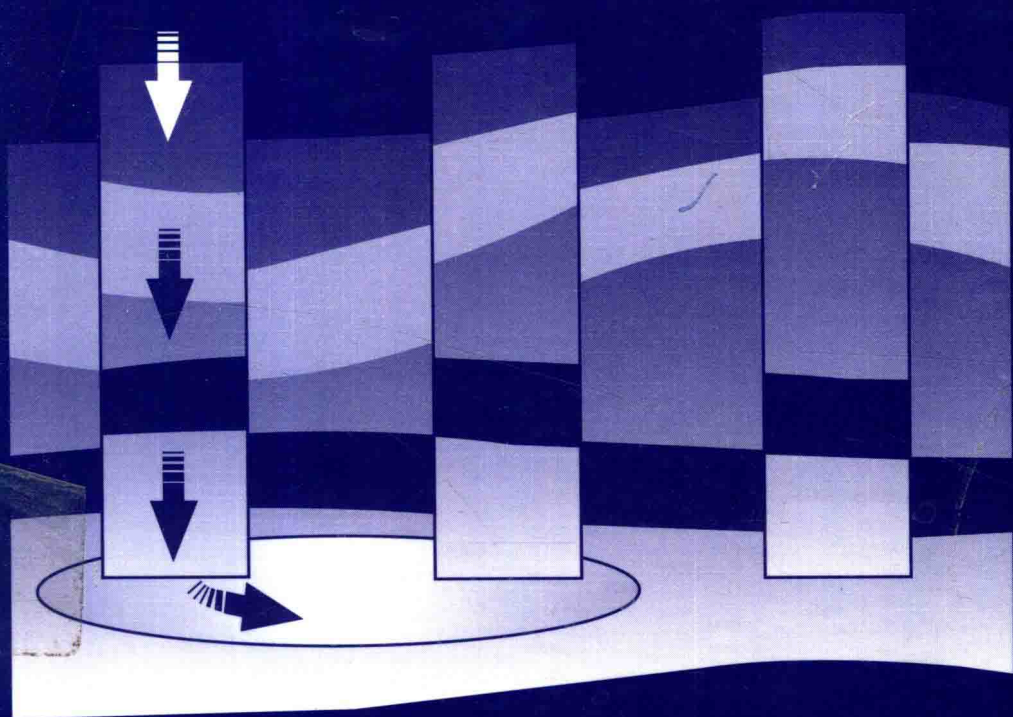# Nonaqueous-Phase Liquids

Remediation of Chlorinated and Recalcitrant Compounds

Editors: Godage B. Wickramanayake and Robert E. Hinchee

Nonaqueous-Phase Liquids

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The First International Conference
on Remediation of Chlorinated and
Recalcitrant Compounds

Monterey, California, May 18–21, 1998

Printed in the United States of America

FOREWORD

Nonaqueous-phase liquids, especially DNAPLs, are among the most challenging contaminants facing environmental remediation professionals. Difficult to detect and stubborn to remove, DNAPLs present a problem at thousands of contaminated sites worldwide. *Nonaqueous-Phase Liquids: Remediation of Chlorinated and Recalcitrant Compounds* brings together the latest research and field studies to provide a systematic overview of the current state of the art in DNAPL remediation approaches. Included in this volume are chapters on characterization of source zones, DNAPL recovery systems, simulation of DNAPL multiphase flow and transport, DNAPL movement and subsurface behavior, fractured media, and NAPL remediation.

This is one of six volumes published in connection with the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, held in May 1998 in Monterey, California. The 1998 Conference was the first in a series of biennial conferences focusing on the more problematic substances—chlorinated solvents, pesticides/herbicides, PCBs/dioxins, MTBE, DNAPLs, and explosives residues—in all environmental media. Physical, chemical, biological, thermal, and combined technologies for dealing with these compounds were discussed. Several sessions dealt with natural attenuation, site characterization, and monitoring technologies. Pilot- and field-scale studies were presented, plus the latest research data from the laboratory. Other sessions focused on human health and ecological risk assessment, regulatory issues, technology acceptance, and resource allocation and cost issues. The conference was attended by scientists, engineers, managers, consultants, and other environmental professionals representing universities, government, site management and regulatory agencies, remediation companies, and research and development firms from around the world.

The inspiration for this Conference first came to Karl Nehring of Battelle, who recognized the opportunity to organize an international meeting that would focus on chlorinated and recalcitrant compounds and cover the range of remediation technologies to encompass physical, chemical, thermal, and biological approaches. The Conference would complement Battelle's other biennial remediation meeting, the In Situ and On-Site Bioremediation Symposium. Jeff Means of Battelle championed the idea of the conference and made available the resources to help turn the idea into reality. As plans progressed, a Conference Steering Committee was formed at Battelle to help plan the technical program. Committee members Abe Chen, Tad Fox, Arun Gavaskar, Neeraj Gupta, Phil Jagucki, Dan Janke, Mark Kelley, Victor Magar, Bob Olfenbuttel, and Bruce Sass communicated with potential session chairs to begin the process of soliciting papers and organizing the technical sessions that eventually were presented in Monterey. Throughout the process of organizing the Conference, Carol Young of Battelle worked tirelessly to keep track of the stream of details, documents, and deadlines involved in an undertaking of this magnitude.

Each section in this and the other five volumes corresponds to a technical session at the Conference. The author of each presentation accepted for the Conference was invited to prepare a short paper formatted according to the specifications provided. Papers were submitted for approximately 60% of the presentations accepted for the conference program. To complete publication shortly after the Conference, no peer review, copy-editing, or typesetting was performed. Thus, the papers within these volumes are printed as submitted by the authors. Because the papers were published as received, differences in national convention and personal style led to variations in such matters as word usage, spelling, abbreviation, the manner in which numbers and measurements are presented, and type style and size.

We would like to thank the Battelle staff who assembled this book and its companion volumes and prepared them for printing. Carol Young, Christina Peterson, Janetta Place, Loretta Bahn, Lynn Copley-Graves, Timothy Lundgren, and Gina Melaragno spent many hours on production tasks. They developed the detailed format specifications sent to each author, tracked papers as received, and examined each to ensure that it met basic page layout requirements, making adjustments when necessary. Then they assembled the volumes, applied headers and page numbers, compiled tables of contents and author and keyword indices, and performed a final page check before submitting the volumes to the publisher. Joseph Sheldrick, manager of Battelle Press, provided valuable production-planning advice and coordinated with the printer; he and Gar Dingess designed the volume covers.

Neither Battelle nor the Conference co-sponsors or supporting organizations reviewed the materials published in these volumes, and their support for the Conference should not be construed as an endorsement of the content.

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Godage B. Wickramanayake and Robert E. Hinchee
Conference Chairman and Co-Chairman

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REMEDIATION OF MULTI-COMPONENT PCB CONTAINING DNAPL RESERVOIRS IN FRACTURED ROCK

Rawson, James R. Y., May, Ralph J. (General Electric Company - Corporate Research & Development, Niskayuna, NY) and Guswa, John H. (HSI GeoTrans, Inc., Harvard, MA)

ABSTRACT: Releases of PCB oil and other non-aqueous phase liquids (NAPL) at General Electric's Hudson Falls plant site have resulted in the formation of localized multi-component DNAPL (dense non-aqueous phase liquid) reservoirs in the underlying fractured rock. Vertical and horizontal fractures in the rock have allowed downward and horizontal migration of the DNAPL from the original points of release to the Hudson River. Compositional analyses of the PCB containing NAPLs have identified three chemically unique DNAPL reservoirs beneath the plant site. The variation in the chemical composition of these reservoirs is probably the result of sequential and localized releases of different types of NAPLs. Periodic compositional analyses of the DNAPL recovered from the same location indicated that the different DNAPL sources continue to mix in the fractured rock. DNAPL seepage to the Hudson River adjacent to the plant has been minimized by the installation of groundwater and DNAPL recovery wells. One such well has eliminated DNAPL discharge to the river from an underwater seep. A mathematical model was developed to estimate the remaining recoverable DNAPL from this groundwater recovery well.

INTRODUCTION

General Electric (GE) Corporation's former Hudson Falls manufacturing plant is situated immediately adjacent to Bakers Falls on the Hudson River. The Hudson Falls plant is located approximately 200 miles north of New York City, NY. The plant previously manufactured capacitors, which contained dielectric fluids consisting of polychlorinated biphenyls (PCBs), primarily Aroclor 1242. The use of PCBs as dielectric fluids was discontinued in 1977. After that, several other dielectric fluids were used in place of PCBs. These fluids consisted of mixtures in various proportions of bis-(2-ethylhexyl)-phthalate (BEHP), phenyl xylyl ethane (PXE) and trichlorobenzene (TCB). During the manufacturing processes at this site, there were a number of incidental releases of the aforementioned dielectric fluids to the underlying soil and bedrock.

The geology beneath the site consists of a shallow clay and glacial till overburden (up to 21 feet thick), the Snake Hill shale formation (150 - 259 feet thick) and two carbonaceous zones extending a total of another 150 to 160 feet in depth. The primary pathways of DNAPL migration in the Snake Hill shale have been through vertical and horizontal fractures. Two major parallel horizontal fault planes delineate the boundaries between the upper and middle and the middle and lower regions of the Snake Hill shale.

GE's former manufacturing buildings sit atop a bluff on the east side of the Hudson River and approximately 100 feet above the base of Bakers Falls. The Snake Hill shale is exposed on both the cliffs adjacent to the river and on Bakers Falls. Bakers Falls Dam is located at the top of the falls and diverts the Hudson River to the west through a power generation station. The total drop in height from the top of Bakers Falls Dam to the base of the falls is 67 feet. The falls, themselves, drop approximately 40 feet. During normal river flow (3000 to 5000 cfs), the power station diverts all of the water in the river through its generators and the falls are dry. Periodically, during routine maintenance at the power station and during high water flow (greater than 5000 cfs), much of the Hudson River flows over the dam onto Bakers Falls.

Subsequent to diverting the river through the power generation station and prior to initiating groundwater remedial efforts at the site, PCB containing DNAPL could be seen seeping from fractures into pools of water on the face of Bakers Falls. Additionally, groundwater containing PCBs flowed from the site into the Hudson River.

In order to control the unacceptable flux of PCBs to the Hudson River, a remedial strategy was developed to preclude PCBs both in the form of DNAPL and as dissolved phase from entering the river. The remedial strategy included constructing a hydraulic capture zone consisting of a series of groundwater recovery wells adjacent to the river. This hydraulic capture zone was intended to prevent the flow of PCB contaminated groundwater to the river. In addition, many of these wells also recovered DNAPL from localized reservoirs, which resulted in reducing the DNAPL pressure head and minimizing the seepage of DNAPL into the Hudson River.

The primary objectives of the work described herein were: (1) determine the chemical composition of the DNAPL recovered from the recovery wells; and, (2) develop a model that estimates the volume of DNAPL that can be recovered from groundwater recovery wells.

MATERIALS AND METHODS

DNAPL samples were collected from both monitoring and recovery wells by either manual bailing or pumping from the bottom of the wells. DNAPL was collected with eye droppers from the seeps on the face of Bakers Falls. The volume of DNAPL recovered from each well and seep was recorded as a function of time. DNAPL samples were collected from 62 different locations. Multiple samples were also collected as a function of the volume (time) of DNAPL produced from a number (48) of these locations.

The chemical composition of 253 different samples of DNAPL was analyzed. The DNAPL was dissolved in hexane and the individual components were separated by gas chromatography (GC) using a 30 meter DB-1 (J&W Inc) fused silica capillary column. The individual peaks were characterized by a mass spectrometer (MS) operated in the scan mode (50 - 550 amu). The major components of the DNAPL consisted of PCBs, BEHP, PXE and TCB. These compounds accounted for more than 99 weight percent of the DNAPL. The GC-MS system was calibrated with standards of Aroclor 1242, bis-(2-ethylhexyl) phthalate (BEHP), phenyl xylyl ethane (PXE) and trichlorobenzene (TCB). The

relative chromatographic area percent of PCBs in the DNAPL was determined by analyzing for selected di- and tetrachloro congeners.

The individual chemical components (PCB, BEHP, PXE or TCB) of the DNAPL were reported as the relative chromatographic area percent (Area%) of the total (PCB, BEHP, PXE and TCB) chromatographic area as shown in equation 1.

$$\frac{\text{Area of individual component}}{(\text{Area PCB} + \text{Area BEHP} + \text{Area PXE} + \text{Area TCB})} \times 100\% \qquad (1)$$

Analysis of the area percent rather than weight percent of the major constituents of DNAPL permitted the characterization of samples that contained emulsions and sediment. It also permitted the analysis of very small volumes of DNAPL that were recovered on Kimwipes® from bailers and other surfaces encountered in the field.

RESULTS AND DISCUSSION

DNAPL Categorization. The chemical composition of DNAPL from various locations in the fractured rock at the Hudson Falls plant site was used to delineate unique reservoirs. This procedure is similar to that which is used to define the location of hydrocarbon sources in the oil industry (Wang et al., 1994). DNAPL samples were characterized by the area percent of PCBs, BEHP, PXE and TCB (see equation 1). Given that the different dielectric fluids were sequentially used, DNAPL, which contained greater than 90 Area% PCBs, was referred to as "old" DNAPL. DNAPL, which contained less than 10 Area% PCBs and primarily BEHP, PXE and/or TCB, was referred to as "new" DNAPL. DNAPL, which contained greater than 10 Area% and less than 90 Area% PCBs, was characterized as "mixed" DNAPL.

In brief, the age (old, new or mixed) of a DNAPL was defined by the Area% PCBs in the sample. Table 1 illustrates the variation seen in the composition and age of DNAPL from several different locations.

TABLE 1. Examples of chemical composition and age of DNAPL samples collected from different locations at Hudson Falls.

Location	PCB Area%	BEHP Area%	PXE Area%	TCB Area%	Category
Seep 1	99.6	0.0	0.0	0.4	Old
HF-108	98.1	0.3	0.0	1.6	Old
RW-2B	71.5	7.6	20.6	0.3	Mixed
RW-100	49.5	42.0	2.8	5.7	Mixed
RW-103	1.7	60.6	37.4	0.3	New
HF-55 BD	7.9	67.0	24.5	0.6	New

Of the 62 different locations from which DNAPL was collected, 34 produced "old" DNAPL, 6 produced "new" DNAPL and 22 produced "mixed" DNAPL. Of the 48 different locations monitored with respect to volume (time) of DNAPL produced, the composition of the DNAPL changed by 10 Area% PCBs or more at 16 different locations. In addition, the composition (Area% PCBs) of the DNAPL changed sufficiently at 3 different locations to warrant recategorization of the age of the DNAPL.

Figure 1 shows a map of the Hudson Falls site that delineates the "old", "new" and "mixed" DNAPL reservoirs. Several conclusions can be drawn from the location of the different DNAPL reservoirs. One, "old" DNAPL (primarily PCBs) is located adjacent to the river and is seeping onto the face of Bakers Falls. Two, "new" DNAPL (primarily BEHP and PXE) is only located under the main manufacturing building. Three, "mixed" DNAPL is located to the east of the main building and south of Bakers Falls immediately adjacent to the river.
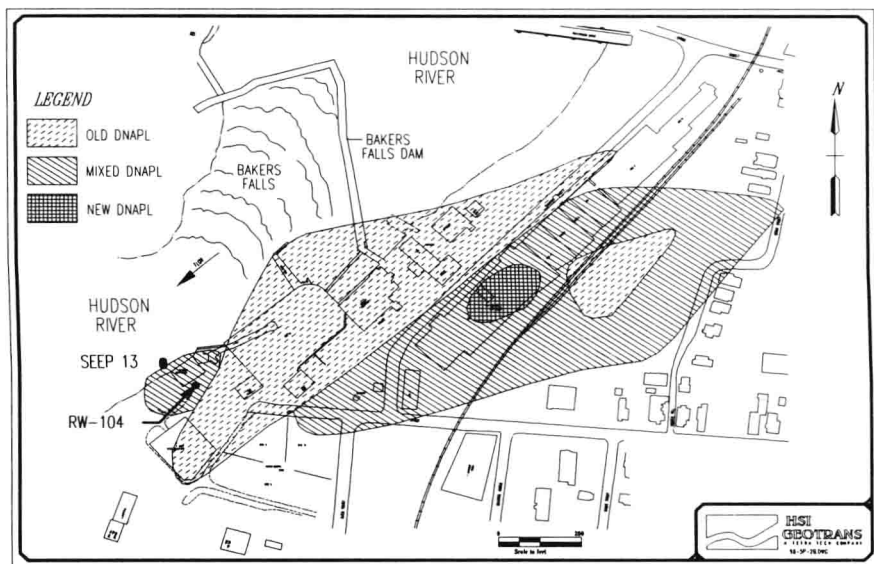
FIGURE 1. DNAPL reservoirs at GE's Hudson Falls plant site

Estimation of recoverable DNAPL volume. The total volume of DNAPL recoverable from a well can be estimated by evaluating the historical performance (volume/time vs time) of the well and assuming that the well will continue to produce DNAPL in the same manner. Generally, the rate of DNAPL recovery decreases exponentially with respect to time, as do hydrocarbon reservoirs (Fetkovich et al., 1987). Equation 2 summarizes the performance of a well that produces DNAPL.

$$P / Po = e^{-kt}, \qquad (2)$$

where Po is the initial DNAPL production rate (L/day) at t = 0 days, P is the DNAPL production rate (L/days) at time t (days) and k is the production rate

constant (day^{-1}). The historical performance of a well can be used to calculate the production rate constant k. The total remaining recoverable DNAPL volume (V) can be estimated using equation 3.

$$V = (P - Pf) / k, \tag{3}$$

where Pf is the final DNAPL production rate (L/day). The time (t-final) at which the DNAPL recovery rate from a given well drops below a significant level (assume 0.1 L/week) can be calculated as shown in equation 4.

$$t\text{-final} = \ln (Po / Pf) / k \tag{4}$$

Influence of recovery wells on seeps. In the Fall of 1996, DNAPL was discovered seeping from a fracture (Seep 13) in the Snake Hill shale formation just south of Bakers Falls and 20 feet below the surface of the Hudson River. An underwater recovery system was immediately installed to capture and recover the DNAPL that seeped (0.15 L/day) from the bedrock at this location. Simultaneously, a groundwater recovery well (RW-104) was installed between the edge of the river where the seep was located and the plant site. The recovery well was located approximately 80 feet to the southeast of the seep and was completed throughout the Snake Hill shale formation. See figure 1 for the location of Seep 13 and RW-104.

Pumping of groundwater from recovery well RW-104 began in January of 1997. Almost immediately, DNAPL began to flow into this well and Seep 13 stopped producing DNAPL. In order to confirm the cause and effect relationship that appeared to exist between the recovery of DNAPL from RW-104 and the cessation of DNAPL seepage from Seep 13, the chemical composition of DNAPL from these two locations was compared to one another at various times. These data are summarized in Table 2.

TABLE 2. Chemical composition of DNAPL collected from Seep 13 and RW-104 at different times.

Date	Location	PCB Area%	BEHP Area%	PXE Area%	TCB Area%	Category
Jan - 97	Seep 13	68.8	15.5	14.8	0.9	Mixed
	RW-104	72.8	16.7	9.8	0.7	Mixed
Oct - 97	Seep 13	51.7	37.6	10.1	0.5	Mixed
	RW-104	55.3	37.0	7.1	0.6	Mixed

The rate of DNAPL production (P - L/day) from RW-104 was monitored over time. At the end of May, 1997, the future performance of this well was evaluated using the equations 2, 3 and 4. At that time, it was estimated that the well RW-104 would produce another 50 L of DNAPL, before the DNAPL production rate would drop below 0.1 L/week. Figure 2 shows the log of the DNAPL production rate (L/day) as a function of time from January through mid-November 1997.

Figure 2 shows that the production rate of DNAPL from RW-104 declined exponentially with respect to time. Using the production rate constant (k), it was estimated that this well would stop producing DNAPL (less than 0.1 L/week) in the first quarter of 1998. After producing another 63 L of DNAPL, the well stopped producing DNAPL in the fourth quarter of 1997.

Hence, it was concluded that RW-104 captured and depleted the DNAPL reservoir that had originally been seeping into the Hudson River. The data in Table 2 also shows that there was a change in the age (0.69 - 0.73 to 0.52 - 0.55) of the DNAPL recovered from this region of the bedrock as a function of time. This change in age was gradual (data not shown) and was probably the result of the influx of newer DNAPL, possibly from under the main building.
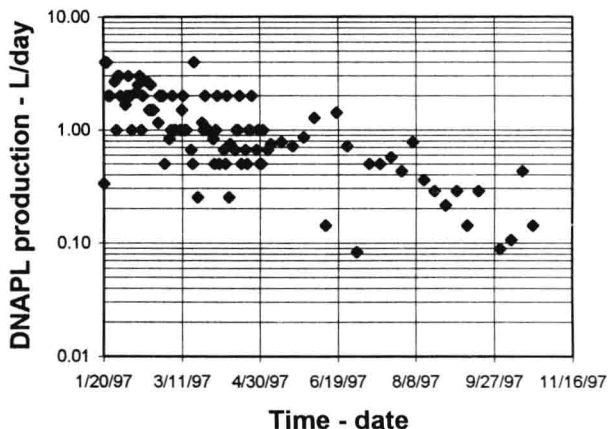
FIGURE 2.   Rate of DNAPL production at RW-104

In conclusion, the results from this work demonstrate that several analytical methods used in the oil industry can be used to delineate DNAPL reservoirs and describe the expected performance of wells that recover DNAPL in fractured rock.

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Evaluating SVE of Chlorinated Compounds From a Landfill in Fractured Limestone

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Texas), and
J.J. Mullen (Air Force Center for Environmental
Excellence(Brooks AFB, Texas)

ABSTRACT: A soil vapor extraction (SVE) treatability study was performed in an area that was trenched into and on top of native limestone to evaluate SVE influence in subsurface soils and surrounding limestone. Chlorinated volatile organic compounds (VOCs) have been detected in the trench soils. Several types of tests employing four different extraction configurations were performed on the 18 well SVE system. Vapor monitoring points (VMPs) and vapor extraction wells (VEWs) not included in each tested extraction configuration were used to monitor soil gas changes and pressure responses throughout the trench. Flow and total volatile hydrocarbon (TVH) measurements were also measured periodically in each of the extracting VEWs to assess contaminant removal contributions from each VEW. Two of the VEWs and one VMP were installed in the fractured limestone to compare extraction efficiencies of wells located outside the main trench limits to the VEWs installed in the trench. Results suggest that subsurface pathways are convoluted, with preferential migration observed in limestone fractures. In fact, flow and mass removal rates from the two VEWs located in the limestone appear capable of exerting greater influence over subsurface soils in the trench than most of the VEWs actually located in the trench.

INTRODUCTION

Chlorinated hydrocarbons were first detected in a water well located near two trenches (solid waste management unit B-3) at Camp Stanley Storage Activity northwest of San Antonio, Texas. A soil gas survey performed as part of a source characterization study identified trichloroethene (TCE) and tetrachloroethene (PCE) with occasional detection of cis-1,2-dichloroethene (cis-1,2- DCE) in the trench area. The presence of these chlorinated hydrocarbons implicated these trenches as a likely source area for the contamination detected in the water well.

The trenches were reportedly created by taking advantage of the natural slope to the west and cutting into the weathered limestone to provide greater disposal volume. The west trench (main trench), which is the deeper of the two trenches, was identified during a soil gas survey as containing the highest levels of VOC contamination. Therefore, it was selected to evaluate the remediation potential of SVE for this site. The general site layout is shown on figure 1.

Objective. The primary objective of the SVE treatability study was to determine the feasibility of SVE to remediate VOCs in the soils of a disposal trench and the surrounding native limestone. A pilot test demonstrated that SVE could significantly reduce VOC concentrations in landfill soils, but also indicated that subsurface air flow pathways are complex. A secondary objective of the treatability study was to evaluate the subsurface influence in subsurface soils, and in the surrounding limestone.

Site Description. Soils in the main trench consist of fill and silty clays with white caliche fragments near the surface, progressing with depth to limestone of the upper Glen Rose formation. The upper Glen Rose is weakly structured in the trench vicinity and exhibits evidence of fractures. The fractures are more common in the upper, more weathered horizons of the limestone. The top of this limestone formation outcrops on the eastern edge of the site and dips to the west where it is encountered at depths to 20 feet bgs. The depth to limestone appears to be variable across the site. The fill material consists of dark brown, reddish brown, and black non-plastic clays with fragments of limestone, plastic, metal debris, and charred wood mixed with poorly sorted coarse sand.

**FIGURE 1
GENERAL SITE
LAYOUT**
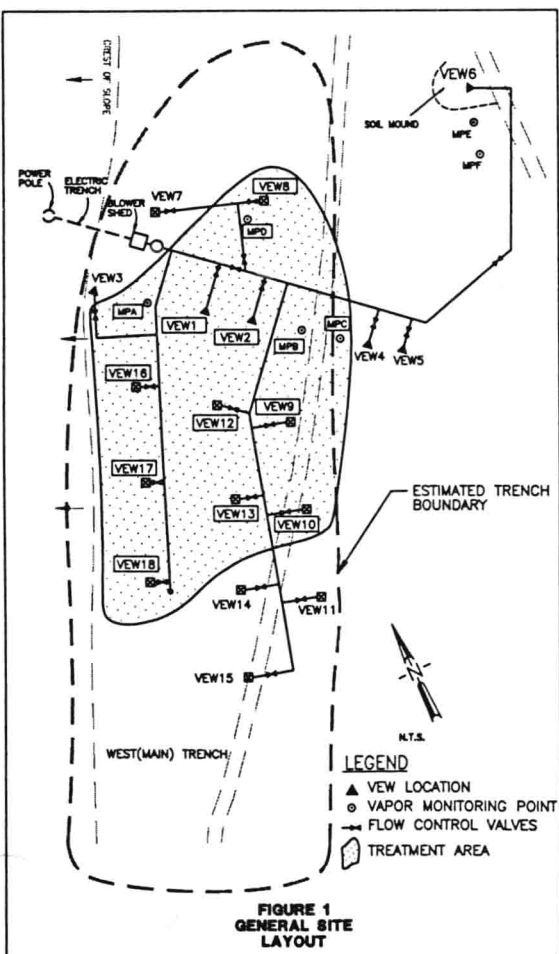
The area of the trench that exceeds current regulatory criteria based on detected VOC concentrations in soils is approximately 9,000 square feet (approximately 75 feet east-west and 120 feet north-south). Trench thickness

estimates where contaminated soils are encountered range from 10 to 15 feet bgs. The average TCE concentration in the trench is 23.0 milligrams per kilogram of soil (mg/kg). The average concentrations of *cis* -1,2-DCE detected is 3.4 mg/kg. The highest VOC concentrations were encountered in the vicinity of VEW-1 and MPA. The portions of the trench that require treatment according to the cleanup criteria are delineated on Figure 1.

SVE Treatability Test System Installation. The as-built SVE system layout is presented on Figure 1. A total of eighteen VEWs and six multi-level VMPs were installed at the site. As a continuing source for migration of VOC migration into the surrounding the fractured limestone, the main trench is the most critical cleanup area, the majority of the VEWs were placed inside the limits of the main trench. VEW-4 and VEW-5 were installed in the limestone outside the trench limits to address the migration of VOCs into the limestone and to assess the potential removal capacity of VEWs located in the native limestone. The VEWs were manifolded together to a single SVE blower with individual control valves to turn on and off the vacuum to each VEW. Each VEW was constructed with a pressure monitoring port, so that it can be used to measure pressure response when not being utilized as an extraction well. The flexibility of the system design allows extraction from any VEW combination, and collection of data from the VEWs and VMPs not included in the extraction configuration. The SVE system operation was authorized without emission control(s) by Texas Natural Resource Conservation Commission standard air exemption which currently limits the system to six VEWs and a maximum VOC emission rate of six pounds per hour.

TREATABILITY TEST METHODS

Two types of tests were performed to collect data for evaluating subsurface influence. The tests included an initial pressure check of the pilot test system after the new VEWs have been installed, and three separate multiple configuration tests (MCTs) to monitor for subsurface pressure and soil gas influence while extracting from different VEW configurations. Flow and TVH emissions data were also collected during each MCT to estimate the mass of VOCs removed from each VEW.

Initial System Check A system check was performed using the four pilot test VEWs. Pressure responses were measured throughout the trench as different configurations of extraction using the existing four VEWs were tested by shutting off air flow from one or more VEWs and then assessing the pressure response from each VEW and VMP at the site. The results of this test were used to determine which portions of the subsurface trench are directly affected by extraction at each of the initial pilot test VEWs.