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REMEDIATION OF A GASOLINE SPILL BY SOIL VAPOR EXTRACTION, LAWRENCE LIVERMORE NATIONAL LABORATORY, LIVERMORE, CA

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ABSTRACT

Lawrence Livermore National Laboratory (LLNL) is conducting a pilot study on a soil vapor extraction system. Approximately 20,000 gallons of gasoline was lost from an underground storage tank prior to 1979. The soil vapor extraction system has operated for 179 days since it was installed in August 1988, removing 2,200 gallons of gasoline (±25%). Three vadose zone monitoring devices were completed in March 1991. These were designed to monitor multiple zones for pressure and vapor concentrations over time.

Soil sampling after venting indicates significantly reduced concentrations of aromatic hydrocarbons at shallow depths. The reduction may be attributed to soil vapor extraction and biological activity. Significant concentrations (up to 440 ppm) remain below a depth of 75 feet. Three factors account for the residual mass: (1) high soil moisture content, (2) fluctuations in capillary fringe height, and (3) volatilization of floating free product.

Residual soil concentrations of the heavier fuel components are up to 1,000 ppm below a depth of 20 ft, increasing to 2,000 ppm below 75 ft. The high moisture content and fluctuations of the capillary fringe may account for this residual. Several impermeable units, containing no residual gasoline components, may have prevented downward migration of gasoline into coarse-grained units.

Initial testing of the new vadose zone monitoring devices has shown no correlation between residual soil and soil vapor concentrations. Concentrations of aromatic hydrocarbons in soil vapor increase with depth, suggesting that volatilization from floating free product may be the primary source of vapor phase hydrocarbons. This lack of correlation between residual soil hydrocarbon concentrations and soil vapor hydrocarbon concentrations suggests that the use of vapor monitoring to assess the efficiency of soil venting may be limited by the presence of floating free product. Tests continue to evaluate this hypothesis.

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INTRODUCTION

Lawrence Livermore National Laboratory (LLNL) is located approximately 40 miles east of San Francisco in the southeastern portion of the Livermore Valley near Livermore, California. In 1979, an underground gasoline tank was found to be leaking. The spill occurred near Building 403 in the southeast corner of LLNL (Fig. 1). The initial investigation confirmed the presence of gasoline contamination in both the soil and ground water. The water table is at a depth of approximately 100 feet. A pilot study on the use of soil vapor extraction in heterogeneous deposits was begun in August 1988. Fieldwork to assess the efficacy of the vapor extraction, including soil sampling and installation of three vadose zone monitoring devices, began in October 1990.

SITE HISTORY

The Building 403 Area was first used as an automotive garage and fuel-dispensing facility by the Livermore Naval Air Station during World War II. LLNL, upon its formation in 1951, continued this use until November 1986. Approximately 9,000 gallons of gasoline leaked into the subsurface in March 1979 (Dresen *et al.*, 1986). The leak is thought to have occurred over a 4-day period in either the southernmost of four underground storage tanks or the distribution lines. After the discovery of this spill, a detailed analysis of inventory records prior to March 1979 revealed that the total amount may have been as much as 17,500 gallons (Nichols *et al.*, 1988).

The four underground storage tanks were removed from service in 1980. The integrity of the southernmost tank (the suspect tank) was tested in April 1980 by filling it half full of water and monitoring the water level for 6 days. No leak was found during this test. It was hypothesized that material in the bottom of the tank shifted, thus blocking the leak point (O. H. Materials, 1985). The underground storage tanks were filled with sand emplaced with a water jet in 1980. The distribution lines were excavated and pressure tested in January 1991. At that time, the lines still held 12 gallons of gasoline. The lines held pressure throughout the 3 days of testing (Gerald Duarte, personal communication, 1990).

SITE CHARACTERIZATION

Initial characterization occurred between February and May of 1984 with the installation of 10 soil borings by LLNL (Fig. 2). The borings were used to better characterize the subsurface geology and the contaminant distribution. Gasoline and its components were found between 20 and 122 feet below the ground surface (O. H. Materials, 1985).

In order to quantify the vertical and horizontal distribution of the subsurface contaminants and test the hydraulic properties of the underlying sediments, five soil borings and five monitor wells were

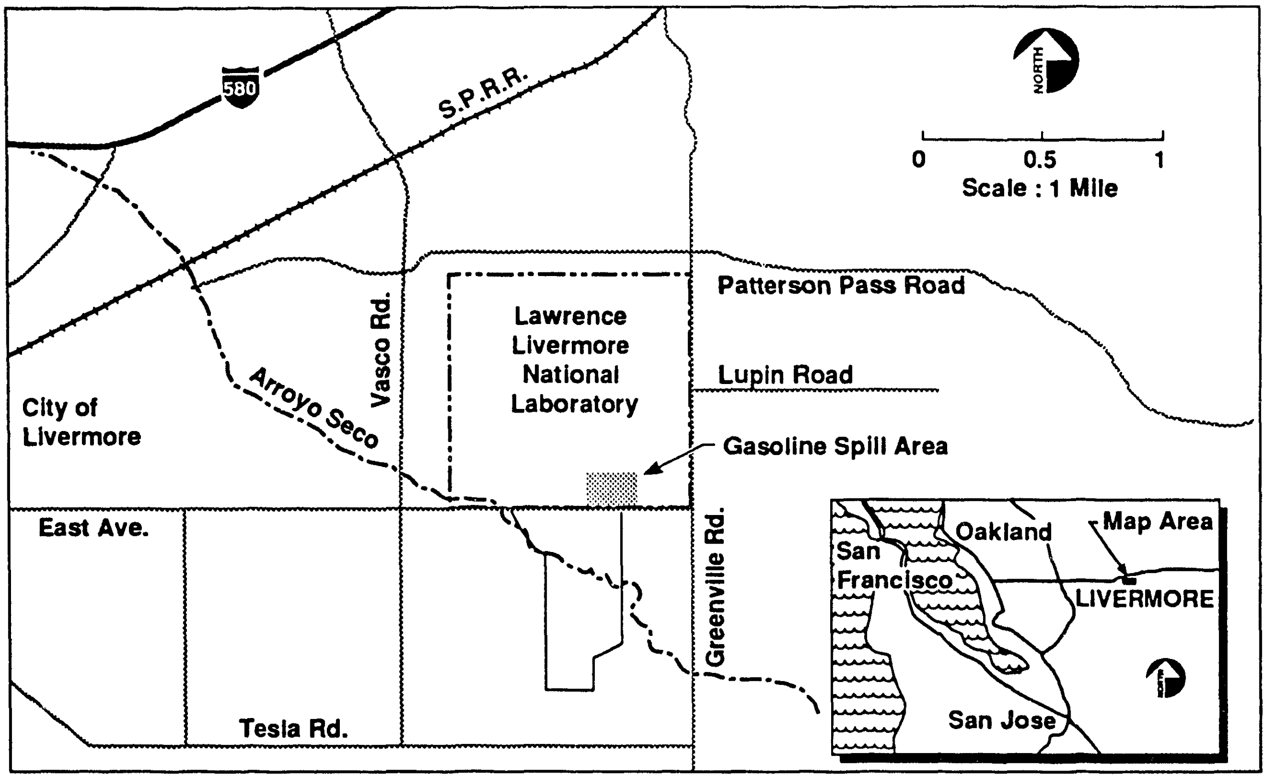

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Figure 1. Site location map (Dresen *et al.* 1986).

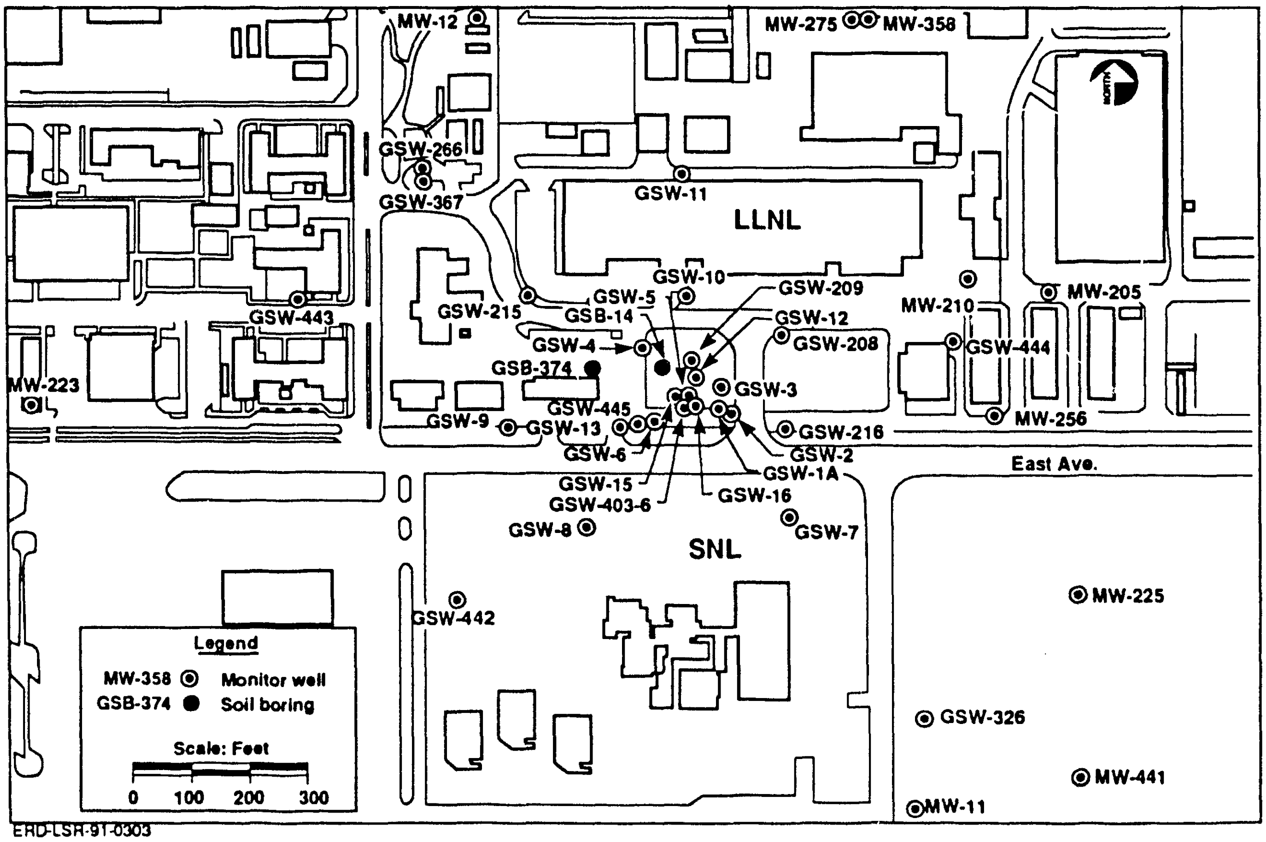

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Figure 2. Well locations, Gasoline Spill Area, as of August 1988. For more detail of study area, see Figure 4 (Nichols *et al.*, 1988).

installed in 1985. The subsurface geology consisted primarily of silts and clays with thin layers of sand above a depth of 75 feet. The sediment 75 to 107 feet below grade consisted of sands and gravels with interbedded clays. Free product was found to be depressing the water table near the center of the plume (O. H. Materials, 1985).

In 1987, 10 additional wells and 2 soil borings were installed. The results of these studies indicated that hydrocarbon distribution in the vadose zone is elliptical in shape with a 30-foot principal axis to the southwest/ northeast. The gasoline appears to have moved vertically. Free product is trapped below clay layers beneath the water table, possibly because the water table has risen approximately 30 feet since the spill occurred (Nichols *et al.*, 1988).

SOIL VAPOR EXTRACTION

Residual soil contamination by gasoline and solvents in the vadose zone has been found to be difficult to mitigate. Excavation is not feasible for areas with a deep water table and deep impacted soil. Soil vapor extraction can be an effective method for treating residual contamination of permeable materials when the compounds are volatile. The efficacy of soil venting is controlled through three basic processes: (1) vapor flowrate; (2) composition of the contaminant; and (3) relation between vapor flowpaths and contaminant distribution. Vapor flowrate is greatest in areas of high permeability. Areas of low permeability will be limited by diffusion because very little or no flow will occur. Vapor flowrate and vapor flowpaths will vary in areas of large heterogeneities (Johnson *et al.*, 1990).

SOIL VAPOR EXTRACTION AT THE GASOLINE SPILL AREA

Vadose zone remediation using soil vapor extraction was initiated in August 1988. The vapor is extracted from a single extraction well, GSW-16, near the center of the spill. GSW-16 is screened in seven individual zones, five within the vadose zone and two in the saturated zone. Vapor extraction can be performed on individual zones or any combination of adjacent zones. Screen placement was made in areas of high concentrations, which were primarily in fine-grained sediment. The vapor is treated by thermal oxidation with the addition of propane as a secondary fuel.

The lower vadose screens of GSW-16 have become blocked. One hypothesis regarding this problem is that grout was pushed into the screens. In August 1989, the screens were scraped with a wire brush to mechanically remove the blockage. A small chunk of a hard, dirty white substance was removed. X-ray diffraction analysis indicated its composition to be primarily quartz and feldspar with a minor amount of calcite. The substance was probably pulled into the screen at the time the vacuum was applied. Calcite formation may be the result of chemical precipitation as water enters the borehole. Another hypothesis is that bacterial activity blocked the pore area surrounding the screened zone. No conclusions have been reached at this time. Attempts to remove the blockages by cyclic pressurizing of the screened zones have been unsuccessful.

The soil vapor extraction system operated for 179 days during a 2.3-year period. An estimated 530 gallons of benzene, toluene, ethylbenzene, and xylenes (BTEX) were removed during this time. This provides an average mass extraction rate of 3.2 gpd. In order to calculate the amount of gasoline removed, we made several assumptions. First was that the amount of BTEX in the free product was representative of fresh gasoline. Second was that all components of gasoline are being extracted in proportion with their content in gasoline. Sampling of the free product indicated BTEX was 27.5% of the total composition; thus, it is estimated that 2,200 (± 25%) gallons of gasoline has been been removed from the subsurface. This probably represents a high end estimate of the total gasoline removed because of the higher vapor pressure of BTEX relative to some of the other components of gasoline. Figure 3 indicates that 50% of the BTEX removed to date was removed in the first 38 days of operation.

PRE-SOIL VENTING SOIL CHARACTERIZATION

The initial characterization of the site was based on the soil borings and monitor wells which were installed between 1984 and 1987 (Fig. 4). Two cross sections, to the NW-SE and SW-NE, are provided to show the initial distribution of BTEX (Fig. 5a and b). The plume is narrow and bell shaped, and its dimensions are 42 feet to the southwest and 23 feet to the southeast using the 1-ppm contour.

METHODOLOGY

Three vadose zone monitoring devices (SVB-GP-008A, SVB-GP-013, and SVB-GP-014) were installed in order to investigate the effects of soil venting on heterogeneous soils. The devices were used to monitor isolated zones throughout the soil profile. Within each monitoring device, at least 5 feet of grout seal was used to isolate the zones of interest. The sandpack consisted of Lonestar 0/30 sand. The sampling port was connected to the surface with 3/16-inch Teflon tubing. Each device is designed to sample the isolated zone for both pressure response and vapor contaminant concentrations.

Extensive sampling was performed during the installation of these monitoring devices to characterize the current soil contaminant distribution and physical properties of the soil. A solid core barrel was used to obtain a 5.75-inch core. The core was extruded from the barrel with a hydraulic press. Samples aliquots were taken from the core by driving a 1.5-inch or 2.5-inch brass liner into the core. The first samples taken were immediately sent for chemical analysis to reduce the amount of time they were exposed to the atmosphere. Soil chemistry samples were sent to certified analytical labs for analysis by EPA method 8020 or modified EPA method 8015. Once soil chemistry samples were

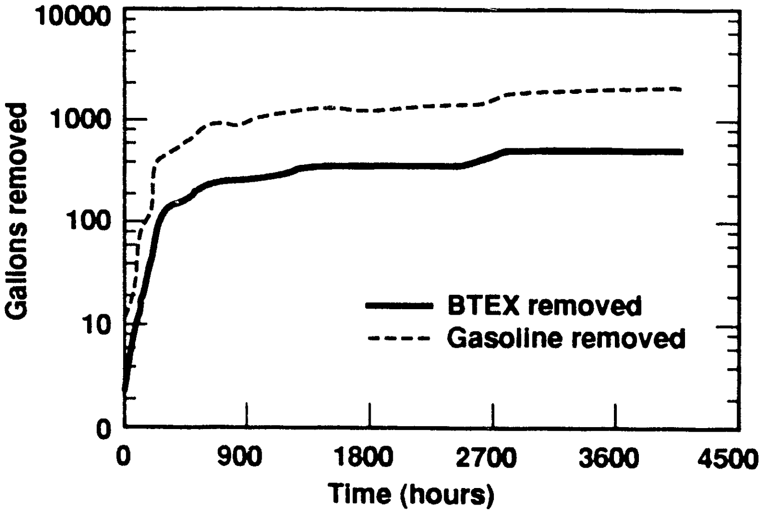

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Figure 3. Estimate of BTEX and gasoline removed with time.

taken, additional samples were taken for bacteriology, permeability, soil-water partitioning coefficient, mineralogy, grain size, carbon exchange capacity, and metals content analyses. After sampling, the lithology was described in detail. All equipment that came into contact with the cores was steam cleaned between coring runs to prevent cross contamination.

Numerous factors were considered in selecting the placement of the monitoring points. The first factor was the depth of the screens in GSW-16. Monitoring points were placed in the same zone or at an equivalent depth to those being used for venting. Lithology was considered because areas of both high and low permeability were observed. The distribution of BTEX and total petroleum hydrocarbons (TPH) as gasoline on soil were also considered. Monitoring points were needed in areas that were apparently being effectively remediated and in those in which high levels of contaminants remained. These monitoring points were placed along a concentration gradient so that we could investigate diffusion.

Vacuum response was monitored at several different monitor wells and the extraction well. SVB-GP-008A, SVB-GP-013, and SVB-GP-014 provided vertical profiles. GSW-2 through GSW-5 and GSW-403-6 provided coverage of the water table. SVB-GP-001, SVB-GP-009, and SVB-GP-012 (completed at depths of 20 feet, 20 feet, and 50 feet, respectively) were also monitored. GSW-15, completed at depths similar to GSW-16, was packed off (isolated) to monitor the screen which was the equivalent of extracting the screen from GSW-16. These 28 monitoring points provided adequate spatial coverage for the zone tests.

Monitoring points that were expected to have large responses were equipped with pressure transducers with a vacuum range of 0 to 10 inches of water. Pressure transducers with a range of 0 to 5 inches of water

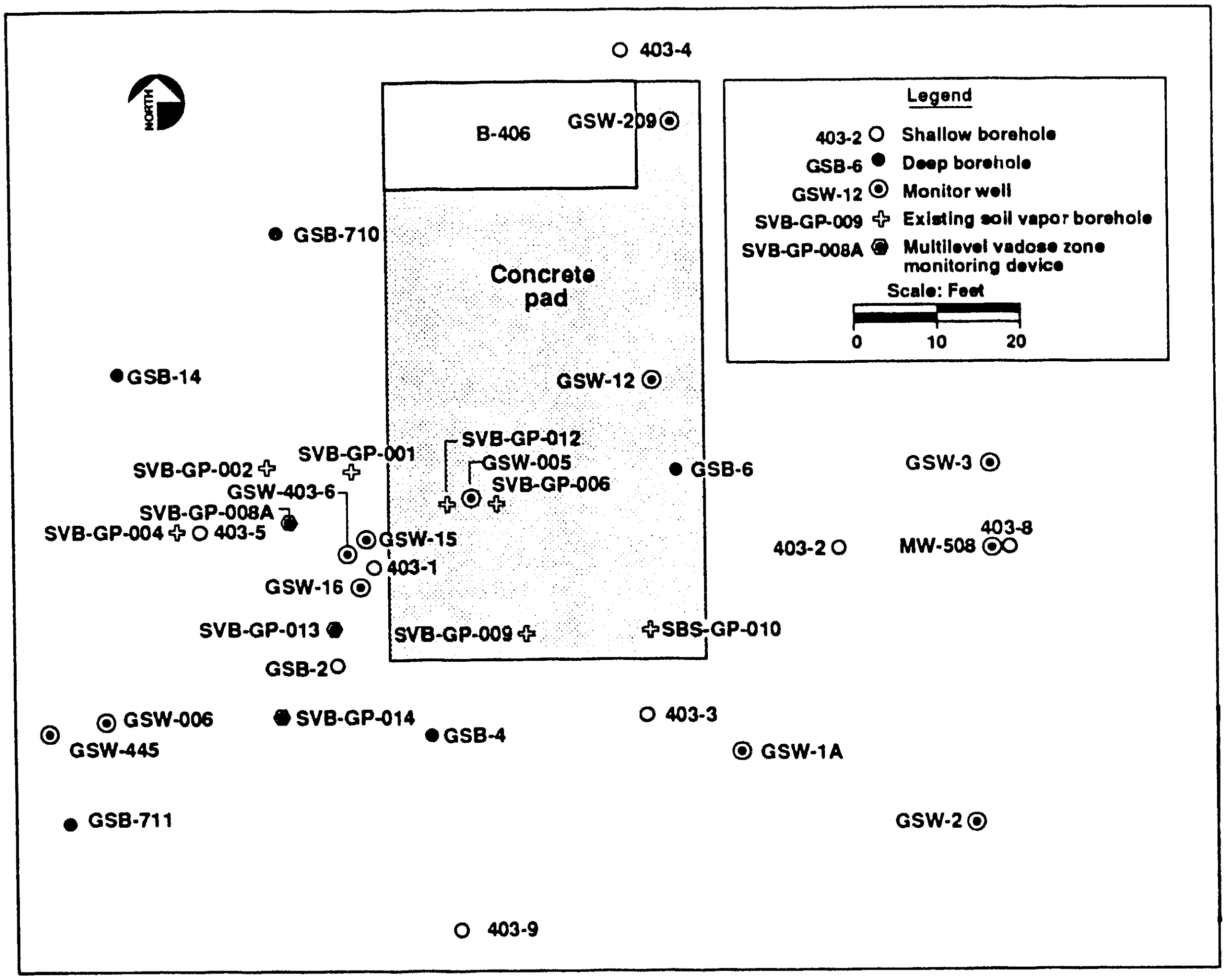

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Figure 4. Wells and boreholes in the Gasoline Spill Area, July 1991.

were used when a moderate response was expected. All other points, except GSW-16 (0 to 30 inches of mercury), used transducers with a range of 0 to 2 inches of water.

Vapor sampling was done with a metal bellows pump capable of applying a vacuum of 30 inches of mercury. A 0.5-micron filter was installed before the pump to protect it from inspiration of fine-grained sediments. The pump was attached to the monitoring tube by a piece of tygon tubing, which was pushed onto barbed fittings. To purge the line and the sandpack, we removed 18 liters of vapor from the monitoring points before sampling. An air-tight syringe was used to obtain the vapor samples. The sample was drawn while pumping by inserting the needle through the tygon tubing, which was changed between samplings.

Vapor samples were analyzed on a Photovac model 70S portable gas chromatograph. Calibrations were run at the beginning and end of each day. Additional calibrations were done as needed. The standard gas used was a National Bureau of Standards approved vapor cannister containing benzene, toluene, ethylbenzene, P-xylene,M-xylene, and O-xylene at concentrations of 50 ppm each.

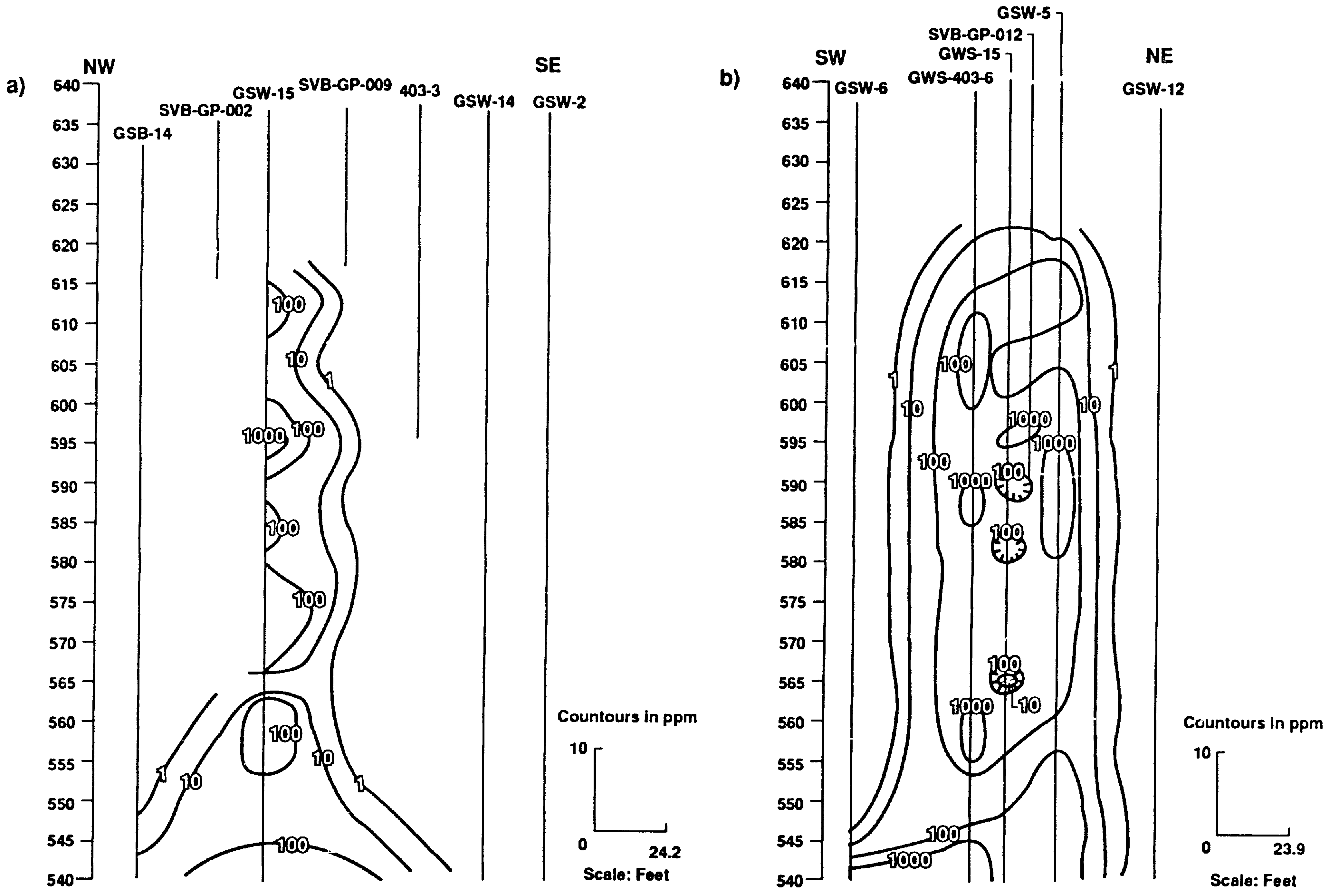

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Figure 5. BTEX concentrations in soil prior to vapor extraction.

A series of calibration analyses were performed prior to the initiation of the vapor extraction tests to compare the results from Photovac analysis with those from a certified analytical laboratory and an on-site (LLNL) laboratory. Two samples from each monitor point were drawn for this test. The first was taken into a gas sampling bag constructed of tedlar, an inert polymer. A syringe sample was taken from the bag for immediate analysis on the Photovac. The tedlar bag was then taken to the LLNL on-site laboratory to be analyzed. The LLNL on-site laboratory analyzed the samples within 4 hours of receiving them. The samples were kept at room temperature until they were analyzed. The second sample drawn was taken immediately after the tedlar bag sample. This sample was placed in a stainless steel cannister and sent to a certified analytical laboratory. Results indicated that the Photovac and the analytical laboratory agreed within an order of magnitude. This level of accuracy is considered reasonable due to the large amount of variability seen in vapor samples.

POST-SOIL VENTING SOIL CHARACTERIZATION

Soil sampling during installation of the three vadose zone monitor devices permitted determination of the effects of the period of extraction on residual soil concentration distribution. A generalized lithologic cross section was constructed to observe the relation between lithology and residual soil contamination (Fig. 6). A cross section, on a north-south line between the three vadose zone monitoring devices, was completed to show the current distribution (Fig. 7). Both BTEX and TPH were contoured to show the differing effects of soil venting on the less volatile compounds.

The BTEX profile shows that a large portion of the soil column has had a majority of the BTEX removed. The remaining BTEX lies mostly at depth near the water table. The TPH still has significant concentrations remaining below a depth of 20 feet. The TPH again shows a large increase near the water table.

DISCUSSION OF POST-SOIL VENTING CHARACTERIZATION

Cross sections drawn before and after soil venting reveal that a significant portion of the vadose zone has had the BTEX removed from the soil. Above a depth of 80 feet, the remaining contaminants are more concentrated in the finer grain sediments. The residual concentrations at depth may be due to several factors. The first factor is the problem with blockages in the lower vadose screens in GSW-16. If multiple zones are being used for extraction, the flow may be preferentially coming from zones at a shallower depth. Another factor is the reduced presence of bacteria, which are found in greater numbers in fine-grained sediments. These bacteria decrease in number between 80 feet and the water table due to the presence of coarser-grained sediments at depth (Paula Krauter, personal communication, 1991).

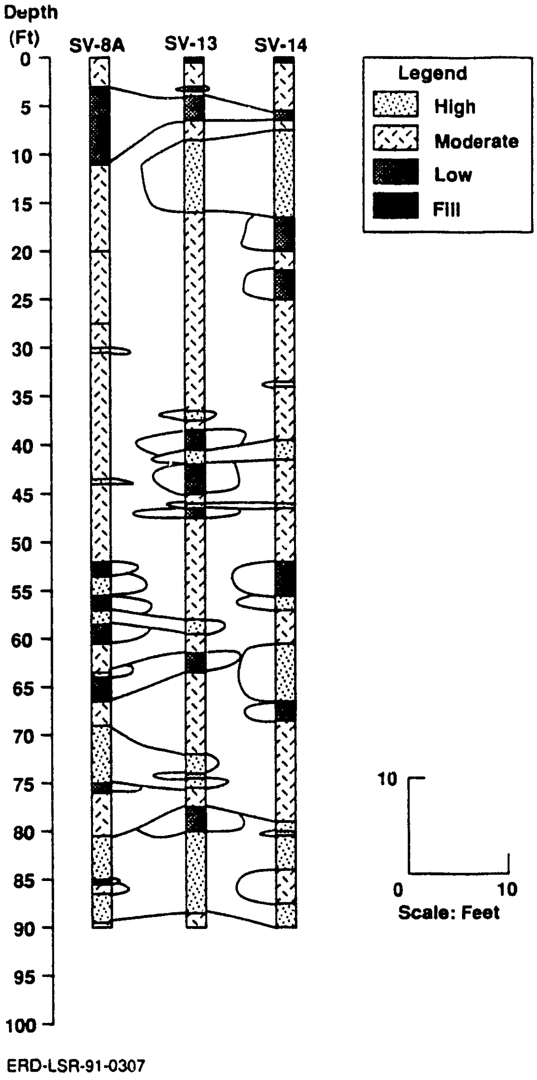

Figure 6. Generalized lithology of Gas Spill Area.

Proximity to the water table may also be a factor. Because there is free product present, volatilization occurs at the surface layer, causing much higher vapor concentrations. This vapor diffuses upwards along the concentration gradient, possibly recondensing on the soil. Soil moisture is another factor that could account for the increased concentrations. In areas of high soil moisture content, effective porosity is reduced, thus preventing the flow of air from reaching the contaminants and transporting them to the extraction well.

At least two processes appear to be reducing levels of BTEX in the vadose zone, soil venting and biological activity. Soil venting activity over the past 2.3 years has definitely removed some of the gasoline. The aromatic compounds BTEX are the most easily removed as they are the most volatile. Biological activity, enhanced by the increased oxygen levels from soil venting, may also be removing BTEX. Oxygen sampling, completed after 5 months of quiescence at the Gasoline Spill Area, revealed that

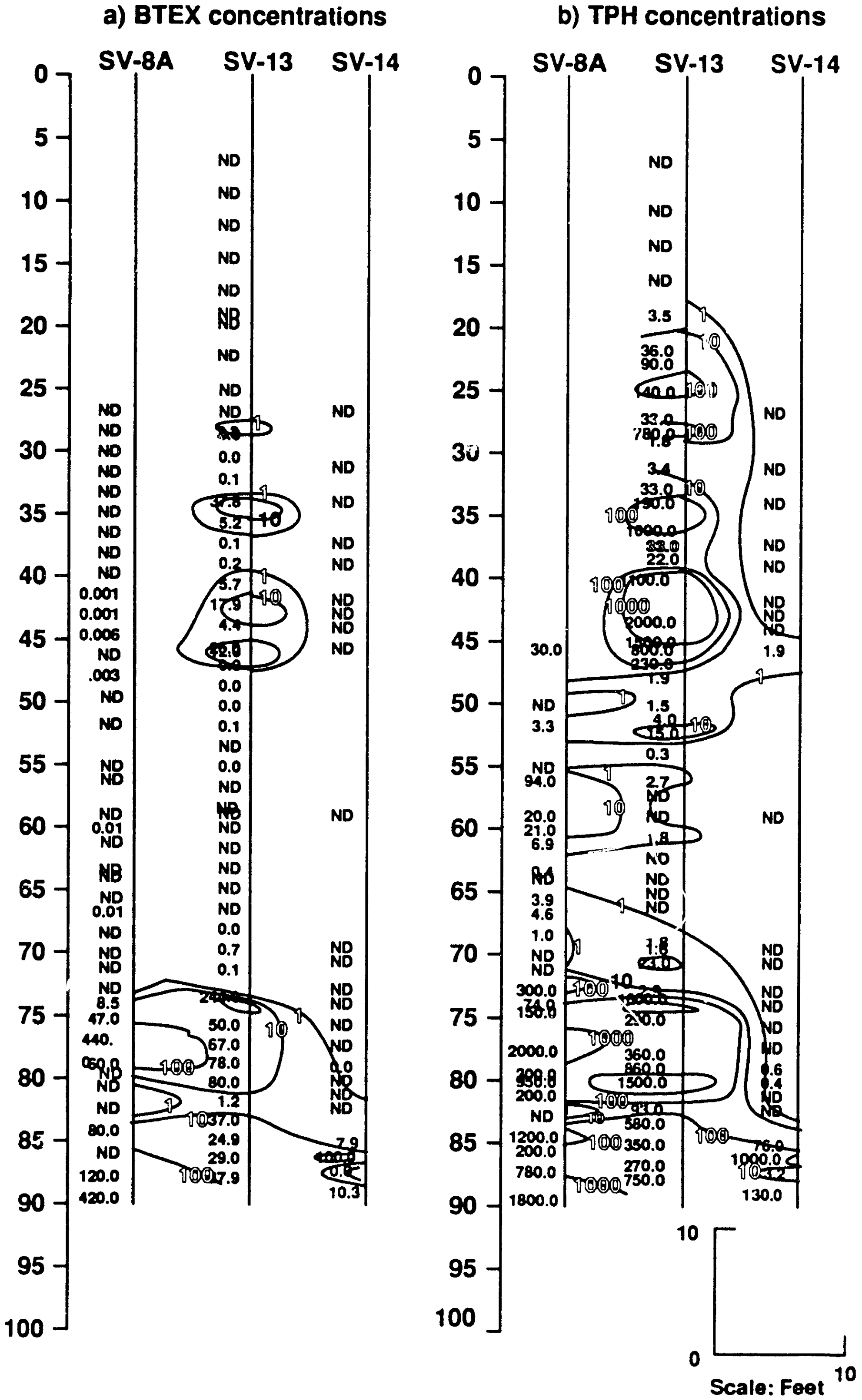

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Figure 7. Concentration in soil after 2.3 years of soil vapor extraction.

oxygen levels at 80 feet below grade were 0% to 0.5%. The reduced oxygen levels may be due to bacterial consumption of oxygen in the biodegradation of the residual gasoline. After 2 weeks of vapor extraction, oxygen levels were 11% to 14% (David Camp, personal communication, 1991). This increase in oxygen will help to stimulate biological activity. Further investigations into this are currently under way.

VAPOR CONTAMINANT DISTRIBUTION

On May 1, 1991, prior to beginning the vapor extraction tests, background vapor sampling was completed for SV-13 and SV-14 (Fig. 8a). The BTEX distribution was narrow and found over the entire soil column below 20 feet. There is only a partial relationship between the vapor concentrations and the residual soil contaminant distribution (compare Figs 7 and 8). Areas of high vapor concentrations (>100 ppm) are found in association with areas of high residual soil contamination. Moderate vapor concentrations (between 10 ppm and 100 ppm) and low vapor concentrations (between 1 ppm and 10 ppm) are found in areas where residual soil contamination is below detection limits.

After the vapor extraction tests were completed, another series of vapor samples was taken to observe any changes (Fig. 8b). After 6 days of operation during a 1-month period, the vapor concentration distribution and the residual soil contaminant distribution showed a strong relationship. The anomalous vapor concentrations which were previously found have been removed.

After 5 days, a follow-up series of vapor samples was taken to observe the recovery (Fig. 8c). The distribution found represented a midpoint between the prior two distributions. The high vapor concentrations are still in the areas of high residual soil contamination. The moderate and low vapor concentrations are moving towards the distribution seen prior to the vapor extraction tests. During periods of quiescence, gasoline vapors diffuse gradually through the porous soil zones.

VAPOR EXTRACTION TESTS

A series of one-day vapor extraction tests was performed to evaluate the effects of each extraction well zone on the surrounding sediment (Table 1). Table 1 shows the completion depths of GSW-16, the vacuums applied, flow rate, BTEX removal concentrations and rates, gasoline removed per test, and the removal rate. The lower four vadose zone screens were each used for one day of extraction. The first zone of the extraction well was not tested because it has very low levels of contaminants remaining. Ideally, each zone was to be pumped at the maximum possible level. The limiting factor on the system is the thermal oxidizer. The flame will blow out if the flow is too great upon entry; thus, shutting down the system. Therefore, the flow at the wellhead had to be reduced, so it was not possible to extract at the maximum possible flow rate. The data presented are the response after 24 hours of

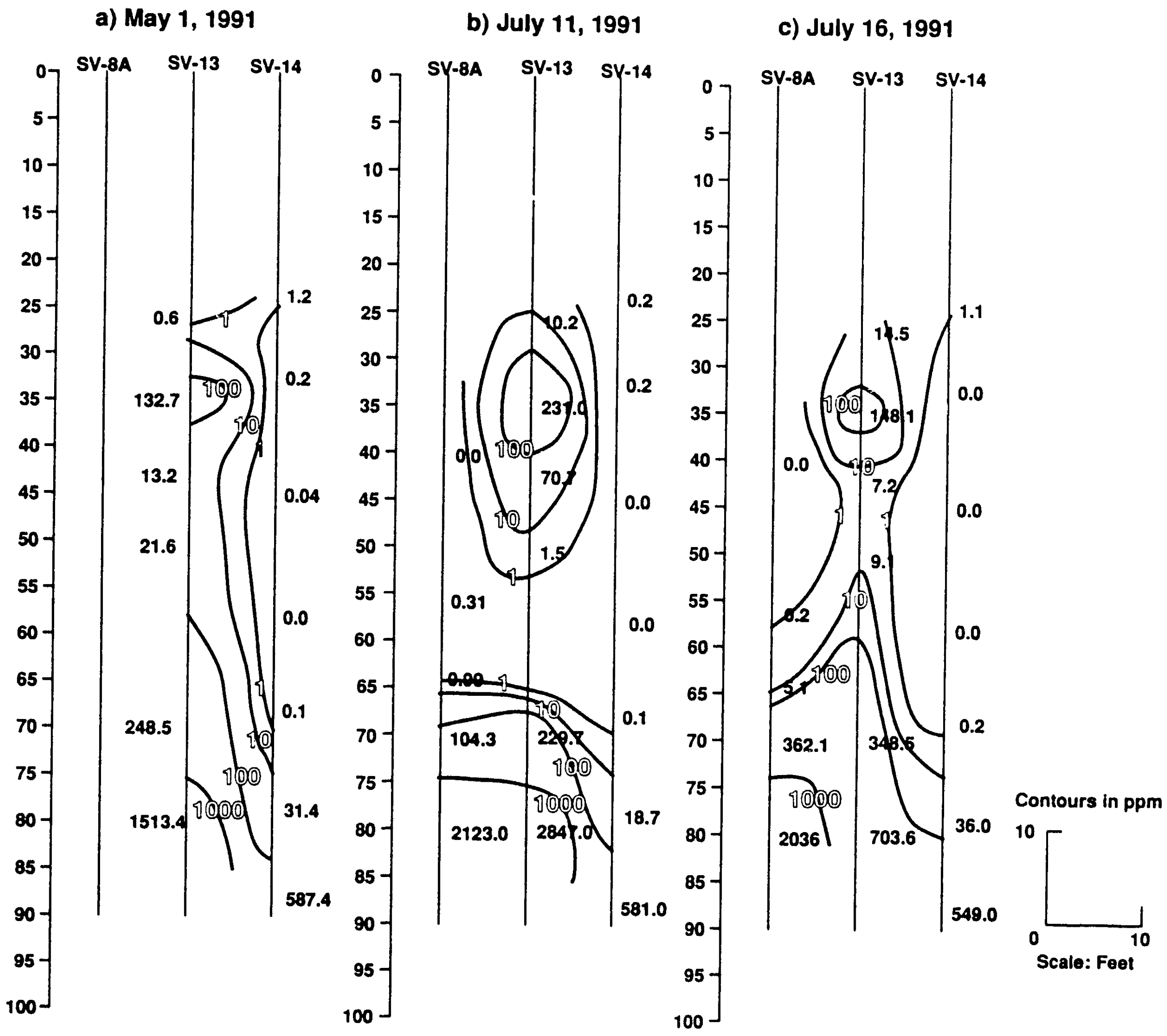

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Figure 8. BTEX concentration in vapor.

Table 1. Response of GSW-16 extraction zones to vapor extraction tests.

Extraction zone	Depth (ft)	Vacuum (in. Hg)	Flow (scfm)	Average vapor BTEX concentration (ppm)	BTEX removed (gal)	Gasoline removed (gal)	Removal rate (gpd)
2	38-43	5.60	21.20	58.10	0.23	0.84	0.78
3	50-55	5.00	26.10	155.60	0.62	2.24	2.15
4	61-66	8.00	26.80	72.90	0.22	0.81	0.85
5	78-83	18.60	16.80	377.90	0.91	3.32	3.39

pumping. The response had reached near steady-state conditions at this time.

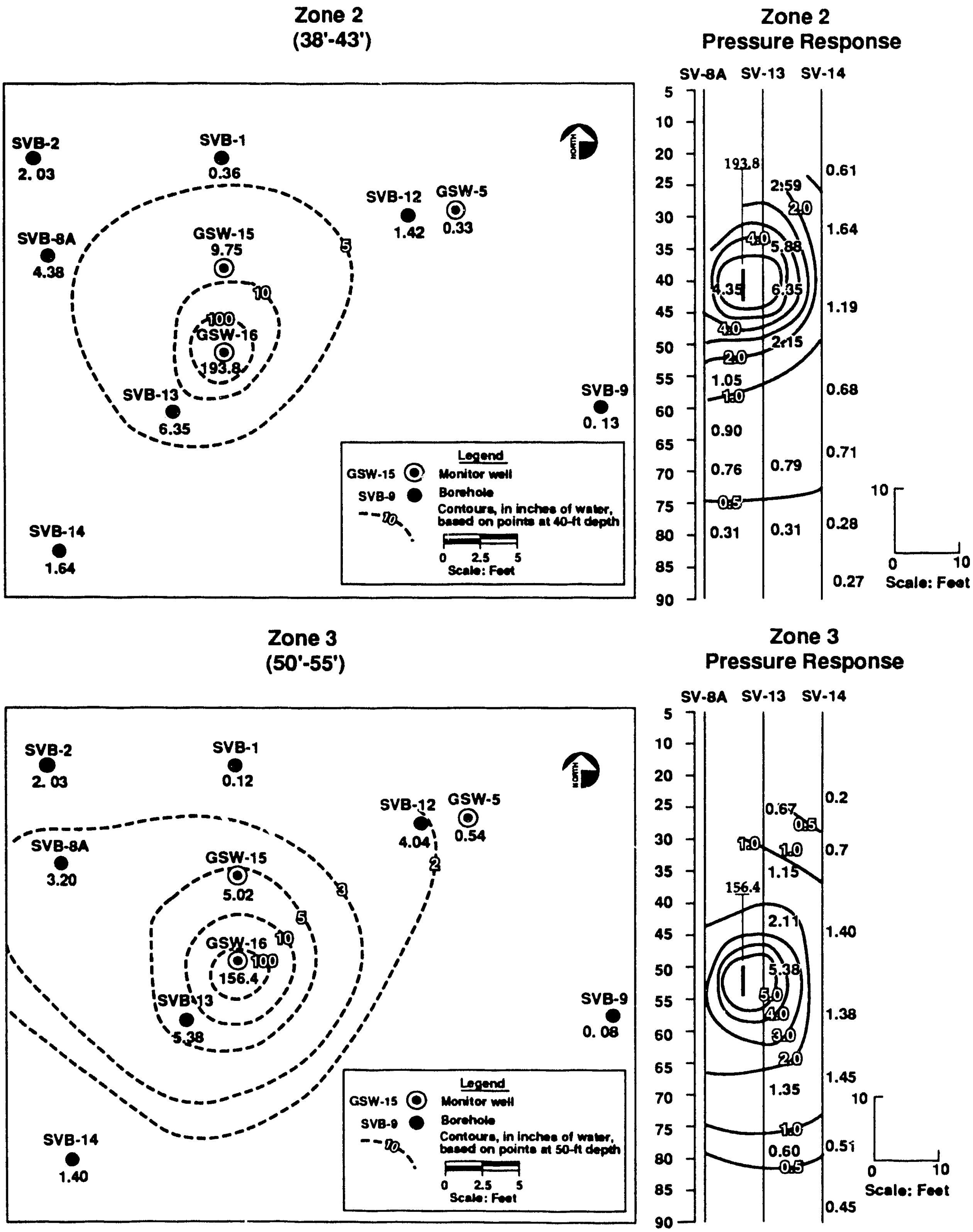
DISCUSSION OF VAPOR EXTRACTION TEST

The vapor extraction tests indicated the similarity between the extraction zones in that responses were essentially spherical in shape (Fig. 9) suggesting vertical communication. A more cylindrical response was expected due to the sedimentary layering in the vicinity. The only zone that showed a more restricted amount of vertical communication was zone 5. The flow from zone 5 was also lower, with a much higher vacuum, than that from the upper zones (Table 1). The use of a 3-D flow model might be useful in understanding the pressure distribution and flow. The overall vertical response was greater than expected because the extraction well is screened primarily in low to moderate permeability sediments. The flow into the extraction well is thought to be primarily through the surrounding higher permeability zones. The flow must then be constricted through the low permeability sediments to enter the extraction well. This would account for the large pressure drop near the extraction well. The north half of the site generally showed greater response than the south. The only evidence of a zone unaffected by soil ventings (i.e., little pressure response) was GSW-15, zone 4, during the GSW-16, zone 4, test.

The vapor concentrations in the extracted soil gas were greatest in the fifth zone. The third extraction zone had higher concentrations than the fourth extraction zone. The gasoline removal rate was correlated with the zones of highest concentrations.

CONCLUSIONS

The soil vapor extraction system at ILNL has been effective in removing BTEX from the soil. The less volatile petroleum compounds are remediated to a lesser degree and are still present in areas where BTEX has been



Zone 2 (38'-43')

Zone 2 Pressure Response

Zone 3 (50'-55')

Zone 3 Pressure Response

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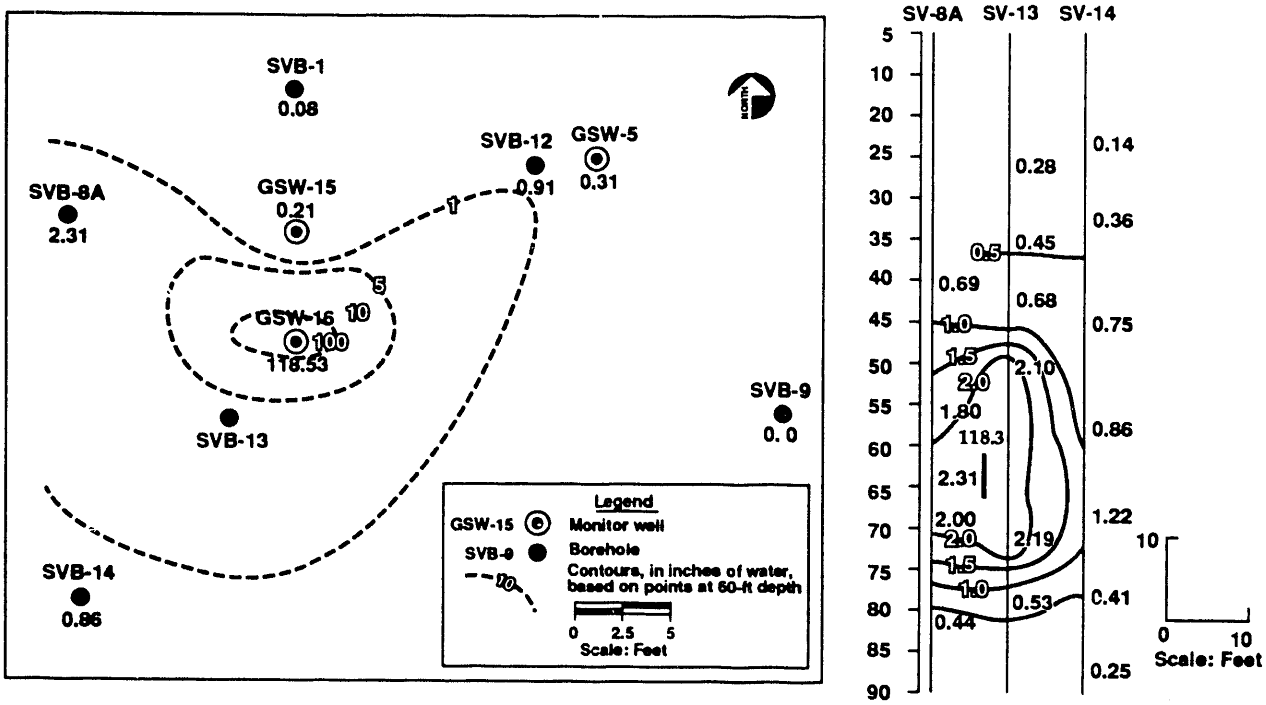
Figure 9. Zone 2 and Zone 3 vapor extraction tests.

Zone 4
(61'-66')

Zone 4
Pressure Response



Zone 5
(78'-83')

Zone 5
Pressure Response

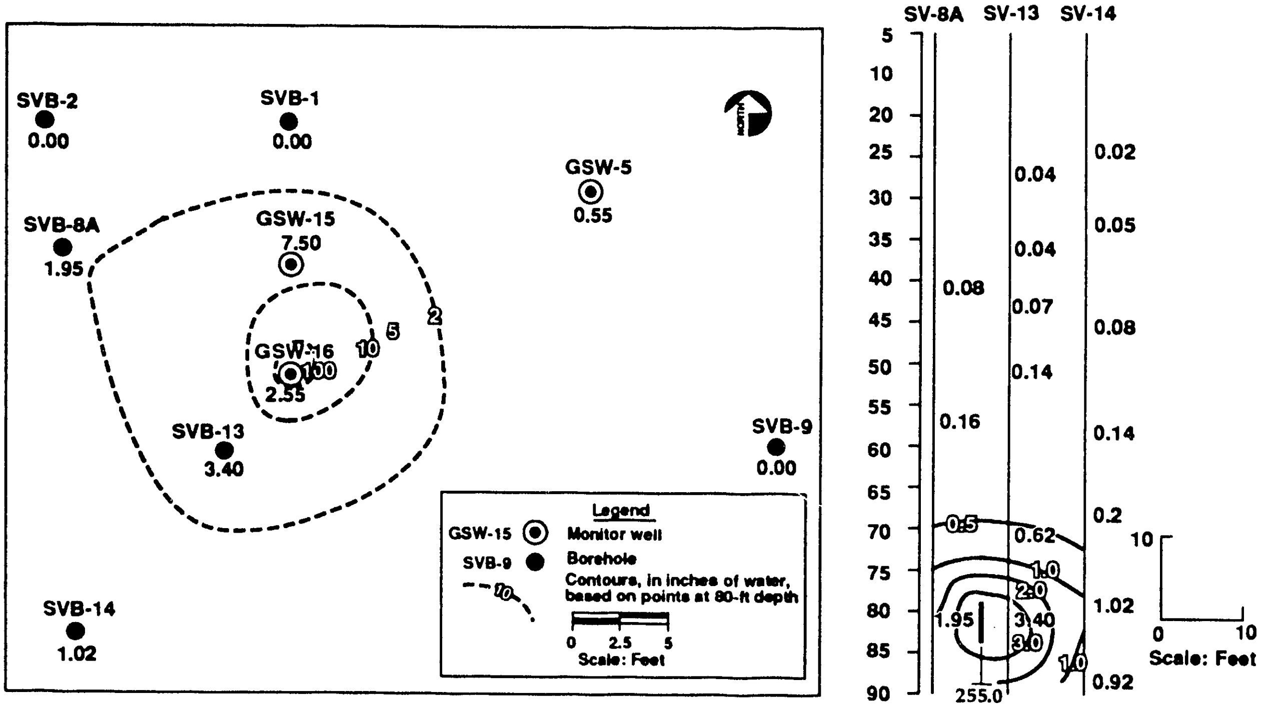


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Figure 9. (Continued)

removed. The residual contamination is associated with the fine-grained sediments, which are more difficult to clean up. The greatest removal rates occurred at the beginning of the extraction process. The decreasing removal rate indicates that cleanup of the remaining residual contamination may take a long time. The soil vapor extraction stimulates biologic activity by increasing oxygen levels. The time required for final cleanup will likely be shortened by aiding the natural biodegradation of the petroleum hydrocarbons.

Soil vapor extraction is more effective in areas of high concentrations of volatile compounds. These areas provide the highest mass extraction rate even though the flow may be less. Areas with greater flow may act as a short circuit by providing preferential flowpaths and bypassing residual contamination held in the fine-grained, low permeability sediments.

The monitoring of vapor concentrations provided only a partially accurate representation of residual soil contamination. Areas of high vapor concentrations (>100 ppm) correlate well with areas that are high in residual soil contamination. The presence of low to moderate levels of vapor contaminants because of vapor diffusion did not correlate well with the amount of residual soil contamination because of vapor transport.

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REFERENCES

Dresen, M. D., Hoffman, F., and Lovejoy, S., Jr. (1986), *Subsurface Distribution of Hydrocarbons in the Building 403 Area at LLNL*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCID-20787).

Johnson, P. C., Kemblowski, M. W., and Colthart, J. D. (1990), "Quantitative Analysis for the Cleanup of Hydrocarbon Contaminated Soils by *In-Situ* Soil Venting," *Groundwater*, vol. 28, no. 3, pp. 413-429.

Nichols, E. M., Dresen, M. D., and Field, J. E. (1988), *Proposal for Pilot Study at LLNL Building 403 Gasoline Station Area*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCAR-10248).

O. H. Materials (1985), *Site Investigation, Hydrocarbon Leak Near Building 403*, Lawrence Livermore National Laboratory Livermore, Calif. (UCRL-15857).

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