

**IN-SITU DNAPL REMEDIATION USING SIX-PHASE HEATING
A CASE STUDY OF A SUCCESSFUL FULL-SCALE DNAPL REMEDIATION**

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EXECUTIVE SUMMARY

Three of the top ten most frequently detected contaminants at hazardous waste sites are Dense non-aqueous phase liquids (DNAPL) compounds. Although much progress has been made recently to develop and improve cleanup technologies, prior to 1999 no proven technology for the restoration of DNAPL source zones. A new commercially available technology, the Six-Phase Heating (SPH) Technology, is presently being implemented at a number of sites for the treatment of DNAPL contamination. The SPH technology has successfully remediated DNAPL sites including the full-scale application of the technology that is documented in this case study. Over a six-month remediation program, the SPH technology successfully removed significant DNAPL pools and dropped groundwater concentrations to below the required site clean up levels. Based on the results of the SPH system, the site owner has received a written closure letter for no further action from the Illinois EPA for the site.

INTRODUCTION

Chlorinated solvents were first manufactured in the United States in the early 1900s and their subsequent use mirrored the economic growth of the country. Production quantities ranged from hundreds of millions, to billions of kilograms (kg) per year. Historical use and disposal practices led to wide spread releases at thousand of locations.

According to a recent National Research Council study, three of the top ten most frequently detected contaminants at hazardous waste sites are Dense non-aqueous phase liquids (DNAPL) compounds (National Research Council, 1994, pg. 26, table 1-1). The Office of Management and Budget estimates that the federal government will spend between \$234 and \$289 billion on environmental remediation over the next 75 years at DoD, DOE, Department of Interior and Agriculture, and NASA sites (Soil and Groundwater, August/September, 1997). Although no specific data is available, we can expect that a significant portion of these budgets will be directed toward DNAPL remediation.

DNAPL REMEDIATION

Although much progress has been made recently to develop and improve cleanup technologies, there still exists no proven technology for the restoration of DNAPL source zones. The difficulty of this challenge is unprecedented in the field of groundwater engineering. Despite recent, notable progress ". . .the technologies available for the removal of DNAPL from the groundwater zone at appreciable rates are still experimental and no DNAPL source zone of significant size has been fully restored using any of them" (Pankow and Cherry, 1996 pg. 503).

Dense non-aqueous phase liquids (DNAPLs) form when chlorinated solvents percolate through a soil column and migrate downward through an aquifer until they encounter an impermeable clay or mudstone aquitard. The DNAPL initially conforms to the surface of the aquitard to form a network of pools and interlacing strings. As the solvent continues to move independently of the

groundwater, it begins to form dendritic branching patterns in microporous zones throughout the aquitard surface and inside the soil column. Over a period of time, the DNAPL can diffuse into impermeable layers, resulting in distributed source terms that are extremely difficult to remove or access. These source terms in the aquitard slowly migrate and disperse into the aquifer, causing direct contamination, as well as degrading slowly to form other hazardous substances, such as vinyl chloride, that threaten human health and inhibit land reutilization.

The removal of volatile organic compounds (VOCs) from tight; silty and clay-rich soil has proven difficult using conventional remediation technologies. Vapor extraction, an *in-situ* technique commonly used for removing volatile organic compounds from the subsurface, is limited in effectiveness for silty and clay-rich soil due to the very low permeability, high moisture content, and binding potential of these lithologies. Additionally, vapor extraction is not possible in under saturated conditions. However, the combination of in situ heating with soil vapor extraction has proven effective for releasing DNAPL from tight soils.

Heating causes DNAPL to partition to the vapor phase, enabling a high degree of removal over relatively brief treatment periods. Typically, the Henry's law constant (representing the equilibrium ratio of vapor phase and dissolved concentrations) increases roughly 15-20 times as temperatures increase from 10 to 100°C (Herron et al, 1998)¹. Heating further enhances vapor partitioning by increasing the aqueous contaminant solubility. Because of elevated vapor concentrations of the contaminant, it has been shown that the boiling point of DNAPL in the surface is reduced significantly below that of either the pure contaminant or of water (De Voe and Udell, 1998)². For example, PCE as a DNAPL boils at 88°C versus 100°C for pure water or 121°C for pure PCE. Boiling results in rapid release of DNAPL from the formation, through pressure induced advection and buoyant forces. It has also been speculated that continuous heating can cause pressure-driven fracturing in low permeability soils, providing a potentially critical release mechanism for removing DNAPL from tight soil layers within the aquifer and soil column. The ability to form micro-fractures in low permeability soils would help explain why diffusive rebound of contaminant concentrations has not typically been observed following thermal remediation. Finally, by increasing subsurface temperatures to the boiling point of water, the Six Phase Heating technology further speeds the removal of contaminants by *in situ* steam stripping. The ability to generate steam *in-situ* represents a significant advantage of SPH over technologies that rely upon hydraulic transport and conductive transfer to deliver heat to the subsurface.

SIX-PHASE HEATING

Six Phase Heating™ (SPH) is a polyphase electrical technique to resistively heat soil and create an in-situ source of steam to strip contaminants, which are then captured using standard soil vapor extraction techniques. The technique was originally developed by Battelle Memorial Institute for the U.S. Department of Energy (DOE) as a method to enhance the removal of volatile organic contaminants (VOCs) from low-permeability soils. It is now provided commercially by Current Environmental Solutions, a joint venture with Battelle Memorial Institute.

The SPH technology uses conventional 60-hertz utility transformers connected in a delta-star configuration to convert the three-phase electricity from standard power lines into six electrical phases delivered to the subsurface. Vertical, angled, or horizontal electrodes inserted using

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standard drilling techniques are used to couple the electrical power to the subsurface. The electrodes are connected in a spatially phase-sequenced pattern so that each electrode conducts to every other electrode in the formation. This results in a remarkably uniform heating pattern. The heating pattern can be adjusted to adapt to the requirements of each site. In general, the design and placement of the SPH electrodes are optimized for each site based on:

1. Size and shape of the remediation area
2. Site lithology and depth to groundwater
3. Subsurface interval(s) and total depth of site impact
4. Total organic carbon content and electrical resistivity of site soil
5. Buried utilities and immediately adjacent surface structures

The SPH power supplies are capable of operating at either 500, 950, or 1,250 kW. Each power supply provides six separate, and simultaneous, electrical outputs with voltages adjustable from 0 to 1,100 V. Electrodes are typically placed in patterns allowing a grouping of six electrodes to be in electrical contact, but out of phase, with each other. At sites with multiple electrode groupings, electrodes at identical phases are all connected to the same transformer.

In addition to the electrodes and power supply, the major components of an SPH treatment system are:

1. A computer control and data acquisition system with fully remote communication.
2. Vapor extraction vents and monitoring wells (temperature and pressure) installed subsurface.
3. An off-gas collection and treatment system (including piping, a blower, a steam condenser, a condensate holding tank and an off-gas treatment unit).

The remote communication systems enables complete system control (including startup, shutdown, voltage and power adjustments) from a remotely located computer via phone lines. The system also transmits data from in situ and aboveground sensors and the operational status of the SPH power supplies. During system operations, CES staff remotely monitor and control the SPH equipment in consultation with on-site personnel.

During the heating process, subsurface vapor extraction wells are used to remove steam and contaminant vapors as they are produced. A steam condenser separates the mixture of soil vapors, steam, and contaminants extracted from the subsurface into condensate and contaminant laden vapor. If these waste streams require pre-treatment before discharge, standard air abatement and water treatment technologies are utilized.

The SPH technique creates a uniform heating pattern by utilizing the electrical resistance of the soil and groundwater within the target treatment volume to heat the volume internally. The soil and groundwater are analogous to a distributed matrix of series and parallel resistors that are continuous throughout the heated volume. Initially, the SPH current causes the soil and

groundwater to heat to the boiling point of water. Steam is then generated throughout the heated volume as though thousands of individual heating elements existed in the heated volume. This integrated process of heating and internal steam generation has proven extremely effective and efficient for thermal remediation in both the vadose zone and in groundwater.

As electric current is conducted through the soil column and aquifer, the current flux is initially highest along paths of low electrical resistance where preferential heating occurs. Over time, chlorinated solvents undergo natural anaerobic dehalogenation, producing daughter compounds and free chloride ions. We have found that the resulting elevated ion content near high *in situ* concentrations of solvent are effective in producing low resistance pathways that are also heated preferentially. Thus, at chlorinated hydrocarbon sites, the most heavily impacted portions of the subsurface are preferentially treated by SPH. Silt or clay lenses in the vadose zone are also heated preferentially because they exhibit an elevated moisture content and relatively low electrical resistivity. These phenomena contribute to accelerated remediation by helping to focus heating where the contaminant is likely to reside and where diffusive processes would normally be rate limiting.

To remove DNAPLs, it is important to heat the upper layer of the aquitard itself, not just the permeable zone. With SPH, simultaneous heating occurs within the aquitard as well as within other low permeability units where the DNAPLs tend to pool. This means that steam is generated continuously along the top units of the aquitard and other low permeability units where the DNAPL resides so that it can pass directly through the DNAPL pools. The physical action of steam escaping these tight soil lenses drives contaminants out of those portions of the soil matrix that tends to lock in contamination via low permeability or capillary forces. Released steam then acts as a carrier gas, sweeping contaminants out of the subsurface and to the soil vapor extraction wells. As this steam moves towards the surface, it strips contaminants from both groundwater and the more permeable portions of the soil matrix.

APPLICATIONS OF THE SPH PROCESS

The SPH technology has been demonstrated on a pilot scale at several sites where it has proven capable of remediating the vadose zone as well as both DNAPL and light non-aqueous phase liquids (LNAPL) from the saturated zone. At the U.S. Department of Energy's Savannah River Site, SPH reduced the concentrations of perchloroethylene (PCE) in clay soil by over 99% in 25 days of heating (Gauglitz et al, 1994)³. The demonstration also showed that the SPH process preferentially heats clay layers over adjacent sandy soil layers.

At the Dover AFB in Delaware, tracers were used to evaluate the effectiveness of SPH to recover DNAPL from an aquifer. The demonstration proved successful in almost fully recovering the DNAPL tracers with no tracer migration documented. The demonstration also illustrated the effectiveness of SPH in boiling a flowing aquifer (Peurrung and Schalla, 1998)⁴.

At a Technology Demonstration Project in Fort Richardson, Alaska in 1997, SPH proved successful in complete recovery of recalcitrant chlorinated compounds from tight saturated soil lithologies. At the Fort Wainwright Site Demonstration Project, in Fairbanks, Alaska in 1998, SPH was used successfully to augment aerobic bioremediation of an LNAPL at a cold weather site by moderate heating coupled with air sparging. Following operations at low temperature, further heating was performed to evaluate removal of gasoline-range organics by thermal

volatilization. A pilot demonstration was also performed for a commercial client in 1998 where SPH was shown capable of removing LNAPL including both gasoline and kerosene from the saturated zone.

The first full-scale commercial application of SPH for the remediation of DNAPL in the saturated zone was the remediation of a former telecommunications manufacturing facility in Skokie, IL.

DESCRIPTION OF THE SKOKIE, IL REMEDIATION

The SPH process was operated at a full scale for six months in 1998 at a large DNAPL site located in Skokie, Illinois, within the greater Chicago area. The site housed an abandoned brick building that served for decades as a telecommunications manufacturing facility. Most of the DNAPL, consisting of pooled trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), and the *cis* isomer of 1,2-dichloroethene (*cis*-DCE), was located beneath the building itself. The site lithology consisted of heterogeneous sandy silts with clay lenses to 18 feet below grade (bg) with hydraulic conductivity ranging from 10^{-4} to 10^{-5} cm/sec. At 18 feet bg, a dense silty clay till or ground moraine formed an aquitard with a hydraulic conductivity of less than 10^{-8} cm/sec. A shallow groundwater table was encountered at 7 feet bg. Most of the remaining solvent mass was known to be pooled on top of the clay till at 18-20 feet bg.

From 1991 to early 1998, ENSR had performed soil and groundwater remediation using a process of steam stripping combined with groundwater and vapor extraction. The steam stripping process was able to remove much of the DNAPL, but had difficulty in three very heterogeneous regions containing large DNAPL pools. After seven years, these technologies reduced overall site impact but had left behind three large hot spot areas. The remaining areas represented about 20,000-sq. ft. of an original 115,000-sq. ft. treatment area. **Figure 1** shows where the remaining DNAPL was located in relation to the main building at the site.

To continue subsurface clean up beyond the limits reached by steaming, groundwater and vapor extraction, the site owner selected the SPH technology. The client's remediation plan focused on removing the remaining DNAPL. Consequently, the remediation goals for the SPH process were established for reduction of chlorinated solvent concentrations to below the State of Illinois RBCA TIER III levels. The Tier III cleanup goals for each contaminant were (based on groundwater concentrations):

1. <17,500 ug/L for TCE,
2. <9,650 ug/L for 1,1,1-TCA
3. <35,500 ug/L *cis* 1,2-DCE

To meet the remediation objectives, a network of 107 electrodes was designed and installed to focus heating at the remaining TCE and TCA pools covering roughly two-thirds of an acre. To access the DNAPL, 85 of the electrodes were constructed directly through the floor of the building as shown **Figure 1**. The electrodes were designed to be electrically conductive throughout a depth interval of 11-21 feet bg so as to boil the groundwater and DNAPL in the interval from 5-24 feet, including the clay aquitard itself at 18 feet bg. The electrodes were

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slotted to serve as vapor extraction wells for removing steam and chlorinated solvents from the subsurface. The slots were positioned above the water table within an upper layer consisting of a structural fill having moderate permeability. A network of 37 soil vapor extraction wells that were installed during earlier site remediation efforts was also used to ensure vapor capture. These wells were screened to 5 feet bg.

Operation of the SPH system was controlled remotely via software, enabling real-time adjustment of electrode voltage to control power delivered to the soil. Thermocouples placed in the soil were used to monitor the heating pattern as a basis for adjusting the distribution of power and also to assist in determining the best electrical configuration for power delivery as the cleanup progressed. The electrical configuration was adjusted in the field by reconnecting electrical jumpers between electrodes to re-focus electrical energy as needed to maintain rapid treatment. During all phases of the operation, the total power, energy delivered, electrical currents, voltage and electrical power factor were measured and recorded along with soil temperatures using a computer based data acquisition and control system.

Treatment progress was monitored by measuring vapor concentrations in the soil offgas exiting the condenser and prior to atmospheric release, by periodically measuring the contaminant concentrations in the off-gas condensate, and by periodically monitoring in situ concentrations through groundwater samples collected from wells. Groundwater samples extracted monthly and analyzed via head space extraction using an HP 5890 gas chromatograph equipped with an electron capture detector (GC/ECD). Standards for TCE, TCA, cis and trans 1,2-DCE and 1,1 DCE were used to calibrate the instrument. A subset of the sample population was analyzed using a gas chromatograph with a mass spectrometer (GC/MS) following EPA Method 8240. The same techniques were used to periodically monitor contaminant concentrations in the collected condensate.

The off gas system consisted of a vacuum extraction blower, a steam condenser, and a condensate holding vessel. Off gas concentrations exiting the condenser were monitored using a flame ionization detector (FID). To correlate the FID signal with total vapor phase contaminant concentrations, grab samples were obtained using Tedlar bags and analyzed using the GC/ECD. The off gas measurements enabled estimates of the rate of contaminant removal and total removed mass throughout the site operation. Roughly 99% of the removed mass was found to remain in the vapor phase past the off-gas condenser while the remaining 1% was collected in the condensed phase. This partitioning reflects the relatively high volatility and modest solubility of the contaminants.

RESULTS AND ECONOMICS

Full-scale operations of the SPH system began on June 4, 1998. Within 60 days, temperatures throughout the entire 24,000 cubic yard treatment volume had reached the boiling point of water. Over an additional 70 days of heating, all of the separate phase DNAPL in the area had been removed and TCE/TCA groundwater concentrations reduced to below the TIER III cleanup levels. Cleanup results are summarized in **Table 1** along with target levels for State of Illinois TIER III and more stringent TIER I requirements. As shown, groundwater concentrations were well below TIER III levels and were approaching TIER I levels throughout the site at the end of site operations on November 20, 1998.

Figure 2 provides a graphical comparison of contaminant concentrations before and after the remediation.

Table 2 lists groundwater concentrations obtained monthly during the remediation process. The concentrations are also plotted as a function of time for TCA and TCE at each monitoring well in **Figures 3 and 4**. Post remediation monitoring data through May of 1999 is also included on Figures 3 and 4. **Based on the results from the operation of the SPH system, the Illinois EPA granted closure to the site owner.**

At the request of the site owner, the total cost of remediation efforts to date could not be disclosed. However, on a per unit basis, the full-scale SPH remediation was completed at a total price of \$35 per cubic yard of treatment area. This cost included the installation and operation of the SPH power system and electrodes as well as vapor extraction, air abatement, and condensate treatment systems. The costs also included project permitting, preparation of work plans, electrical use, waste disposal, interim sampling, and progress reporting. A total of 1,775 MW-hr of electrical energy had been consumed by the SPH system.

CONCLUSIONS

During the first two months of this successful DNAPL remediation project, SPH was able to rapidly increase the temperature of a large saturated volume to the boiling point of the DNAPL. Following a total treatment operation of six months, 23,000 cubic yards of soil and aquifer contained DNAPL pools in tight heterogeneous soil were remediated to well below the site cleanup goals set by the Illinois State RBCA Tier III standards. Based upon these results, the Illinois EPA granted site closure to the site owner.

REFERENCES

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Table 1. Groundwater Quality Before and After Start of SPH Remediation

Well No.	Compound	RBCA Tier III Clean-up Level (ug/l)	RBCA Tier I Clean-up Level (ug/l)	Prior to SPH Remediation 1998 (ug/l)	October 1998 (ug/l)	November 1998 (ug/l)	Reduction
B3	cis 1,2-DCE	35,500	350	49,000	780	390	99.2%
	1,1,1-TCA	9,650	1,000	82,000	ND	ND	>99.9%
	TCE	17,500	25	58,000	790	250	99.6%
Ba6	cis 1,2-DCE	35,500	350	18,000	200	1,200	93.3%
	1,1,1-TCA	9,650	1,000	66,000	ND	ND	>99.9%
	TCE	17,500	25	23,000	510	470	98.0%
C4	cis 1,2-DCE	35,500	350	160,000	1,300	550	99.7%
	1,1,1-TCA	9,650	1,000	13,000	ND	ND	>99.2%
	TCE	17,500	25	120,000	1,600	ND	98.7%
Ca6	cis 1,2-DCE	35,500	350	52,000	4,100	250	99.5%
	1,1,1-TCA	9,650	1,000	16,000	14	ND	>99.9%
	TCE	17,500	25	230,000	81,000	1,600	99.3%
Da2	cis 1,2-DCE	35,500	350	18,000	120	3,000	83.3%
	1,1,1-TCA	9,650	1,000	94,000	290	ND	>99.9%
	TCE	17,500	25	370,000	8,800	320	99.9%
F13	cis 1,2-DCE	35,500	350	510	480	38	92.5%
	1,1,1-TCA	9,650	1,000	150,000	ND	ND	>99.9%
	TCE	17,500	25	2,900	260	12	99.6%
Fa2	cis 1,2-DCE	35,500	350	3,900	470	210	94.6%
	1,1,1-TCA	9,650	1,000	24,000	ND	ND	>99.8%
	TCE	17,500	25	22,000	1,200	ND	94.5%
Average	cis 1,2-DCE	35,500	350	43,100	1,060	810	98.1%
	1,1,1-TCA	9,650	1,000	63,600	44	1	>99.8%
	TCE	17,500	25	118,000	13,500	380	99.7%

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Table 2. Monthly Groundwater Quality

Cis 1,2,-DCE							
Sampling Date	3/24/98	6/26/98	7/15/98	8/20/98	9/17/98	10/6/98	11/20/98
Tier 1 Cleanup Goal	350	350	350	350	350	350	350
Tier 3 Cleanup Goal	35500	35500	35500	35500	35500	35500	35500
Well B3	48000	22000	390	18000	4200	780	390
Well Ba6	9800	18000			3500	200	1200
Well C4	43000	160000	22000	47000	16000	1300	550
Well Ca6	1800	52000	1800	52000	8400	22000	250
Well Da2	18000	8100	4000	11000	9100	7300	3000
Well F13	510	500	1000	218	120	480	38
Well Fa2	3900	2400	50	850	590	470	210

1,1,1-TCA							
Sampling Date	3/24/98	6/26/98	7/15/98	8/20/98	9/17/98	10/6/98	11/20/98
Tier 1 Cleanup Goal	1000	1000	1000	1000	1000	1000	1000
Tier 3 Cleanup Goal	8850	8850	8850	8850	8850	8850	8850
Well B3	82000	4000	500	17000	500	500	500
Well Ba6	88000	52000			2600	50	50
Well C4	11000	13000	8800	1000	1000	100	100
Well Ca6	10000		1200	4200	2000	2000	20
Well Da2	28000	94000	51000	5600	5000	500	100
Well F13	16000	150000	14000	2000	100	250	250
Well Fa2	24000	810	420	200	100	50	50

TCE							
Sampling Date	3/24/98	6/26/98	7/15/98	8/20/98	9/17/98	10/6/98	11/20/98
Tier 1 Cleanup Goal	25	25	25	25	25	25	25
Tier 3 Cleanup Goal	17500	17500	17500	17500	17500	17500	17500
Well B3	34000	640	240	58000	2900	790	250
Well Ba6	7000	23000			10000	510	470
Well C4	75000	24000	89000	120000	17000	1600	55
Well Ca6	83000		5200	230000	12000	81000	1600
Well Da2	47000	130000	230000	44000	370000	8800	320
Well F13	800	2800	1000	830	400	260	12
Well Fa2	22000	4800	880	3100	280	1200	12

Figure 1. Site Initial Conditions

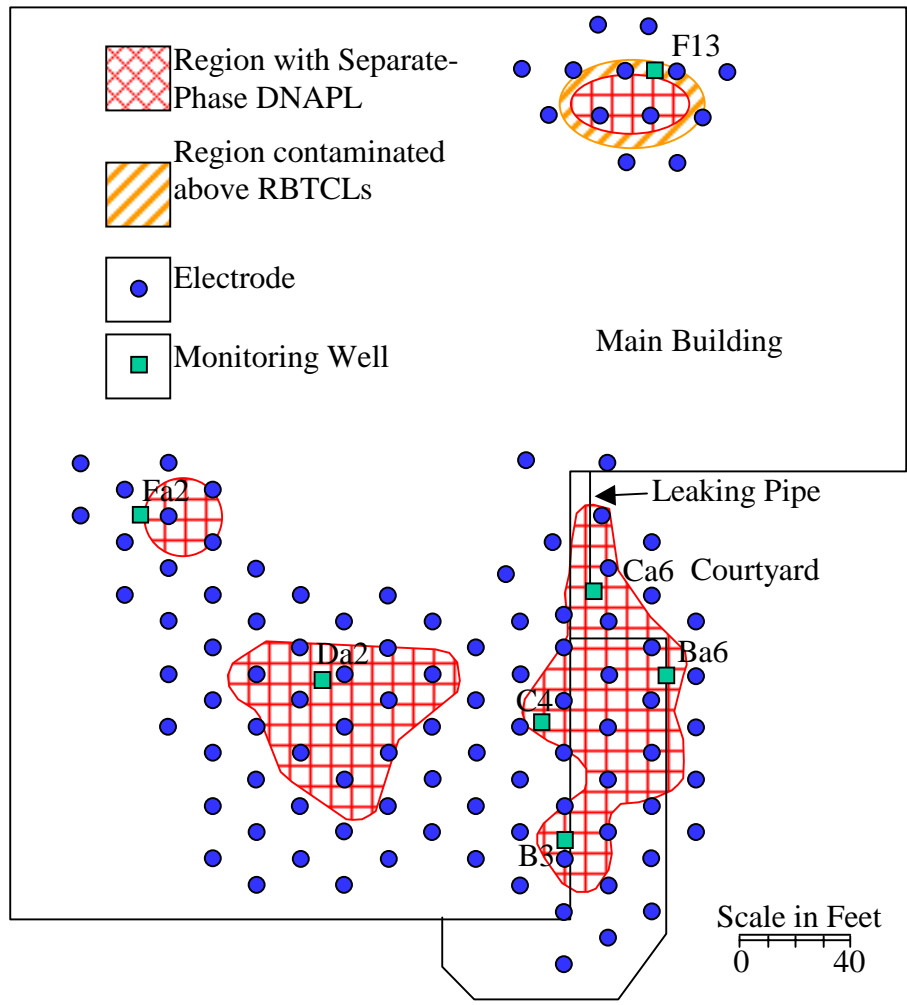


Figure 2. SPH Electrode Layout

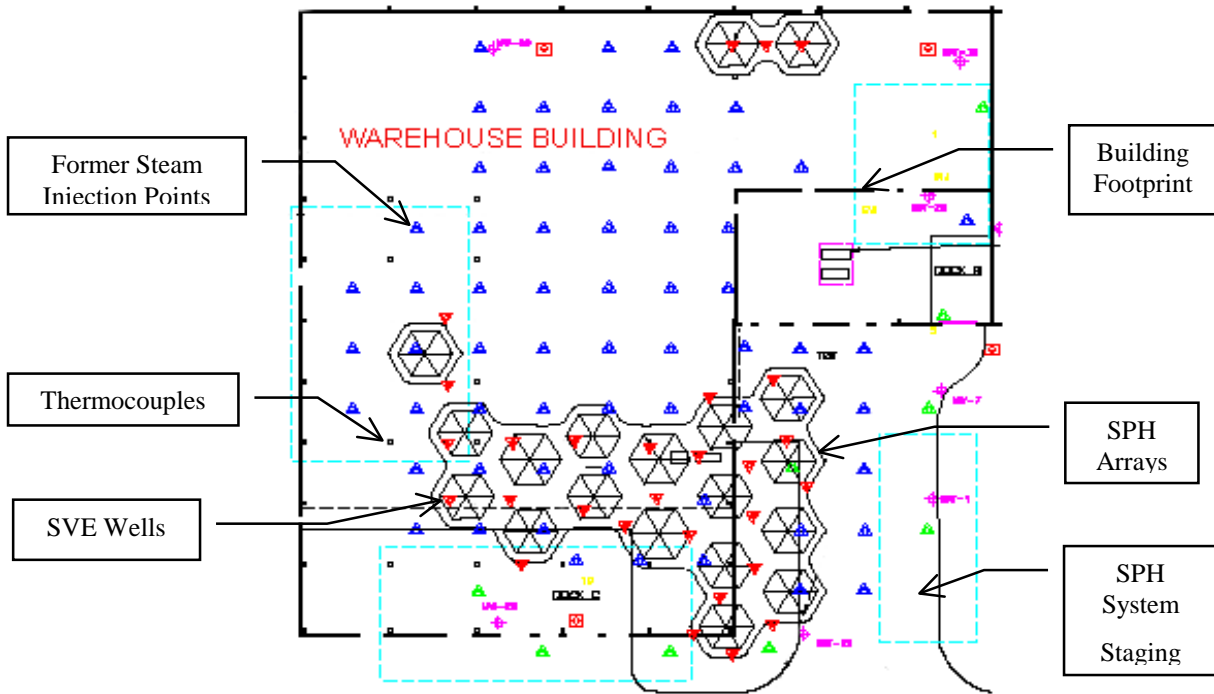


Figure 3. Average Groundwater Quality Before and During SPH Remediation

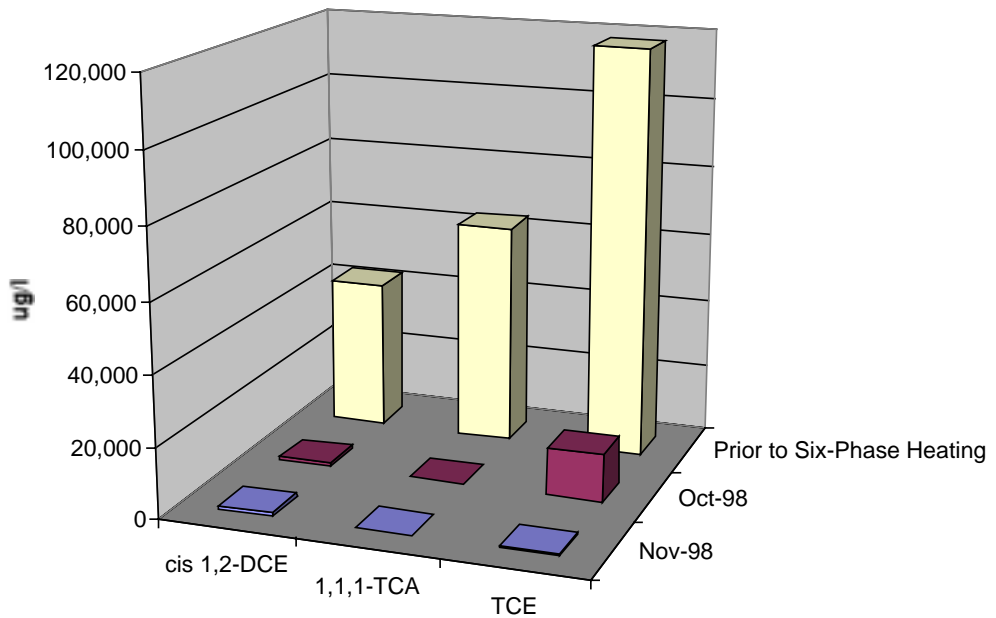


Figure 4. Monthly 1,1,1-TCA Concentrations in Groundwater

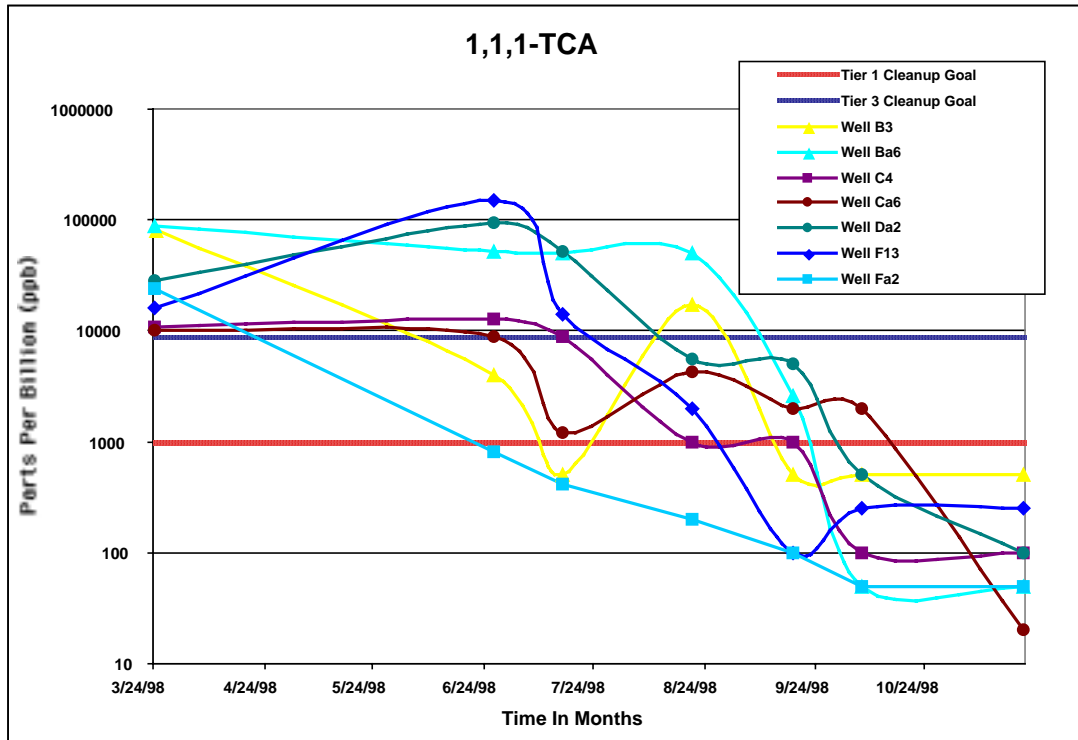


Figure 5. Monthly TCE Concentrations in Groundwater

