor monitoring probes were installed at heights of 1, 2, and 5 ft above the capillary zone. In-situ vapor samples were obtained periodically from these probes to measure changes in vapor concentration and composition while extracting vapors from the vacuum well at three different flow rates, (i.e., 18.5 scfm, 22.6 scfm, and 39.8 scfm). In-situ vapor samples were collected

with a gas-tight syringe and injected directly into a portable gas chromatograph to quantify and speciate the vapors. Vacuum levels were also measured, in inches of water, at each vapor sampling probe and at the vacuum well to determine the area of influence during each venting test.

The first experiment was conducted with the vacuum pump extracting vapors from the vacuum well, Cell A, at an average rate of 22.6 scfm. During this 12-day test, an average equivalent volume of 4.28 gal per day of hydrocarbon product (measured as hexane) was removed from the formation. Changes in static pressures were observed at distances up to 45 ft from the vacuum well. Decreases in vapor concentrations from the baseline level (those measured prior to activating the vacuum system) ranged from 39% to 98%, depending on the probe's depth and distance from the vacuum well.

The second experiment was conducted in Cell B with the vacuum pump operating at an average flow rate of 18.5 scfm. An average equivalent volume of 3.12 gal per day of hydrocarbon product was removed during the 10-day test period. During this test, changes in pressure in the soil formation were observed at a distance of 52 ft from the vacuum well. Decreases in vapor concentrations from baseline levels ranged from 12% to 99%, depending upon the distance from the vacuum well.

A third test was again conducted in Cell A with the vacuum pump extracting vapors from the vacuum well at an average rate of 39.8 scfm. During the 15-day test period, an average equivalent volume of 5.86 gal per day of hydrocarbon product was removed from the soil. As with the first test, significant reductions in vapor concentrations were observed. The vapor concentration reductions ranged from 19% to 99%. Changes in the static pressure in the soil formation were observed at distances of 44 ft from the vacuum well. After operating the system for 10 days at the 39.8 scfm flow rate with the air inlet wells open to the atmosphere, the air inlet wells were capped and changes in the static pressure were observed at each of the vapor probes in the test cell. With air inlet wells capped, the pattern of reduced pressure became concentric about the vacuum well within

4 hr, and pressure changes were observed at distances of 110 ft from the vacuum well. This effectively doubled the radius of influence of the system with the flow rate remaining constant.

The effective radius of influence for each cell evacuation rate was determined by measuring the static pressures at each vapor recovery well. The radius of influence in each cell extended approximately 50 ft from the vapor recovery wells during the low flow experiments and approximately 110 ft during the high flow experiments. In all cases, a plot of the vacuum (in inches of water) versus distance from the vacuum well very closely approximates an exponential decay function.

An estimate of the cumulative hydrocarbon product recovered during each of the three experiments was 166 gal. Cumulative product recoveries ranged from 31.2 gal in Cell B (18.5 scfm) to 87.9 gal in Cell A (39.8 scfm). The results of the experiment clearly show that the amount of product recovered was directly related to the cell venting rate and the concentration of vapors in the recovery well exhaust. The concentration of hydrocarbon vapors in the vapor recovery well exhaust remained relatively constant during each venting period. As a result, the estimated cumulative product recoveries were observed to increase in a linear fashion with respect to time.

These experiments show that soil venting is not only an effective means of removing hazardous hydrocarbon vapors from the unsaturated soil zone, but may also be used to augment conventional recovery equipment as a primary means of eliminating spilled hydrocarbons in a shallow aquifer. Data collected during this study will be useful in optimizing the design of subsurface venting systems for removing spilled hydrocarbons and controlling hydrocarbon vapors in the soil.

2.0 INTRODUCTION

This report presents the results of a study which was designed to evaluate the effectiveness of subsurface ventilation techniques in controlling and removing hydrocarbon vapors from a soil formation at the site of a gasoline spill. The spilled product had entered a shallow aquifer approximately five years earlier and conventional recovery methods had been used to recover a substantial quantity of the liquid product.

The purpose of this study was to design, install, operate, and evaluate a subsurface ventilation system which could be used to augment conventional recovery methods used to mitigate hydrocarbon spills. The main emphasis of this effort was to evaluate the effectiveness of forced venting in controlling and removing hydrocarbon vapors from the underground environment. In addition, sampling and analytical procedures were developed specifically for this study to measure the effectiveness of the hydrocarbon recovery and vapor control during venting. The data collected during this program will be useful in optimizing the design of subsurface ventilation systems used to mitigate spills of this type.

A brief summary of the results of this study are presented in Section 1.0. A description of the system design and installation procedures are provided in Section 3.0. Also summarized in Section 3.0 are the procedures employed to evaluate the effectiveness of the subsurface ventilation techniques used during this study. The results of this study are presented in Section 4.0. A summary of the results and the conclusions drawn from this study are presented in Section 5.0.

3.0 TECHNICAL APPROACH

This section describes the experimental approach used to evaluate the effectiveness of subsurface venting of gasoline vapors.

3.1 Site Description

A subsurface hydrocarbon venting study was conducted at a petroleum fuels marketing terminal. This site was selected for the following reasons:

- o The ground water aquifer in the immediate vicinity of the terminal was contaminated with gasoline product from a spill which had occurred approximately five years earlier;
- o Conventional liquid product recovery methods have been used at this site to recover a significant quantity of the spilled product;
- o The soil formation at the site was quite porous and permeable and was conducive for using subsurface soil ventilation techniques to control and eliminate hydrocarbon vapors in the soil;
- o The site offered a hydrocarbon lens with an area of continuous vapors which extended beyond the confines of the venting cells;
- o The depth to ground water was sufficient for installation of a venting system to simulate interception of hydrocarbon vapors prior to entering common subsurface structures such as residential/commercial basements, utility vaults, etc.; and

- o The concentration and volatility of the hydrocarbon vapor near the capillary zone were adequate for conducting a pilot study to evaluate the ventilation system design employed.

A plot plan of the study area is shown in Figure 3-1. The area selected for installation of the subsurface ventilation system was located approximately 100 yd southwest of the point where the gasoline product entered the ground. The venting system was installed in a rectangular area 60 ft long and 110 ft wide.

A sieve analysis of core samples taken from a study area adjacent to the venting test cells indicated that the soil formation was uniformly comprised of sand and fine sand fractions with some traces of silt and clay interspersed with occasional traces of coarse gravel. Sieve analyses of core samples collected from the venting system study area revealed similar results. The analysis of core samples shows that soil porosities ranged from 30 to 47% at depths ranging from 20 to 21.5 ft.

Prior to installing the ventilation system, vapor headspace samples were collected from product recovery wells in close proximity to the venting study area. The results of the product headspace analyses indicated that the vapors were weathered gasoline product, owing to the noticeable absence of very light hydrocarbon fractions. The analysis results of the headspace samples indicated that the vapor composition was comprised primarily of C_4 - C_6 fractions (~60-70%).

The approximate depth to ground water in the study area was 24.5 ft. The thickness of the free product lens as measured in the observation well on the surface of the water table was approximately 19.2 in. This was determined from direct measurements of two product monitoring wells. Observations of the split spoon samples show the capillary zone was approximately twelve (12) in. thick and was located approximately 22 to 23 ft below land surface (BLS).

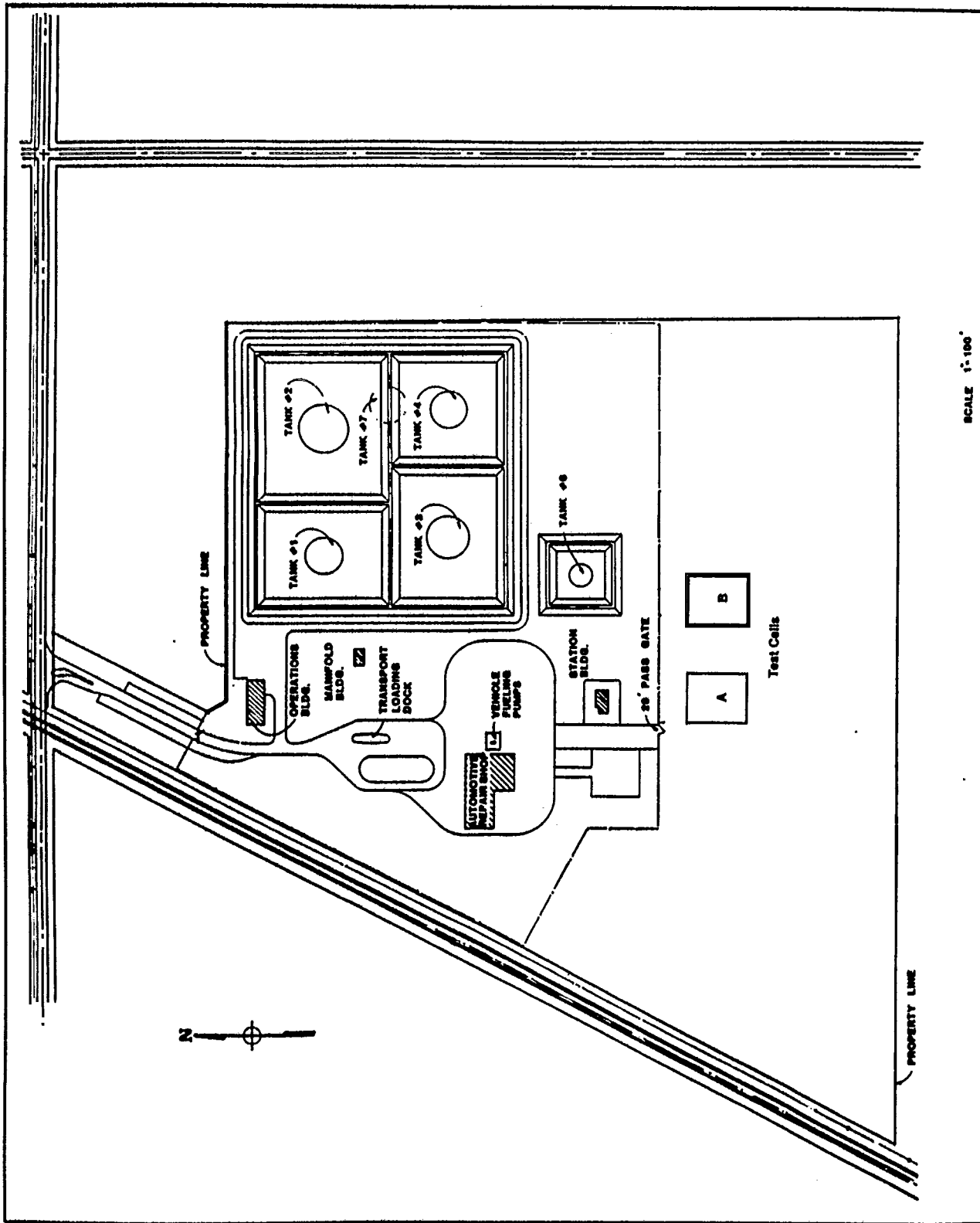


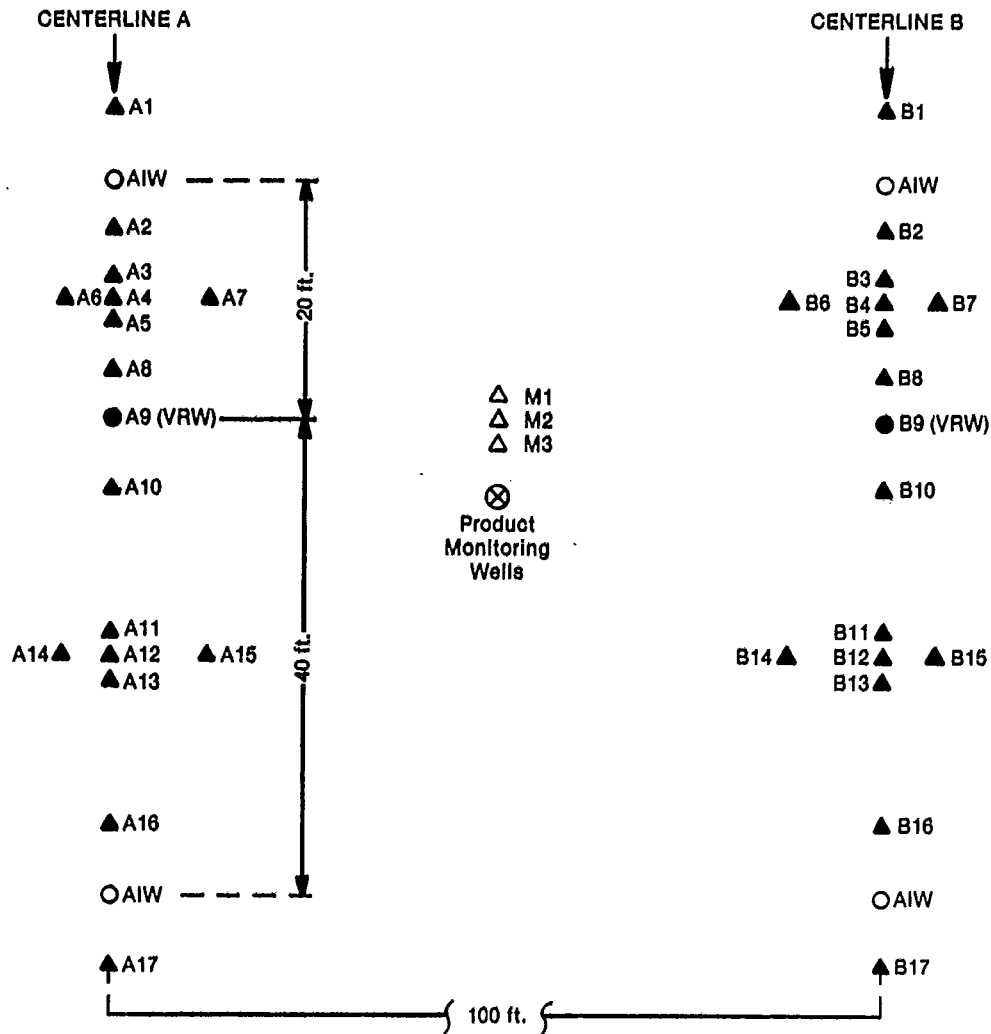
Figure 3-1. Plot Plan of the Study Area

A distinct color change was observed in split spoon samples collected within the vent system area beginning at a depth of 19.5 ft (BLS). Core samples collected at this depth were reddish brown in appearance, and a very distinct hydrocarbon odor was detected. Split spoon samples collected at shallower depths were tannish in color and no distinct hydrocarbon odor was detected. The split spoon samples collected at depths below 19.5 ft BLS were observed to turn grey in color after being exposed to the air. Samples collected at approximately 22 ft BLS and deeper appeared to be saturated with hydrocarbon product, thus indicating the upper boundary of the hydrocarbon capillary zone.

The depths selected for installation of the vapor recovery wells, air inlet wells, and vapor sampling probes used in the venting system were based on the results of the composition of the product vapor and split spoon analysis results.

3.2 Venting System Design

The venting system design evaluated incorporated some of the design features and recommendations obtained from an earlier API-sponsored laboratory study (1). A single vent system geometry was evaluated at varying flow rates. The venting system consisted of two parallel cells with identical dimensions. A diagram of the ventilation system is shown in Figure 3-2. Preliminary split spoon samples were taken to determine the boundaries of the hydrocarbon capillary zone prior to installation of the ventilation system. These data were then used to determine the proper depths for the vapor probes, air inlet wells (AIWs) and vapor recovery wells (VWRs). Each test cell contained one VRW positioned between two AIWs in a straight line configuration. The distance between the first AIW and the VRW was 20 ft and the distance between the second AIW and the VWR was 40 ft. The rationale for this test cell configuration was to evaluate the effect of different distances between the air inlet and vapor recovery wells with regard to control efficiency and elimination of hydrocarbon vapors in the soil. The air inlet and vapor recovery wells in each cell were drilled and



- ▲ Vapor Sampling Probes
- VRW = Vapor Recovery Well
- AIW = Air Inlet Well
- ⊗ Product Monitoring Well
- △ Vapor Monitoring Probe

Probe Depth

13 feet BLS
16 feet BLS
14-20 feet BLS
20 feet BLS
21 feet BLS

Probe Number

M1
3, 11,
9
1, 2, 4, 6, 7, 8, 10, 12, 14, 15, 16, 17, M2
5, 13, M3

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Note: M probes were located midway between centerlines A and B.

Figure 3-2. Two-Cell Venting System Configuration

cased with 2-in. ID pipe to a depth of 20 ft. Each AIW and VRW was screened from a depth of 14 to 20 ft.

The horizontal distance between the VRWs in the two parallel cells was 100 ft. Sixteen vapor sampling probes were installed at various locations and depths in each cell (see Figure 3-2). An oblique view of one-half of a single vent cell configuration is shown in Figure 3-3. This figure is a three-dimensional representation of a single test cell illustrating the various depths and relative distances between the air inlet wells, vapor probes, and vapor recovery wells. The vapor sampling probes were used to measure changes in the vertical and horizontal distribution of hydrocarbon vapors over time during each venting period. The exact dimensions of each cell are given in Table 3-1.

A preliminary analysis of core samples from the study site revealed that there were no layers or continuous lenses of impermeable material in the soil column. In an attempt to induce as nearly as possible horizontal flow of air and vapor in each test cell, an impermeable plastic liner was used to cover approximately 150% of the test area. This was done to:

- o Minimize rainfall influences;
- o Simulate the effect of a structure or parking lot; and
- o Isolate the air inlet wells as primary atmospheric air inlet points.

The impermeable cap was constructed of 6 mil plastic liner placed over the ground surface in each test cell. Each liner was covered with a 3-in. layer of sand to protect the liner from weather and foot/vehicular traffic. The capped area was elevated approximately 1 ft above the natural grade at the center, and evenly sloped to existing grade toward the outer perimeter of each cell. Additional grading was required along the eastern

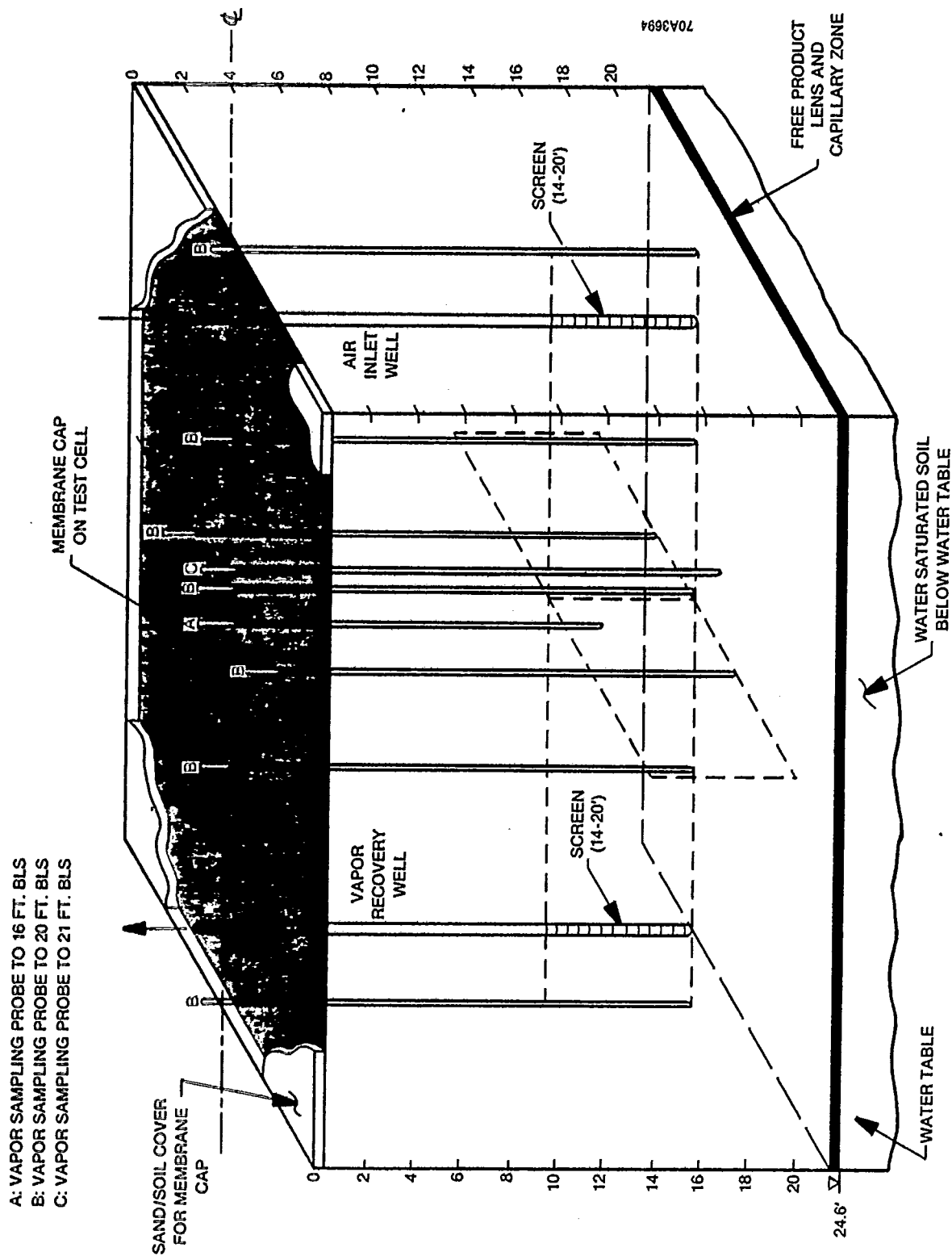


Figure 3-3. Oblique View of Subsurface Hydrocarbon Venting System

TABLE 3-1. VENTING SYSTEM DIMENSIONS

Cell	Probe #	Horizontal Distance from Recovery Well (ft)	Probe Depth (ft)	Offset Distance from Centerline of Cell (ft)	Cell	Probe #	Horizontal Distance from Recovery Well (ft)	Probe Depth (ft)	Offset Distance from Centerline of Cell (ft)
A	A-1	25	20	--	B	B-1	25	20.5	--
A	AIW-1 ^b	20	14-20 ^d	--	B	AIW-1	20	14.5-20.5	--
A	A-2	18	20	--	B	B-2	18	20.5	--
A	A-3	13	16	--	B	B-3	13	16	--
A	A-4	10	20	--	B	B-4	10	20.5	--
A	A-5	7	21	--	B	B-5	7	21.5	--
A	A-6	10	20	5	B	B-6	10	20.5	10
A	A-7	10	20	10	B	B-7	10	20.5	5
A	A-8	4	20	--	B	B-8	4	20.5	--
A	A-9(VRW) ^c	0	14-20	--	B	B-9(VRW)	0	14.5-20.5	--
A	A-10	10	20	--	B	B-10	10	20.5	--
A	A-11	15	16	--	B	B-11	15	20.5	--
A	A-12	20	20	--	B	B-12	20	20.5	--
A	A-13	25	21	--	B	B-13	25	21.5	--
A	A-14	20	20	5	B	B-14	20	20.5	10
A	A-15	20	20	10	B	B-15	20	20.5	5
A	A-16	32	20	--	B	B-16	32	20.5	--
A	AIW-2	39	14-20	--	B	AIW-2	39	14.5-20.5	--
A	A-17	44	20	--	B	B-17	44	20.5	--

^arefer to Figure 3-1.^bair inlet well^cvapor recovery well^dscreened depth

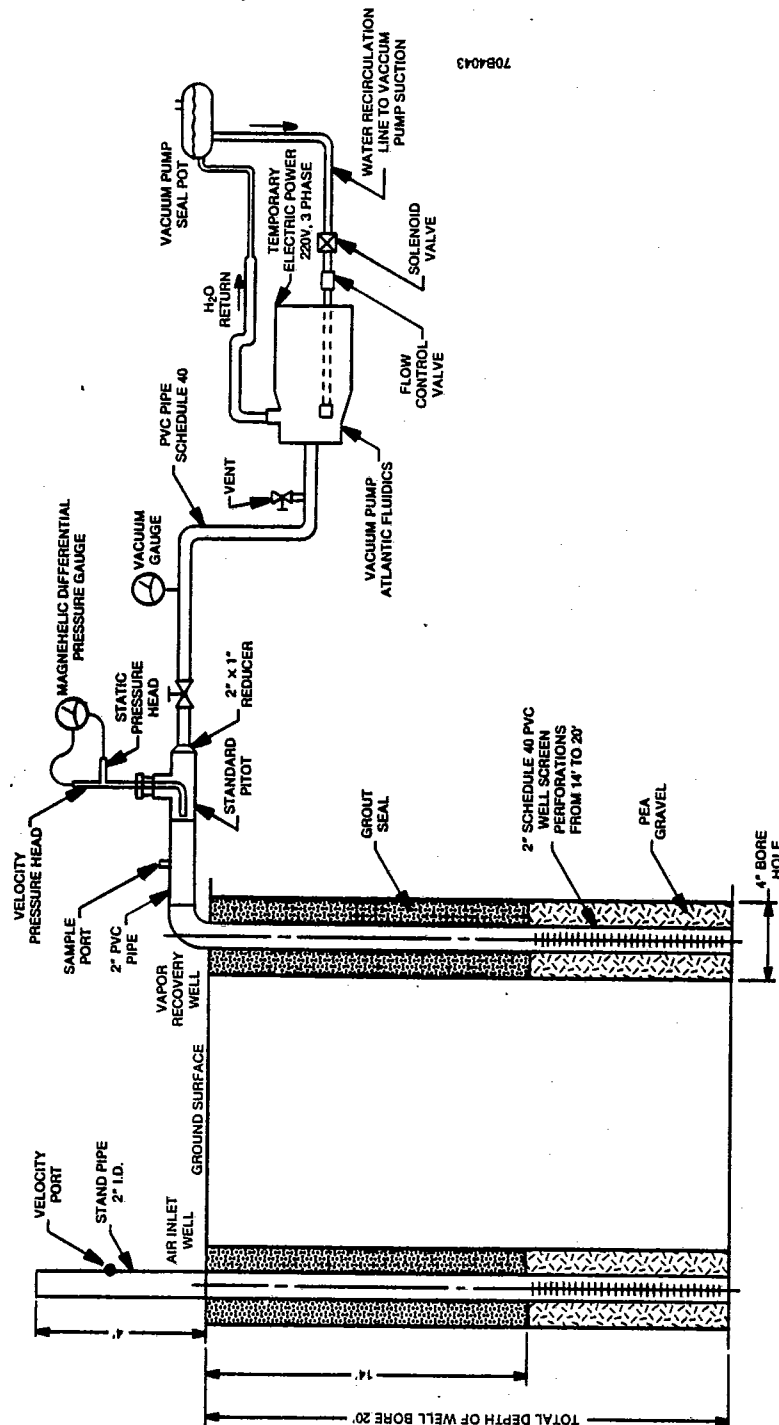
boundaries of the venting system (e.g., Cell B) to divert surface water runoff from other areas of the site.

A product monitoring well drilled to ground water was located approximately midway (50 ft) between the two test cells. In addition, three vapor sampling probes were installed near the product well at different depths (e.g., 13, 20, and 21 ft). These vapor probes were used as control probes to monitor the potential influence of one cell on the adjacent cell.

The venting system was designed to evaluate two lateral spacing geometries between the air inlet wells and vapor recovery wells (e.g., 20 ft and 40 ft) at two different flow rates. Flow rates of 18 scfm and 45 scfm were selected to study the hydrocarbon vapor removal of the system.

The vacuum and air inlet wells were constructed identically. First, a 4-in. bore hole was augered to a depth of 20 ft. Schedule 40 PVC plastic pipe, 2-in. ID, was used to case from the surface to 14 ft in each vacuum and air inlet well. Hydrophylic Industries 0.010-in. slotted casing was used to case the interval from 14 to 20 ft. The bottom of the screen was fitted with a slip cap. After setting the casing in each hole, the annular space of the bore hole was filled with pea gravel to a depth of 14 ft BLS and a grout seal was installed from 14 ft to the surface. The details of the air inlet and vapor recovery well construction are shown in Figure 3-4.

The well construction was designed to facilitate lateral flow of air and vapors through a substantial cross-sectional area of the vadose zone, thereby creating a barrier for vapor migration to the surface. This design was thought to be ideal for controlling or eliminating vapors at depths typical for construction of basements, substructures, or utility vaults. No attempt was made to evaluate other well screening configurations during this study.



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Figure 3-4. Schematic Diagram of Subsurface Venting System

Two liquid ring vacuum pumps were used to generate the required air flow rates evaluated during this study. The pumps were manufactured by Atlantic Fluidics. This pump design was selected since they have no metal to metal contacts (as do piston-type pumps), thereby reducing the possibility of vapor ignition.

A model A-20 pump was used during the low flow venting periods. The model A-20 is designed to pump 32 CFM at a maximum vacuum of 24 in. Hg. During the high flow venting period, a model A-100 pump designed to pump 100 scfm at a maximum vacuum of 25 in. Hg was used. Both pumps required circulating water for the liquid seal.

During operation (see Figure 3-4), the suction side of the pump was connected directly to the vacuum well screens by a 2-in. diameter PVC pipe. A standard pitot tube was installed between the wellhead and a vacuum flow control valve. The flow rate was calculated from differential pressure measurements made with a magnehelic gauge. A 1-in. ball control valve installed in the vacuum line was used to regulate the vacuum/flow.

A 2-in. diameter PVC standpipe 2 ft in length was attached to the wellhead of each air inlet well. A small hole located approximately eight pipe diameters below the standpipe inlet was used for the insertion of a hot wire anemometer in order to measure the air inlet rates.

3.3 Venting Experiment Test Sequence

Three experiments were performed to evaluate the effectiveness of the vent system configuration. Only one test cell was vented at a time during each of the three experiments. Two separate venting experiments were conducted in Test Cell A and one experiment was conducted in Test Cell B. Prior to start-up, baseline soil vapor concentrations were measured at the vapor probes installed in both test cells and at the control probes positioned in the center of the study area.

During the first venting experiment, Test Cell A was operated continuously for a period of 12 days until steady-state conditions were achieved. An average vacuum flow rate of 22.0 ± 2.0 scfm (1360 scfh) was maintained during Experiment 1. In this experiment, Test Cell A was operated with the air inlet wells open. Venting terminated in Test Cell A after 12 days and the cell was allowed to re-equilibrate for a period of 14 days before conducting Experiment 3.

Test Cell B operated continuously for a period of 10 days during Experiment 2. An average flow rate of 18.5 ± 2.3 scfm (110 scfh) was maintained during the experiment. Similarly, Test Cell B was also operated with the inlet wells open.

Upon completion of Experiment 2, Test Cell A was vented at a high flow rate for a period of 15 days. The average vacuum flow maintained during this period was 39.8 ± 1.0 scfm (2390 scfh). During the first 10 days of the experiment, Test Cell A was vented with the air inlet wells open. The air inlet wells were capped on the tenth day of the experiment, and the test cell was vented for an additional five days. The air inlet wells were capped to determine what effect these wells played in controlling or eliminating hydrocarbon vapors in the soil.

The test sequence used to evaluate the effectiveness of the vent system configuration is summarized in Table 3-2.

3.4 Venting System Installation Procedures

This section describes the procedures which were used to install the ventilation system at the test site.

3.4.1 Initial Site Characterization and Preparation

Prior to installing the various components of the ventilation system (e.g., vapor probes, air inlet wells, vapor recovery wells, vacuum

TABLE 3-2. TEST SEQUENCE SUMMARY

Date	Comment	Average Cell Flow Rate (SCFM)
09-17 to 09-28-84	Install venting system and validate sampling protocol	--
09-29-84	Collect core samples in Test Cell A	--
10-01 to 10-03-84	Perform baseline vapor probe measurements in Test Cells A and B	--
10-03-84	Start-up venting system in Cell A (Experiment 1) with air inlet wells open	22.6 $\pm$ 2.0
10-15-84	Terminate venting in Test Cell A and collect core samples in both Test Cells A and B	--
10-15-84	Perform baseline measurements in Test Cell B at each vapor probe	--
10-17-84	Start-up venting system in Test Cell B (Experiment 2) with air inlet wells open	18.5 $\pm$ 2.3
10-25-84	Drill new product well (F-3)	--
10-27-84	Terminate venting in Test Cell B and collect core samples	--
10-29-84	Perform baseline vapor probe measurements at each vapor probe and start-up vent system (Experiment 3) with air inlet wells open	39.8 $\pm$ 1.0
11-09-84	Cap air inlet wells and collect vapor probe static pressures daily	39.8 $\pm$ 1.0
11-13-84	Terminate venting in Test Cell A and collect core samples	--
11-14-84	Terminate study	

pumps, and product monitoring wells) headspace samples from various product monitoring wells and split spoon samples obtained from the proposed study area were collected and analyzed (see Section 3.5.8). Based on the results of these analyses, the decision was made to locate the subsurface venting system in an area near an existing product monitoring well (F-2). The preliminary core sampling data were used to accurately locate the hydrocarbon capillary zone. This information was then used to select the proper depths for installation of the vapor sampling probes, air inlet wells, and vapor recovery well.

Prior to installation of the subsurface venting system, the study area was cleared with a front-end loader/maintainer. The locations selected for installation of the vapor sampling probes, vapor recovery wells, and air inlet wells in each test cell were measured and marked. Preparations were then made to install the vacuum pumps and power drop.

3.4.2 Vacuum System and Product Well Installation

The vacuum system described in Section 3.2 was installed midway between the two test cells (approximately 50 ft from the centerline of each cell). A 1-in. diameter PVC pipe was connected from the vacuum pumps to each individual vapor recovery well.

A product recovery well, located approximately 3 ft from the control vapor probes (M-1 through M-3), was drilled to ground water. The well was drilled approximately two weeks after venting had begun. The new product well (F-3) was drilled in close proximity (~5 ft) to an existing product monitoring well F-2. Three Type K thermocouples were taped to the outer casing of the product recovery well at depths of 16, 20, and 21 ft below surface level.

3.4.3 Vapor Sampling Probes Design and Installation

The vapor probes used for this study were specially designed to map the concentration and composition of hydrocarbon vapors in the soil at various depths and distances from each vapor recovery well. A schematic diagram of the vapor sampling probe is shown in Figure 3-5. Each probe consists of a hollow steel drive tip attached to a 1-in. diameter steel drive shaft. A 1/8-in. diameter seamless stainless steel sample line connected to the drive tip with a stainless steel NPT to Swagelok® union was inserted through the drive shaft. The drive tip was mounted to the end of the steel drive shaft using a metal collar, O-ring, and lockwasher attachment. The O-ring washer was used to seal the drive tip to the collar, thus preventing a short circuit between the hollow cavity of the drive tip and the outer steel drive shaft.

The ground probes were installed in the vadose zone at depths ranging from 16 to 22 ft below the ground surface. A 4-in. hollow stem auger was used to drill a pilot hole within 2 ft of the final depth. Each probe was then inserted into the pilot hole and driven to the final depth using an impact hammer. The annular space around each probe shaft was filled with cement grout to seal the probe and prevent the migration of soil vapors to the surface.

After installation (but prior to grouting), each vapor probe was pressurized to 200 lb to clear the perforations in each drive tip and to check for leaks between the drive tip and the outer drive shaft. This procedure was also effective in determining if a probe had penetrated into the free product zone. A resonating bubbling sound could be heard if the drive tip penetrated through the saturated free product zone. Probes were pulled and reset if the drive tip was observed to have penetrated through the capillary zone or developed leaks through the outer drive shaft.

The end of each vapor probe sampling line was fitted with a Swagelok® union fitted with a silicon rubber septum. A gas-tight syringe

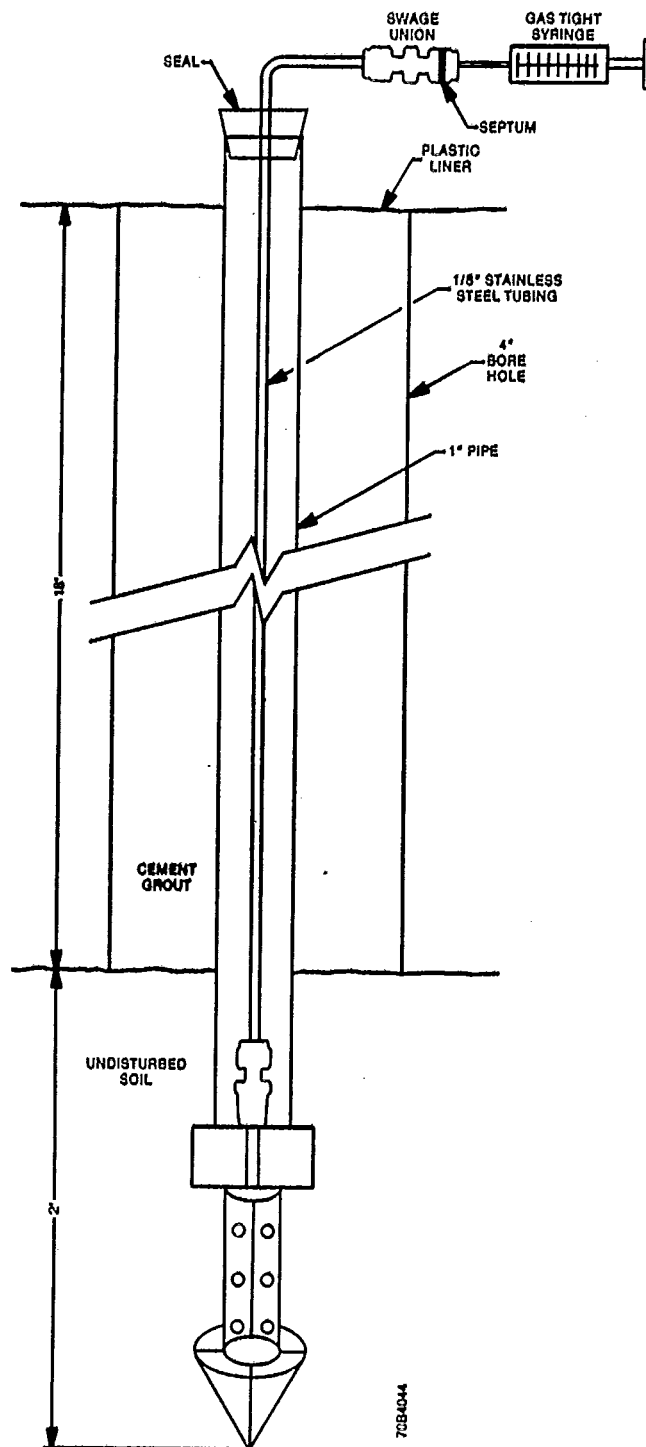


Figure 3-5. Schematic Diagram of Vapor Sampling Probe

was inserted into the septum fitting to withdraw vapor samples from each probe for analysis of vapor concentration and composition using GC analysis techniques. The vapor probes used in this study were designed to minimize the internal volume of the sample transfer line while maximizing the external probe surface area to provide an accurate measurement of soil hydrocarbon vapors in the immediate vicinity of each probe.

3.4.4 Validation of Vapor Probe Sampling Techniques

Initially, four vapor sampling probes were assembled and installed. Two probes were installed to a depth of 20 ft in each of the two test cells. These probes were used to determine the uniformity of the vapor concentrations and composition in each test cell. In addition, the data from the probes were used to validate the sampling and analytical protocol employed during this study. The results of the initial measurements indicated that the vapors appeared to be uniformly distributed horizontally in Cell A, but were somewhat more variable and lower in concentration in Cell B. The composition of vapors were homogeneous in both test cells. Repeated sampling of a single probe indicated that the sampling and analytical techniques were reproducible.

3.4.5 System Operation

During each venting period, the appropriate vacuum pump configuration was connected to the vapor recovery well in the cell under test. A standard pitot tube was used to obtain cell flow rate measurements. The cell flow rate measurements were corrected to standard conditions (e.g., 68°F and 29.92 in. Hg). After start-up, minor adjustments of the cell vacuum were made until the desired flow rate was achieved. The vacuum pressure corresponding to the desired flow rate was noted and the vacuum system was then maintained at the same conditions until each experiment was terminated. Duct velocity measurements were made on a daily basis during each venting experiment.

3.5 Sampling and Measurement Procedures

A variety of measurements were made during this study to monitor the effect of subsurface ventilation on the vertical and horizontal distribution of hydrocarbon vapors in the soil. A number of core samples were collected before, during, and after the venting study in an effort to characterize the hydrocarbon vapors present in the interstitial spaces between the soil particles and the volatile/semi-volatile hydrocarbons adsorbed on the soil particles.

During the ventilation study, the following parameters were measured to evaluate the effectiveness of the subsurface ventilation system. These included:

- o Hydrocarbon concentration and composition from each vapor recovery well;
- o Soil vapor concentration and composition at various depths and distances from the vapor recovery and air inlet wells;
- o Air flow rate measurements at each air inlet and vapor recovery well;
- o Static pressure measurements at each vapor sampling probe;
- o Estimates of hydrocarbon vapor and product removal rates;
- o Soil temperature at three levels;
- o Hydrocarbon product lens thickness and depth to ground water as measured in the observation well;

- o Physical characterization of the soil formation (e.g., particle size, permeability, bulk density, particle density, total porosity, moisture, pH, conductivity);
- o Characterization of interstitial pore space hydrocarbon vapors; and
- o Characterization of volatile/semi-volatile hydrocarbons absorbed on the soil particles.

The sampling and analytical techniques used to evaluate the sub-surface ventilation system removal effectiveness are described below.

3.5.1 Determination of Vapor Recovery Well Hydrocarbon Concentration and Composition

The concentration and composition of hydrocarbon vapors in the vapor well exhaust were determined by periodically sampling the effluent from each vapor recovery well (VRW). A gas-tight syringe was used to withdraw a known volume of gas from a sample port mounted on the wellhead of each VRW. Each sample was analyzed on site by GC-FID using the procedures described in Section 3.5.9. The elapsed time between sample collection and analysis was approximately five minutes. The analysis results were used to determine the concentration and relative composition of hydrocarbons in the VRW effluent exhaust. In addition, the data were used to estimate vapor emission and product recovery rates during each venting period.

The direct vapor sampling technique used in this study is much preferred over sorbent tube collection methods. Direct vapor analysis is less subject to sampling errors due to variable collection efficiencies, artifact formation, variable solvent recovery efficiencies, sorbent concentration, and sample degradation.

3.5.2 Vapor Probe Measurements

Subsurface vapor sampling probes were used to characterize the concentration of hydrocarbon vapors at various distances from the air inlet wells and vapor recovery wells during each venting experiment. A description of the vapor probe is given in Section 3.4.3.

A gas-tight syringe was used to withdraw vapor samples for analysis using the GC-FID techniques described in Section 3.5.9. During sampling, a 10 milliliter (mL) gas-tight syringe was used to withdraw a sample from the perforated drive tip located at the base of each sample probe shaft. The sample was withdrawn from the probe tip by inserting the gas-tight syringe through a septum fitting attached to the end of the sample line (see Figure 3-5). The 10 mL syringe was used to purge the sample line by withdrawing 30 mL of vapor (~9 residence volumes) before collecting a sample in a 1 mL gas-tight syringe. The sample was then injected directly into a gas chromatograph and analyzed for vapor concentration and composition. Between sampling, the gas-tight syringe was flushed vigorously with ultrapure air and sample blanks were analyzed periodically to ensure accurate sampling.

3.5.3 Air Flow Rate Measurements from Air Inlet and Vapor Recovery Wells

Air flow rate measurements were made daily at each air inlet well and vapor recovery well under test. The effluent velocity from the vapor recovery well was used to determine the exhaust flow rate which in turn was used to calculate estimates of product vapor and liquid product recovery rates. Flow rate measurements made at the air inlet wells determined the ratio of inlet air to exhaust air.

Vapor recovery well flow rate measurements were made using an inline standard pitot mounted between the wellhead and the vacuum/flow control valve. A magnehelic differential pressure gauge was used to measure the difference between the velocity pressure head and the duct static pressure

(ΔP). The static pressure was obtained by measuring the difference between the duct static head and ambient pressure. Barometric pressure and temperature measurements were also made to correct the actual flow rate measurements to standard conditions (68°F and 29.92 in. Hg).

The equations used to compute the vapor recovery well flow rates are as follows:

$$P_d = P_a + P_s \quad (1)$$

$$V_s = 85.48 \sqrt{(T_d)(\Delta P)/(MW)(P_d)} \quad (2)$$

$$Q_a = (V_s)(A)(3600) \quad (3)$$

$$Q_s = (Q_a)(528^\circ R/T_d)(P_d/29.92) \quad (4)$$

where: P_d = absolute duct pressure (in. Hg)
 P_a = ambient pressure (in. Hg)
 P_s = static pressure (in. Hg)
 V_s = vapor recovery well velocity (ft/sec)
 pitot
 85.48 = pitot tube constant
 T_d = duct temperature (°R)
 ΔP = differential pressure (in. H₂O)
 MW = average molecular weight (28.08 lb/lb-mole)
 Q_a = actual flow rate (ft³/hr)
 A = cross-sectional area of duct (ft²)
 Q_s = standard flow rate (scfh)
 528°R = standard temperature in °R (68°F)
 29.92 in. Hg = standard atmosphere

Air inlet flow rates were made with a temperature compensated hot wire anemometer. This sensor measures the velocity of the gas stream by sensing the cooling effect due to a moving stream over a uniformly heated

metal sphere. The anemometer was inserted through a small opening in the air inlet standpipe where the air enters the well. The measurement point was located approximately 8 duct diameters below the duct entrance. The hot wire anemometer was purchased new for this project and was factory calibrated in a laminar flow chamber.

3.5.4 Vapor Probe Static Measurements

Static pressure measurements were made at each vapor probe at least once during each venting experiment. The static measurements were made by connecting one end of a magnehelic gauge to the sample line on each vapor probe and measuring the static pressure (probe vacuum) relative to ambient pressure. These measurements were made to document the evacuated zones of influence at various distances and depths within each test cell during the venting study.

3.5.5 Soil Temperature Measurements

The soil temperature was measured at three different depths (e.g., 16, 20, and 21 ft) at the observation well. The soil temperature was measured at the product recovery well (F-3) located midway between the two test cells. A digital electronic readout displayed the temperature reading from each thermocouple.

3.5.6 Hydrocarbon Thickness and Depth to Ground Water

An electronic device which senses the difference in conductance between hydrocarbons and water measured the thickness of the free hydrocarbon layer in the observation well. The depth to ground water was measured with the same device.

3.5.7 Physical Characterization of Soil Core Samples

The physical measurement parameters used to characterize the soil core samples are described in this section.

Sample Collection - Core samples were collected using a split spoon core sampling tool. A hollow stem auger was used to core down to within 18 in. of the sampling depth. A split spoon tool equipped with three 1 1/2-in. diameter brass sample sleeves each 6 in. in length was driven to final depth. The split spoon was withdrawn from the bore hole and the brass sleeves containing the soil samples were removed. Core samples designated for hydrocarbon characterization were capped with specially machined aluminum end caps. A diagram of the core sample sleeve is shown in Figure 3-6.

Split spoon samples were collected in each test cell before and after each venting period. Two split spoon samples were collected from each core hole at 19-20.5-ft and 20.5-22.0-ft depth intervals. Selected samples were chosen for analysis. The samples were then labeled and shipped to Radian laboratories in Austin, Texas in refrigerated containers.

Particle Size - Particle size determinations were made using ASTM Method D422. This method requires that a hydrometer be used to determine particle density. The sample was passed through a dry sieve to determine the particle size distribution.

Permeability - The permeability coefficient of the soil was measured on sleeved core samples using a constant head permeameter and U.S. Army Corps of Engineers Method EM 1110-2-1906.

The test cores were left in the inner brass sleeves in which they were sampled. Porous polyethylene discs were placed over each end of the cylinder. The entire cylinder was sealed in a permeameter and saturated with water to remove all air voids. This was accomplished by initially applying a large back pressure to the test specimens. Then under a constant

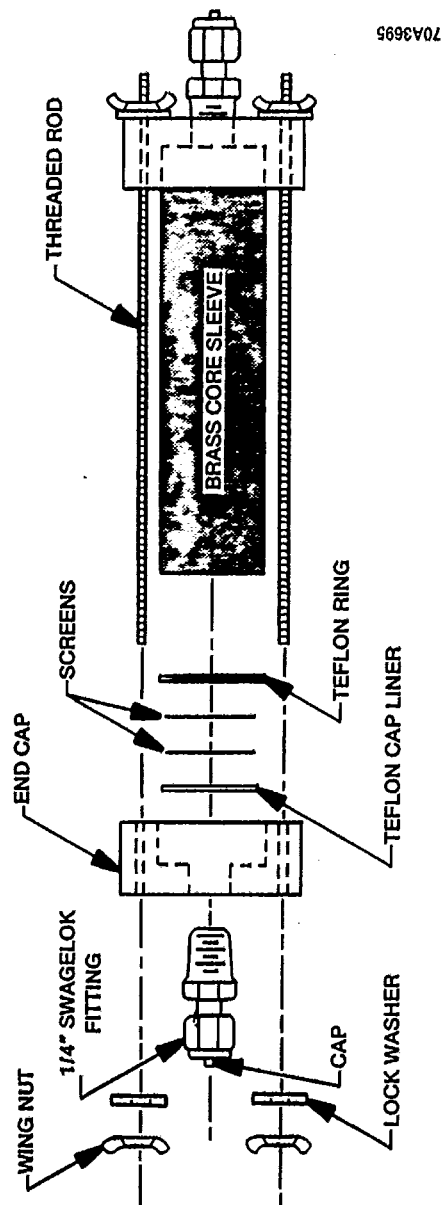


Figure 3-6. Soil Core Sample Sleeve with Machined End Caps

head of pressure, water flowed through the test specimen. The permeability coefficient, K , was calculated from the following equation:

$$K = (vh/tPA) \quad (5)$$

where: K = permeability coefficient (cm/sec)
 v = volume of leachate (cm³)
 h = height (or length) of soil core specimen (cm)
 t = time of test duration (sec)
 P = pressure (cm of water), and
 A = cross-sectional area of core specimen (cm²)

Bulk Density - The bulk density of the soil represents the combined mass of solids, liquids, and air contained in the undisturbed bulk soil sample volume. Soil samples collected in undisturbed cores were used to determine bulk density. Each sealed core sample was carefully measured for volume determination. After recording the volume, the entire soil sample was transferred to a tared watch glass and placed in an oven at $110 \pm 5^\circ\text{C}$ until a constant weight was obtained. The bulk density was calculated using the following equation:

$$D = M/V_b \quad (6)$$

where: D = the bulk density (g/cm³)
 M = oven dry weight (g)
 V_b = bulk volume (cm³)

Particle Density - The particle density of a sample describes the mass and volume occupied by the solid particles in the soil sample. Particle density was determined on oven-dried samples of soil according to ASTM D854. This method consisted of placing the dried soil in a pycnometer (constant volume vessel) and filling all voids with hexane. The particle density of the soil can be calculated based on the volume of hexane displaced by the soil and the dry weight of the soil. An exception to the ASTM

method was taken in reporting the results. Instead of reporting the particle density as a specific gravity (i.e., relative to water), it was reported as a mass per unit volume (g/cm^3).

Total Porosity - Total porosity represents the void space in undisturbed soil. Total porosity was calculated from the bulk density and particle density measurements.

The bulk density of the soil was measured on an undisturbed core sample as described in previous Equation 6. The particle density which describes the volume of soil occupied by solid particles was determined by the following equation:

$$P = M/V_p \quad (7)$$

where: P = particle density (g/cm^3)
 M = mass of oven dry soil (g), and
 V_p = volume occupied by solid particles having a mass M (cm^3)

The fraction of space in a soil column occupied by solid particles in a bulk soil sample is defined as V_p/V_b is equal to D/P by solving from Equations 6 and 7. Total porosity, S_t , represents the percentage of the bulk volume occupied by nonsolids (i.e., the air and liquids in void spaces) as calculated below:

$$S_t = 100 [1-(D/P)] \quad (8)$$

Moisture Content - Selected core samples were analyzed for moisture content using ASTM Method D2216. Soil samples were transferred from the core sleeve to a sealed container and weighed. The soil samples were placed in a drying oven at $110 \pm 5^\circ\text{C}$ with the container open. The samples were dried to a constant weight. The container was emptied of its contents and cleaned prior to determining the tare weight of the container. The moisture content, W , of the sample was calculated as follows:

$$W = [(w_1 - w_2) / (w_2 - w_c)] \times 100 \quad (9)$$

where: W = moisture content %

w_1 = mass of container with moist specimen (g)

w_2 = mass of container with oven dried specimen (g)

w_c = mass of container (g)

Soil pH Value - Hydrogen ion activity was determined with an Orion 701A digital temperature compensated pH analyzer equipped with a glass electrode pair. EPA Method 150.1 was used to determine hydrogen in activity (pH) in selected soil core samples.

Conductivity - Conductivity was measured in selected core samples using EPA Method 120.1. The specific conductance was measured with a Lab-Line LECTRO Model MCI-MARK IV.

3.5.8 Analysis of Volatile Organics in Soil Core Samples

The analysis of volatile organics in soil can be broken down into three categories: a) organics in the interstitial pore space; b) organics adsorbed to the soil particles, and c) organics within the soil particles. Since the soil cores sampled consisted primarily of sand with small amounts of clay interspersed, only the first two cases were considered for this study. In any given soil, there exists a dynamic equilibrium between organics in the gas phase, trapped between the soil particles, and the organics adhering to the particles themselves. Any attempt to remove the organics either on or between the soil particles can disturb the equilibrium and give misleading analytical results. The procedures used to analyze organics in soil and at the same time minimize the disruption to the equilibrium are described herein.

Determination of Sorbed Organics on Soil Particles - Extractable volatile organic carbon (VOC) fractions were removed from soil samples in the following manner. A weighed amount of soil was suspended in tetraglyme

and allowed to equilibrate undisturbed for at least one hour. The concentration of the solution was 1 gram of soil in 1 mL tetraglyme. An aliquot of the extract, no more than 100 μ L, was placed in a Belar tube containing 5 mL of organic-free water and purged with inert gas. Loss of volatile fractions was prevented by minimizing exposure of the extract to air during the transfer.

Determination of Interstitial Soil Vapor Concentrations

(Headspace) - A soil headspace technique was used to determine VOC concentrations in porous, dry soil samples. Headspace samples were collected using a 5 mL gas-tight syringe. A cleaning wire was inserted into the syringe needle to prevent plugging. A syringe needle, equipped with a pressure-lock valve, was inserted into the center of the soil core, with care taken to minimize disturbance of the soil. Once the needle was positioned, the cleaning wire was removed and the syringe was attached to the needle. The headspace was allowed to equilibrate for 5 minutes before collecting the headspace sample. The pressure-lock valve on the syringe was opened prior to sampling and then closed immediately after withdrawing the sample. The pressure-lock valve was then re-opened while the needle tip was immersed in a beaker of water. If no bubbles were observed or if water was drawn into the syringe, no soil headspace was collected. If this occurred, the needle was examined and the sampling procedure was repeated. The headspace sample was injected directly into the cryotrapping system. The syringe plunger was then pushed to the desired injection volume, and the sample was injected into the GC for analysis.

Analytical Conditions - The analytical procedure consisted of the following operations:

- o Collection of VOCs through a Permapure® drier onto a cryogenic trap;
- o Flash thermal desorption onto a fused silica capillary GC column;

- o Detection of the VOCs by flame ionization detector (FID), photoionization detector (PID), and Hall electrolytic conductivity detector (HECD); and
- o Computer-assisted data reduction.

Table 3-3 presents the detailed analytical conditions for each of these operations.

3.5.9 On-Site Analysis of Hydrocarbon Vapor Samples

A Shimadzu Model GC Mini 2 gas chromatograph equipped with a flame ionization detector (GC-FID) was used on site to immediately analyze the hydrocarbon vapor samples collected from the vapor recovery wells and vapor sampling probes. The GC was equipped with a heated sample inlet and a temperature programmed oven. A Hewlett-Packard Model 3390A integrator was used to generate sample chromatograms and reduced run reports.

The analytical column used to separate the various hydrocarbon component fractions consisted of an 8 ft by 1/8-in. stainless steel column packed with 20% SP 2100 and 0.1% Carbowax 1500 on 100/120 mesh Supelcoport. All analyses were made at isothermal column oven conditions of 100°C. A nitrogen carrier flow of 40 mL/min was maintained during each run. The detector inlet was maintained at a temperature of 250°C.

Gas-tight syringes were used to inject samples collected from the vapor recovery wells and vapor sampling probes. Injection sizes ranged from 0.1 to 1 mL depending on the expected concentration range of the sample analyzed.

Two types of gas standards were used to calibrate the field GC. These consisted of quantitative and qualitative standards. The FID detector response was multipoint, calibrated daily with a series of three benzene in air standards obtained from Scott Environmental. The concentration of each

TABLE 3-3. GC-FID/PID ANALYTICAL CONDITIONS

Instrument: Varian 3700 GC or equivalent interfaced to a laboratory data system possessing a minimum of 48K of RAM

Detectors: FID, PID, HECD (Halogen Mode)

FID/PID Split Ratio: 4:1

GC Column: (2) 60m x 0.32mm ID SE-30 fused silica capillary columns,
 $d_f = 1 \mu\text{m}$

GC Carrier Gas: Helium @ 2 mL/min

Column Head Pressure: 13 psig

Injector: Cryogenic trap

Transfer Lines and Valve Oven Temperature: 110°C

Cryotrap Desorb Temperature: 180°C

GC Program: -50°C to 100°C @ 6°/min, IH - 2 min.

benzene standard was 10, 100, and 1000 ppm-V, respectively. The total organic response (TOC) in parts-per-million carbon (ppm-C) was obtained for concentrations ranging over three orders of magnitude. An average response factor for benzene was used to determine the concentration for each chromatographic peak. The sum of the responses for all peaks was used to determine the total hydrocarbon response. A seven-component qualitative standard obtained from Scott Environmental was analyzed daily to estimate the retention times of the individual carbon fractions. The qualitative standard contained methane, ethane, propane, N-butane, N-pentane, N-hexane, and N-heptane in air.

A semi-qualitative analysis of the hydrocarbon vapors was obtained by dividing the chromatogram up into various carbon fractions. The carbon fractions reported during this study are as follows:

- o C₁-C₂
- o C₃-C₄
- o C₃-C₆ and
- o C₇ +

The sum of the responses of the individual carbon fractions was computed for each analysis. The response of the individual fractions was reported in ppm-C.

3.5.10 Estimates of Hydrocarbon Vapor and Product Removal Rates

Estimates of hydrocarbon vapor and product removal rates were used to evaluate the effectiveness of the venting system design. Measurement of the hydrocarbon concentration and flow rate of the vapor recovery well exhaust was used to calculate the hydrocarbon vapor mass recovery rates and liquid product removal rates. In addition, cumulative product recovery estimates were calculated for each venting rate.

Before the vapor and liquid recovery estimates could be calculated, it was necessary to convert the vapor recovery well concentrations from a ppm-C (parts-per-million carbon) basis to a ppm-V (parts-per-million volume) basis and derive an average molecular weight for the hydrocarbon product vapor. The concentration of each hydrocarbon fraction was converted to ppm-V by dividing the concentration in ppm-C by the average carbon number for each component fraction. The average carbon number was estimated based on the relative concentration of each component class observed in the soil headspace samples. Each component class was then summed to obtain the total hydrocarbon (THC) concentration reported in ppm-V. Based on these data, it was further determined that the average carbon number for the hydrocarbon vapors was 6. Therefore, an average molecular weight of 86.18 (N-hexane) was used to estimate the vapor and product recovery rates obtained during the venting study.

The equation used to estimate the hydrocarbon vapor recovery rates follows:

$$V_r \text{ (lb/hr)} = (V_c \text{ ppm-V}) / (10^6 \text{ ppm-V}) (86.18 \text{ lb/lb-mole}) \\ (1.0 \text{ lb-mole/385.36 SCF}) (Q \text{ (SCF/hr)}) \quad (10)$$

or

$$V_r \text{ (lb/hr)} = (V_c)(Q)(2.24 \times 10^{-7})$$

where: V_r = vapor recovery rate (lb/hr)
 V_c = vapor concentration (ppm-V)
 86.18 = average molecular weight by vapor (lb/lb-mole)
 Q = venting rate (SCF/hr)

The following equation was used to compute the liquid product recovery rate:

$$LP_r = (V_r)/(P_d) \quad (11)$$

where: LP_r = liquid product recovery rate (gal/hr)
 V_r = vapor recovery rate (lb/hr)
 P_d = product density (5.51 lb/gal)

3.6 Sampling Frequency

The sampling and measurement frequency for those parameters used to evaluate the hydrocarbon vapor removal efficiency of the subsurface venting system are described in this section. The sampling and measurement procedures were divided into two categories: on-site sampling and analysis and off-site analysis.

The types of sampling and analyses performed on site included:

- o sampling and analysis of hydrocarbon vapors from vapor probes and vapor recovery wells;
- o measurement of air inlet and vapor recovery well flow rates;
- o measurement of soil temperature at three depths;
- o analysis of QC standards;
- o measurement of product lens thickness and depth to ground water; and
- o periodic collection of soil core samples for detailed characterization.

Types of analyses conducted off site included:

- o analysis of soil core samples for hydrocarbon product adsorbed to soil particles;
- o analysis of soil core samples for interstitial hydrocarbon vapors in the soil column pore space;
- o physical characterization of the soil core samples (e.g., particle size, permeability, particle density, bulk density, porosity, moisture, pH, and conductivity); and
- o analysis of hydrocarbon product samples for volatile hydrocarbons (headspace).

Prior to start-up of the ventilation system, the hydrocarbon vapor levels in the soil were measured at each vapor probe in each test cell. After start-up of the venting system, only one test cell was operated at a time (see Table 3-2). During each experiment, all 16 vapor probes in the cell under test were sampled the first day after venting was begun and every other day thereafter. Each day one probe was chosen randomly to be resampled. The sampling schedule for each group of vapor probes was as follows:

Probe Number	Air Inlet Well Spacing	Sampling Frequency
1,2,3,4,5,6,7,8	20 ft	Every other day
9 (Vapor Recovery Well)	N/A	Daily
10,11,12,13,14,15,16,17	40 ft	Every other day

Air flow rate measurements were made at each air inlet well and vapor recovery well on a daily basis. Soil temperature at all depths, ambient temperature, barometric pressure, lens thickness, and depth to groundwater measurements were made daily.

Some measurements made on site were obtained on a periodic basis. Static pressure measurements from each vapor sampling probe were obtained at least once during each venting experiment. During the latter part of the A-cell high flow venting experiment (Experiment 3), static pressure measurements were made daily in the vapor probes in Cell A. These measurements were made with the air inlet wells capped. In addition, soil hydrocarbon vapor measurements were obtained periodically at the control vapor probes during each venting experiment.

Soil core samples from each test cell were collected before and after start-up each venting study experiment. Split spoon samples were collected at two depths ranging from 19.5 ft to 22 ft at 18-in. depth intervals. Nine core samples were collected during the venting study. Selected samples were analyzed for interstitial pore vapor concentrations and adsorbed hydrocarbon product. Eight core samples were selected for physical characterization for all parameters except permeability (e.g., particle size, permeability, particle density, bulk density, porosity, moisture, pH, and conductivity). Four of the eight core samples were analyzed for permeability (two in each cell).

4.0 DATA PRESENTATION

The results of the subsurface hydrocarbon venting study are presented in this section.

4.1 Initial Baseline Characterization

Prior to start-up of the subsurface hydrocarbon venting system, an initial characterization of the baseline concentration of hydrocarbon vapors was performed. The results of the initial baseline survey are presented in Table 4-1. As expected, the baseline vapor profiles indicate a very distinct vertical distribution of hydrocarbons in each cell. Typically, the vapors were more concentrated at depths approaching the capillary zone. The vertical distribution of the soil hydrocarbon vapors ranged over three orders of magnitude in concentration from depths of 1 to 5 ft above the capillary zone. The soil hydrocarbon vapors were the most concentrated in the measurement zone 1 ft above the capillary zone (21 ft BLS).

Baseline vapor concentrations measured at 16 ft BLS ranged from 58 to 113 ppm-V. The vapor concentrations between the depth of 20 and 20.5 ft BLS ranged from 3,450 to 28,000 ppm-V. The vapor concentrations ranged from 11,000 to 51,500 ppm-V at depths ranging from 21 to 21.5 ft BLS.

In general, the baseline vapor concentrations were more uniformly distributed in Cell A than Cell B. The baseline vapor concentrations in Test Cell B were more highly concentrated in the 20-ft air inlet spacing than the 40-ft air inlet spacing. The difference in the lateral distribution of vapors in Cell B may have been the result of:

- o irregularities in the soil formation, and/or
- o positioning of the B-cell on the boundary edge of the free product plume.

TABLE 4-1. INITIAL BASELINE HYDROCARBON VAPOR CONCENTRATION PROFILE (BEFORE
START-UP OF VENTING SYSTEM)

Probe #	Cell A			Cell B			M-Cell ^a		
	Hydrocarbon Conc. (ppm-V)	Hydrocarbon Conc. (ppm-C)	Probe Depth (ft)	Hydrocarbon Conc. (ppm-V)	Hydrocarbon Conc. (ppm-C)	Probe Depth (ft)	Hydrocarbon Conc. (ppm-V)	Hydrocarbon Conc. (ppm-C)	Probe Depth (ft)
1	25,100	142,000	20	19,300	109,000	20.5	55	308	14
2	18,300	103,000	20	12,600	71,200	20.5	21,200	118,000	20
3	58	327	16	113	638	16.0	38,700	216,000	21
4	13,800	78,000	20	11,900	67,200	20.5			
5	19,600	111,000	21	15,100	85,300	21.5			
6	18,200	103,000	20	14,700	83,100	20.5			
7	24,300	137,000	20	17,000	96,100	20.5			
8	25,200	142,000	20	9,260	52,300	20.5			
9 VENT ^b	—	—	14-20	—	—	14-20.5			
10	28,000	158,000	20	3,450	19,500	20.5			
11	80	452	16	64	362	16.0			
12	19,200	108,480	20	5,580	31,500	20.5			
13	51,500	291,000	21	11,000	62,200	21.5			
14	23,300	132,000	20	4,890	27,600	20.5			
15	23,500	132,000	20	4,660	26,300	20.5			
16	20,200	114,000	20	6,850	38,700	20.5			
17	23,300	132,000	20	6,430	36,300	20.5			

^aControl probes located midway between A Cell and B Cell

^bVapor recovery well