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Cost and Performance Report

(ER-201027)

Enhanced Attenuation of Unsaturated Chlorinated Solvent Source Zones using Direct Hydrogen Delivery

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
AFCEC	Air Force Civil Engineer Center
ASTM	American Society for Testing and Materials
bgs	below ground surface
C_3H_8	propane
cis-1,2-DCE	*cis*-1,2-dichloroethene
cm/s	centimeters per second
CO_2	carbon dioxide
CVOC	chlorinated volatile organic compound
cy	cubic yard
DHC	*Dehalococcoides*
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
ft^2	square feet
ft/day	feet per day
GAC	Granular Activated Carbon
GAO	Government Accountability Office
GC/MS	gas chromatograph/mass spectrometer
GEDIT	Gaseous Electron Donor Injection Technology
gpm	gallons per minute
He	helium
H_2	hydrogen
H_2T	Hydrogen-Based Treatment
HRC®	Hydrogen Releasing Compound®
K	hydraulic conductivity
LEL	lower explosive limit
LPG	liquefied petroleum gas
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
mg	milligram
MW	monitoring well

ACRONYMS AND ABBREVIATIONS (continued)

N_2	nitrogen
ND	non-detect
NDEQ	Nebraska Department of Environmental Quality
NFPA	National Fire Protection Association
O&M	Operation and Maintenance
O_2	Oxygen
PCE	perchloroethene
PID	photoionization detector
ppbv	parts per billion by volume
ppmv	part per million by volume
PVC	polyvinyl chloride
RACER	Remedial Action Cost Engineering and Requirements
RL	Reporting Limit
ROI	Radius of Influence
scfm	standard cubic feet per minute
SRT	Sustainable Remediation Tool
SVE	soil vapor extraction
1,1,1-TCA	1,1,1-trichloroethane
TCE	trichloroethene
trans-1,2-DCE	*trans*-1,2-dichloroethene
USCS	Unified Soil Classification System
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
VOC	volatile organic chemical

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

As of 2005, the Department of Defense (DoD) has identified nearly 6,000 sites at its facilities that require groundwater remediation and has invested $20 billion for site cleanup over a ten-year period (Government Accountability Office [GAO], 2005). At many of these sites, unsaturated chlorinated volatile organic compounds (CVOC) source zones located above the water table are producing and sustaining groundwater plumes. Many of these unsaturated sources are currently being treated with soil vapor extraction (SVE) technologies. Long-term SVE projects can be very costly, as the treatment process for the recovered vapors is expensive.

The overall objective of this project is to show if Hydrogen-Based Treatment (H_2T) can serve as a remediation technology for the unsaturated zone, either as the initial remediation technology applied at a site or as a polishing technology that will allow DoD site managers to shut down an existing expensive, low performance SVE system, but where monitored natural attenuation may not be sufficient to control the groundwater plume that is sourced by the residual contaminants in the unsaturated zone. With such a technology, the cost for remediating these groundwater plumes can be greatly reduced, and a much more sustainable remedy can be implemented. This demonstration answers key questions about the performance, implementability, and cost of the technology. If successful, the H_2T system can serve as a cost-effective and more sustainable remediation technology (i.e., lower carbon-footprint) for unsaturated soils containing chlorinated solvents.

TECHNOLOGY DESCRIPTION

"Anaerobic Bioventing" is an attractive option for unsaturated zone remediation because gases can disperse farther into the unsaturated materials than liquids. Gases can also potentially diffuse more thoroughly through the subsurface, to some extent minimizing the problems of preferential flow pathways that are more common with liquid flow. Previous studies have shown that anaerobic biotreatment of CVOCs in the unsaturated soils (i.e., anaerobic bioventing) has potential as a remediation alternative for unsaturated soils. In H_2T, reductive dechlorination and bioventing are combined to create a remediation technology for sites where the unsaturated zone requires some type of treatment of chlorinated solvents. This approach for bioremediation of unsaturated soils containing chlorinated solvents was originally proposed in a patent by Hughes et al. (1997).

In the H_2T system, a mixture of nitrogen (N_2), hydrogen (H_2), propane (C_3H_8), and carbon dioxide (CO_2) gases are injected into an unsaturated treatment zone through a series of widely spaced injection points to degrade chlorinated organic compounds. Nitrogen serves as a non-explosive carrier gas to flush oxygen from the soil gas, enhancing conditions for the anaerobic degradation of chlorinated solvents. Propane is used as an inexpensive electron donor for scavenging oxygen (i.e., naturally-occurring aerobic bacteria will use the propane to remove oxygen). Hydrogen is used as the electron donor for dechlorinating bacteria to stimulate biodegradation of chlorinated organic compounds, forming innocuous daughter products such as ethane or ethene. Nitrogen and hydrogen can be purchased regularly and delivered to the site (which are refilled or changed out regularly by the gas provider as part of the gas delivery contract) or generated on-site depending on the size of H_2T application (i.e., total flowrate and treatment time).

The stoichiometry of the dechlorination reaction indicates that for every one milligram (mg) of hydrogen utilized by dechlorinating bacteria, 21 mg of perchloroethene (PCE) can be completely converted to ethene. In the unsaturated zone, the H_2T process relies on a gas injection skid consisting of piping, gages, safety equipment, process control system, and gas supply vessels that could connect to a piping manifold and injection wells at the site. At some sites, one advantageous configuration could be the conversion of a low-performance SVE system to H_2T, where the existing SVE blower and treatment system is decommissioned and replaced by the H_2T injection skid connected to the existing manifold and injection wells.

DEMONSTRATION RESULTS

Over the six-month demonstration, we injected a total of 830,000 standard cubic feet of gas was injected into a fine-grained vadose zone at a former missile silo site in Nebraska with the following average composition: 10% hydrogen, 79% nitrogen, 10% propane, and 1% carbon dioxide. The hydrogen gas was designed to stimulate biodegradation of the chlorinated solvent contaminants that persisted in this zone even after three years of SVE. Because of inconclusive sampling results during the test, the total gas flow rate and hydrogen composition were doubled for the last month of the injection phase and the total gas flow rate was increased from 2.5 standard cubic feet per minute (scfm) to 5.0 scfm and hydrogen composition was increased from 10% to 20%. An increase in hydrogen and propane concentrations and decrease in oxygen concentrations were observed at the monitoring points after increase in the flow rate and hydrogen composition.

Mass in Treatment Zone	Pre-Test (grams)	Post-Test (grams)	Percent (%) Change
TCE	289	127	-56%
*cis*1,2-DCE+*trans*1,2-DCE	472	589	+24%
Total	**760**	**717**	**-6%**

TCE = trichloroethene *cis*-1,2-DCE = *cis*-1,2-dichloroethene *trans*-1,2-DCE = *trans*-1,2-dichloroethene

The molar mass of chlorinated compounds was unchanged (7.1 moles before and after). Therefore while the system was successful at converting TCE, a "*cis*-DCE stall" condition at the site appeared to be present at the site. Key conclusions from the test:

- The H_2T process removed half the TCE from the test zone that was remaining after this zone had been treated with SVE for three years. This indicates the process may be effective for treating finer-grained units that are difficult to treat with SVE.
- In-test measurements of redox-related parameters (oxygen, methane) indicated that deeply anaerobic conditions were not achieved uniformly through the test zone, a likely contributing factor for the observed *cis*-DCE stall condition. For example, the average oxygen content in the treatment zone soils during test ranged from 0.1% to 11%, indicating partial anaerobic conditions for most of the treatment zone.
- Lab microcosm work where the gas mixture was added to soil samples from the site indicated that samples that had been bioaugmented with dechlorinating bacteria

performed much better than unamended soils, indicating a dechlorinating bacterial limitation at the site. Additional microcosm results indicated that low moisture may have been a contributing factor to this bacterial limitation. The research team concluded that the system's inability to create deeply anaerobic conditions was likely a major factor in the *cis*-DCE stall issue.

- It is possible to safely injection the hydrogen, nitrogen, propane, carbon dioxide gas mixture in the test zone. The radius of influence from the injection point was approximately 15 feet.
- In-test vapor volatile organic chemical (VOC) monitoring data were not very helpful in evaluating the progress of remediation.
- The H_2T system for this test was more successful than the existing SVE system at removing TCE from the fine-grained soils at this test site, but was not successful at removing a significant fraction of the *cis*-DCE. To help drive a full-scale H_2T drive a treatment zone to deeply anaerobic conditions, some type of barriers over the top and around the sides of the treatment zone (even something as simple as adding water to reduce the gas permeability of the soils) might help break out of a *cis*-DCE stall condition.

The pre-test success criteria and outcomes are summarized below:

Performance Objective	Success Criteria	Success Criteria Achieved?
Achievement of a greater radius of influence (ROI)	ROI that is 50% greater compared to ROI of liquid addition to the unsaturated zone.	**YES** ROI for He was 15 feet • Low O_2 concentration in monitoring wells (MW) up to 40 feet (ft) • H_2, and propane detected in MWs up to 40 ft
Greater reduction in baseline (no action) mass	50% or greater reduction in baseline (no action) mass and/or estimated mass flux.	**YES FOR TCE, NO FOR DAUGHTER PRODUCTS** • TCE mass reduced by 56% over six months. (This was TCE remaining in soil after 3 years of SVE operation). • Number of soil samples above 57micrograms per kilogram (µg/kg) standard dropped from 27% to 10% • Total moles of CVOC unchanged due to apparent *cis*-DCE stall.
Higher cost savings compared to the continued operation of an SVE system	Greater cost savings compared to the continued operation of a SVE system or use of an injection-based system.	**SOMETIMES** • For full-scale application, H_2T unit costs (in $/cubic yard [cy]) were $39 versus $97 for excavation versus $37 for SVE (although continued SVE appeared to be ineffective.) • Continued operation of SVE for two years was estimated to be $20/cy versus $39/cy for H_2T. However, the H_2T process was more efficient at removing TCE (but not daughter products) from fine-grained soils than SVE.
Reduction in the carbon footprint compared to SVE	50% reduction in the carbon footprint compared to SVE w/ oxidizer or carbon.	**MOSTLY YES** • H_2T carbon footprint was 8 tons of CO_2 compared to 21 tons for SVE (high end). • H_2T CO_2 footprint was 43% of SVE (low end)
Safety	Flammability of less than 10% of lower explosive limit (LEL) at surface.	**YES** • No health and safety incidents occurred • H_2 and propane never detected in ambient air.
Ease of Use	Lower time requirement for system setup and operation. compared to SVE	**YES** One field technician did the weekly operation and maintenance (O&M), made the pressure-flow readings, and collected the data.

IMPLEMENATION ISSUES

Key H_2T implementation issues are summarized below.

- Specific permits for H_2T may be required by local codes and will include drilling, well installation permits, and hazardous materials storage permits. Other permits may be necessary and will be dependent on local codes.
- One of the main safety concerns associated with H_2T application is the flammability of hydrogen and liquefied petroleum gas (LPG) and the potential production of methane gas. It was shown in this demonstration that the safety concerns could be addressed easily by following the safety codes (e.g., National Fire Protection Association [NFPA]50A, NFPA55, etc.).
- Soil permeability and heterogeneity, soil moisture, etc. can greatly affect the performance of H_2T system.
- A suitable population of dechlorinating organisms (*Dehalococcoides* [DHC]) is needed to ensure complete conversion of PCE or TCE to non-toxic products (e.g., ethane).
- In-test measurements of redox-related parameters (oxygen, methane) indicated that deeply anaerobic conditions were not achieved uniformly through the test zone, a likely contributing factor for the observed *cis*-DCE stall condition. Although the H_2T process is best suited for fine-grained soils with a reasonable degree of pneumatic interconnectivity, the structure of silty, loess-like soil at the site may have included some micro-fractures, which probably conveyed the majority of the volume of gas around some areas within the treatment zone. The disconnected zones of low permeability may have retained enough oxygen to inhibit reductive dechlorination within these zones. The research team concluded that the system's inability to create deeply anaerobic conditions was likely a major factor in the *cis*-DCE stall issue.
- Lab microcosm work where the gas mixture was added to soil samples from the site showed that samples that had been bioaugmented with dechlorinating bacteria performed much better than unamended soils, indicating a dechlorinating bacterial limitation at the site. The team strongly recommends that one should understand the bacterial limitation and issues involved with vadose zone bioaugmentation before attempting this technology. Future practitioners considering this alternative should first conduct lab testing with and without bioaugmentation long enough to know whether there is a microbial limitation, and then measure the electron acceptor influxes to estimate initial and sustained hydrogen demand, before designing and implementing a field pilot test.
- Additional microcosm results indicated that low moisture may have been a contributing factor to this bacterial limitation. Lab microcosm work showed that a high moisture content (30%) promoted the most complete reductive dechlorination under conditions with high electron donor concentration (10%) and bioaugmentation. However, lower moisture contents (17% to 19%) promoted reductive dechlorination of TCE to *cis*-1,2-DCE more effectively than a high moisture content (30%) when the electron donor concentration was low (1%). The later condition for moisture content and electron donor concentration was similar to the condition observed in the field.

- When liquid nitrogen was supplied in a commercially available trailer, approximately 20-30% of the liquid nitrogen was wasted due to ventilation to the atmosphere. The lost volume of nitrogen from tube trailers should be considered when the de*cis*ion for using tube trailers versus nitrogen generator is being made.
- If generators are to be used at a site, whether the generators are powered by fuel or electricity, the safety concerns must be addressed with regard to the placement of the generators and their proximity to the treatment area.
- Using both hydrogen and LPG at the site increases safety concerns, and relevant safety codes must be followed for the distance between LPG tank and the hydrogen cylinders (i.e., 30 feet for this demonstration). For large-scale projects where an on-site hydrogen generator is used, it is more economical to replace LPG by hydrogen gas.

IMPLEMENTATION COST

A cost model was developed for H_2T system. Four scenarios were considered and compared in this cost assessment based on data collected during this H_2T demonstration. In each scenario the H_2T system was compared with an alternative SVE system or soil excavation. Unit cost for a full-scale H_2T system (assumed to be about 50,000 cy) is projected to be \$49/cy. This would compare to the following costs per cubic yards: \$37 for a new-build SVE system; \$20 to keep an existing SVE system in operation for another two years; and \$97 for excavation. Sensitivity analyses were performed to evaluate the effect of gas flowrate and ROI on the unit cost of H_2T implementation.

It was concluded that while the cost of H_2T was greater than SVE system operation, the de*cis*ion to switch to H_2T operation over an SVE system should be made based on the overall performance and not only on the cost assessments. For example, in the demonstration site where an SVE system was operating since 2008, the SVE system was not able to reduce the mass in the vadose zone due to the very low permeability soil (i.e., clayey silt loess material), likely due to preferential removal from a high-permeability layer at the bottom of the treatment interval. Small molecules of hydrogen gas, on the other hand, were able to diffuse into the small pores of the low-permeability soil.

1.0 INTRODUCTION

1.1 BACKGROUND

As of 2005, the U.S. Department of Defense (DoD) has identified nearly 6,000 sites at its facilities that require groundwater remediation and has invested $20 billion for site cleanup over a 10-year period (Government Accountability Office [GAO], 2005). At many of these sites, unsaturated chlorinated volatile organic compound (CVOC) source zones located above the water table are producing and sustaining groundwater plumes. Many of these unsaturated sources are currently being treated with soil vapor extraction (SVE) technologies. Long-term SVE projects can be very costly, as the treatment process for the recovered vapors is expensive.

A low-cost, more passive treatment technology for unsaturated zones contaminated with chlorinated solvents was tested during this project. This technology can be applied when DOD site managers would like to shut down an existing SVE system, but where monitored natural attenuation may not be sufficient to control the groundwater plume that is sourced by the residual contaminants in the unsaturated zone. With such a technology, the cost for remediating these groundwater plumes can be greatly reduced, and a much more sustainable remedy can be implemented. “Anaerobic Bioventing” is an attractive option for unsaturated zone remediation because gases can disperse farther into the unsaturated materials than liquids. Gases can also potentially diffuse more thoroughly through the subsurface, to some extent minimizing the problems of preferential flow pathways that are more common with liquid flow.

Several studies have been conducted on the use of hydrogen as an electron donor for the anaerobic bioremediation of saturated and unsaturated porous media (Evans and Trute, 2006; Mihopoulos et al., 2002; Newell et al., 1997; Aziz et al., 2003a; Aziz et al., 2003b; Mihopoulos et al., 2000; Shah et al., 2001; Mihopoulos et al., 2001, Evans et al., 2009). Hydrogen technology using pure H_2 gas has been extensively tested as a treatment technology for groundwater (Air Force Civil Engineer Center [AFCEC], 2004; GSI, 2003; Fisher et al., 1999; Newell et al., 2001) and showed good performance where H_2 injections alone were able to promote vigorous biodegradation. The biological reduction of VOCs using hydrogen in groundwater has been pioneered by the AFCEC.

In general, these studies indicate that anaerobic biotreatment of CVOCs in the unsaturated soils (e.g., anaerobic bioventing) has potential as a remediation alternative for unsaturated soils. Since the technology relies on some very important technical criteria that can affect the performance of the technology (e.g., radius of influence, bioavailability, surface cover, etc.), field-scale application of this technology requires verification through a field-scale demonstration.

1.2 OBJECTIVE OF THE DEMONSTRATION

The overall objective of this project is to determine if H_2T can serve as a remediation technology for the unsaturated zone, either as the initial remediation technology applied at a site or as a polishing technology that will allow site managers to shut down expensive, low performance SVE systems that are no longer cost effective. H_2T is implemented by injecting a primarily inert gas mixture of nitrogen (N_2), propane (C_3H_8), hydrogen (H_2), and carbon dioxide (CO_2) gas through a series of widely spaced injection points to degrade chlorinated organic compounds.

The nitrogen (N_2) serves as a non-explosive carrier gas for the process. The propane serves as an inexpensive electron donor that naturally-occurring bacteria can use to remove oxygen from the vadose zone and control gas buoyancy. The hydrogen stimulates dechlorinating bacteria to biodegrade chlorinated organic compounds, forming innocuous daughter products such as ethane or ethene. This demonstration answers key questions about the performance, implementability, and cost of the technology. If successful, the H_2T system can serve as a cost-effective and more sustainable remediation technology (i.e., lower carbon-footprint) for unsaturated soils containing chlorinated solvents.

1.3 REGULATORY DRIVERS

Two main drivers for cleanup of TCE in soil at many sites is protection of groundwater and/or vapor intrusion. The current maximum contaminant level (MCL) established by the United States Environmental Protection Agency (USEPA) is 5 micrograms per liter (µg/L), while the maximum contaminant level goal (MCLG) for TCE is zero. Various states also may have drinking water regulations that apply to TCE. The Nebraska Department of Environmental Quality (NDEQ) has established a remediation goal of 57.0 µg/kg for TCE concentration in soil.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

In-situ biodegradation of chlorinated solvents (called reductive dechlorination) and bioventing are two proven remediation technologies with extensive application in groundwater and the unsaturated zone, respectively. Most of the groundwater applications of reductive dechlorination are based on the addition of soluble or semi-soluble substrates (i.e., molasses, lactate, Hydrogen Releasing Compound® [HRC®] polymers, edible oils) where the substrates ferment to form dissolved hydrogen (as a waste product), and then the dissolved hydrogen is used by dechlorinating bacteria to degrade chlorinated solvents. The role of hydrogen as an electron donor is widely recognized as the key factor governing the dechlorination of chlorinated compounds (Holliger et al., 1993; DiStefano et al., 1992; Maymo-Gatell et al., 1995; Gossett and Zinder, 1996; Smatlak et al., 1996; Hughes et al., 1997; Evans and Trute, 2006; Shah et al., 2001). There have been a wide variety of injection schemes, ranging from direct push of the amendments to groundwater recirculation systems. The addition of liquids to the unsaturated zone is difficult. However, relatively few biodegradation projects of this type have been performed in the unsaturated zone.

Bioventing (where air is injected at slow rates into the unsaturated zone) has proven to be very effective in remediating releases of petroleum products including gasoline, jet fuels, kerosene, and diesel fuel. Several field demonstrations and pilot applications of bioventing were reported in the literature for petroleum sites (for example, Ely and Heffner, 1988; Hinchee et al., 1991a; Hinchee et al., 1991b; Miller and Hinchee, 1990; Thomas and Ward, 1989; Urlings et al., 1990). Bioventing typically is applied in situ to the unsaturated zone and is applicable to any chemical that can be biodegraded rapidly by aerobic processes, and has been implemented primarily at petroleum-contaminated sites. Conventional bioventing using air has not been used for remediating releases of most chlorinated solvents such as perchloroethene (PCE), TCE, or other more highly chlorinated compounds because these compounds either do not degrade or degrade relatively slowly in aerobic environments.

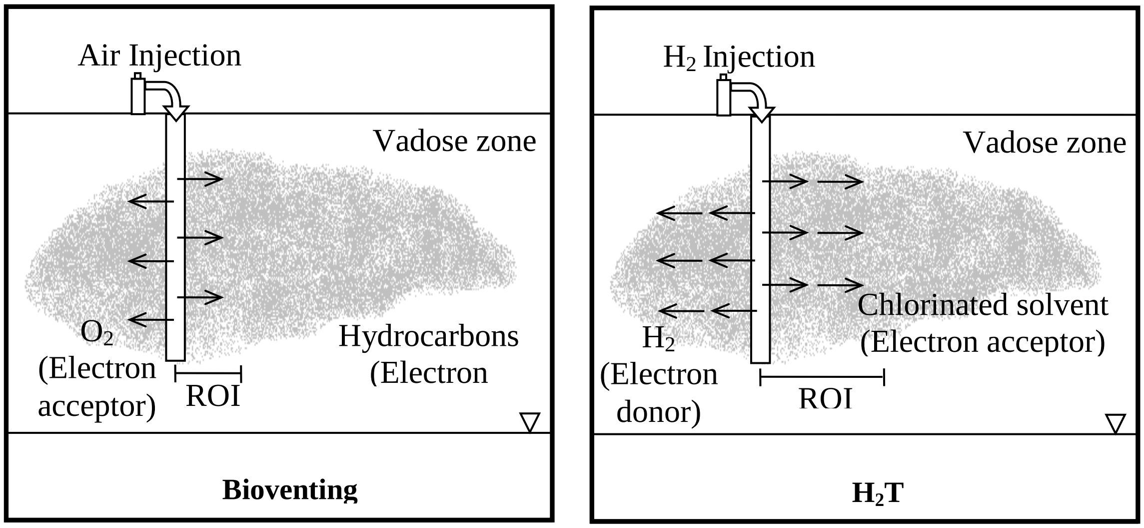

Figure 1. Comparison of H_2T and bioventing.

In the H_2T, reductive dechlorination and bioventing are combined to create a remediation technology (hydrogen-based treatment or H_2T) for sites where the unsaturated zone requires some type of treatment of chlorinated solvents. This approach for bioremediation of unsaturated soils containing chlorinated solvents was originally proposed in a patent by Hughes et al. (1997). Figure 1 shows the comparison of H_2T and bioventing. Biodegradation of the soil contaminant is facilitated by the injection of gaseous oxygen in bioventing or hydrogen gas in H_2T.

In the H_2T system, a mixture of nitrogen, hydrogen, propane, and carbon dioxide gases are injected into an unsaturated treatment zone. Nitrogen serves to flush oxygen from the soil gas, enhancing conditions for the anaerobic degradation of chlorinated solvents. Propane is used as an electron donor for scavenging oxygen (i.e., aerobic bacteria will use the propane to remove oxygen). Hydrogen is used as the electron donor for dechlorinating bacteria. Nitrogen and hydrogen can be purchased and delivered to the site, (which are refilled or changed out regularly by the gas provider as part of the gas delivery contract), or generated on-site depending on the size of H_2T application (i.e., total flowrate and treatment time). The stoichiometry of the dechlorination reaction indicates that for every one milligram (mg) of hydrogen utilized by dechlorinating bacteria, 21 mg of PCE can be completely converted to ethene.

In the unsaturated zone, the H_2T process relies on a gas injection skid consisting of piping, gages, safety equipment, process control system, and gas supply vessels that could connect to a piping manifold and injection wells at the site. At some sites, one advantageous configuration is conversion of a low-performance SVE system to H_2T, where the existing SVE blower and treatment system is decommissioned and replaced by the H_2T injection skid connected to the existing manifold and injection wells.

Hydrogen-based biodegradation can be applied in three ways:

1) As a replacement for traditional soil treatment technologies (SVE, excavation, liquid-based biodegradation, thermal treatment, or chemical oxidation) at sites where no treatment has yet occurred;
2) As a polishing step to replace expensive SVE systems that are no longer removing large amounts of contaminant mass; and
3) Potentially as a method to eliminate migration of solvent vapors to indoor air. In some cases, the existing SVE system hardware (injection points, manifolds, monitoring points) can be retrofitted to accommodate H_2 injection.

H_2T technology development is very similar to the gaseous Electron donor injection technology (GEDIT) that has been described in detail previously (Evans, et al., 2009; Evans and Trute, 2006; Evans, 2007). The previous Environmental Security Technology Certification Program (ESTCP) project (ER-200511) applied the GEDIT to perchlorate remediation (Evans et al., 2009). For that perchlorate remediation project, a gas mixture consisting of 79% N_2, 10% C_3H_8, 1% CO_2, and 10% H_2 was injected into the subsurface. Because the results of that project demonstrated success in the degradation of perchlorate, a similar gas mixture was used for this demonstration.

Several bench-scale and field-scale studies summarized above indicate that anaerobic biotreatment of chlorinated solvents in the unsaturated soils is possible. H_2T can be used in the vadose zone with sufficiently anaerobic conditions to attain reductive dechlorination. In general, any contaminant that can be anaerobically biodegraded is a potential candidate for H_2T (Evans and Trute, 2006; Evans et al., 2009; Mihopoulos et al., 2000; 2001; 2002; Tezel et al., 2004; Shah et al., 2001).

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.2.1 Advantages

The H_2T system has the following advantages compared to SVE and liquid-based unsaturated zone bioremediation projects.

Advantages compared to an SVE system are:

1) H_2T system does not require costly surface treatment equipment, such as thermal oxidizers;
2) H_2T system likely to be more sustainable from an environment perspective than SVE, which uses thermal oxidizers or regenerated activated carbon; and
3) Easier to permit in areas with stringent air discharge regulations.

Advantages compared to liquid-based bioremediation of the unsaturated zone are:

1) Larger radius of influence for gas injection than liquid chemical addition such as molasses or permanganate, thereby reducing costs;
2) Increased treatment of lower-permeability units due to the high diffusion coefficient of the hydrogen; and
3) Injection equipment operates automatically and requires little space.

2.2.2 Limitations

The main limitations to the H_2T process are as follows:

Safety concerns:

1) Use of hydrogen and liquefied petroleum gas (LPG) can a concern to some facilities and fire safety personnel on active sites;
2) Special knowledge is required to design the injection skid; and
3) Compressed and/or liquefied gases are used, and adequate safety procedures are needed when handling these materials.

Efficiency and reaction concerns:

1) Diffusion of oxygen from the surface can reduce the efficiency of the process, as this oxygen will remove electron donor. If oxygen diffusion is significant, then higher rates of nitrogen and electron donor gas addition may be required, thereby increasing costs.
2) At some sites, there may not be adequate dechlorinating bacteria present to degrade the chlorinated solvents.
3) At some sites, the radius of influence of the gas injection point may be limited due to diffusion of oxygen from the surface.

3.0 PERFORMANCE OBJECTIVES

The technical performance objectives of this project were evaluated through the collection of soil and vapor data within the treatment area. Performance objectives, along with the data collected to meet these objectives and the final performance results, are presented in Table 1.

Table 1. Performance objectives and results of H_2T demonstration.

Performance Objective	Performance Monitoring Data Used to Evaluate Objectives	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
Achievement of a greater ROI	Measure Helium, H_2, O_2 and propane concentration in the monitoring points. Monitoring points were located 10, 15, 20, and 40 ft from injection points.	ROI that is 50% greater compared to ROI of liquid addition to the unsaturated zone	**YES** • ROI for He was 15 ft • Low O_2 concentration in monitoring wells (MW) up to 40 ft • H_2, and propane detected in MWs up to 40 ft
Greater reduction in baseline (no action) mass	Estimate contaminant mass from volume-weighted TCE and *cis*-1,2-DCE concentrations in treatment zone soil samples for before (48 samples) and after (48 samples) demonstration.	50% or greater reduction in baseline (no action) mass and/or estimated mass flux	**NO** • TCE mass reduced by 56% • Number of soil samples above 57 µg/kg standard dropped from 27% to 10% • Total moles of CVOC unchanged
Higher cost savings compared to the continued operation of an SVE system	Calculate the cost of H_2T application compared to SVE and soil excavation by collecting the following data: ROI to estimate number of injection points; capital Cost (injection skid; manifold system, wells); gas cost; Operation and Maintenance (O&M) cost (operator cost; electricity); soil and vapor monitoring.	Greater cost savings compared to the continued operation of a SVE system or use of an injection-based system.	**SOMETIMES** • For full-scale application, H_2T unit costs (in $/cy) were $39 versus $97 for excavation versus $37 for SVE (although continued SVE appeared to be ineffective). • Continued operation of SVE for two years was estimated to be $20/cy versus $39/cy for H_2T. However, the H_2T process was more efficient at removing TCE (but not daughter products) from fine-grained soils than SVE.
Reduction in the carbon footprint compared to SVE	Estimate carbon footprint (H_2T: estimate volume of gasoline used by site operators to reach site; compile mass of key materials (polyvinyl chloride [PVC], steel, concrete); any electricity use. SVE: same but add natural gas use).	50% reduction in the carbon footprint compared to SVE using thermal oxidizer or activated carbon.	**MOSTLY YES** • H_2T carbon footprint was 8 tons of CO_2 compared to 21 tons for SVE (high end) • H_2T carbon footprint was 43% of SVE (low end)
Safety	Measure flammability, H_2 and propane air emission. Soil gas monitoring that includes explosivity measurements using explosivity meter.	Flammabilities of less than 10% of LEL for H_2 /propane mixture at surface	**YES** • No health and safety incidents occurred • H_2, and propane were never detected in ambient air
Qualitative Performance Objectives			
Ease of Use	Required operator manpower records for both SVE system that is used before H_2T and for H_2T system. Feedback from field personnel regarding ease of use of H_2T compared to SVE.	Lower time requirement for system setup and data collection	**YES** One field technician did the weekly O&M, made the pressure and flow readings and collected the data.

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4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

Atlas Missile Site 10 in Former Lincoln Air Force Base (AFB) was selected for the demonstration located in York, Nebraska (Figure 2).

Figure 2. Former Lincoln atlas missile site map, York, Nebraska.

Site 10 is the former Atlas "F" missile facility operated by the Former Lincoln AFB from 1960 to 1964. The major structure at the site is the underground missile silo, which is 174 ft in depth and 52 ft in diameter. Historic operations at the former missile silo have resulted in TCE concentrations in soil and groundwater that exceed NDEQ regulatory standards for CVOCs. Site 10 was deactivated and conveyed to a private individual in 1965.

Between 1999 and 2005, soil investigations were conducted to determine the levels of TCE concentrations in soil. These investigations were primarily focused on the pathway from the septic tank to the leach field. The septic system investigation revealed an area measuring approximately 8,978 square feet (ft^2) with TCE soil concentrations above the NDEQ remediation goal of 57.0 µg/kg, as shown in Figure 3 (red line). In 2006, a series of soil borings were completed at the site to investigate TCE concentrations in soil (Kemron, 2007).

The full-scale SVE well locations installed in September-October 2008 are shown in Figure 3. The vapor extracted from the wells was passed through an air/water separator. Generated fluids from the vapor separator were pumped to a nearby groundwater treatment system. Effluent vapors were discharged into the atmosphere (Kemron, 2009).

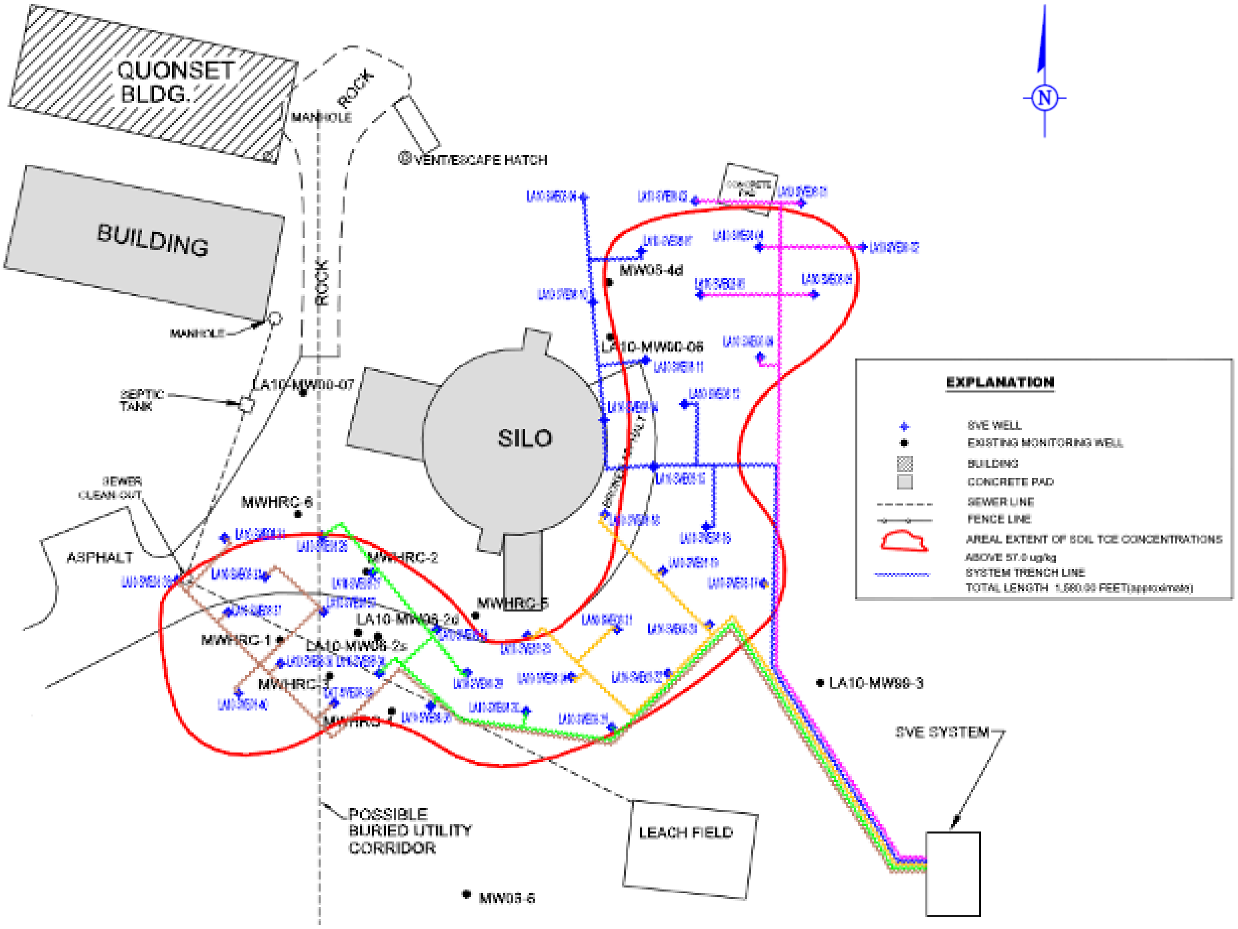

Figure 3. SVE system map.
(Source: Kemron, 2009)

4.2 SITE GEOLOGY/HYDROGEOLOGY

There are four distinct stratiographic layers typically found onsite: Peorian loess and Loveland loess (relatively low permeability), and the Grand Island Formation and glacial deposits (relatively high permeability). During the silo construction, an open cut excavation was used until groundwater was encountered. This resulted in a bowl shaped excavation, which was approximately 49.5 ft in depth and 325 ft in diameter. Once construction was complete, the inferred backfill was the stockpiled soil from the excavation.

The resulting composition of the soils around the silo is a mixture of silty clays with lenses of fine to coarse sands. Two units exist in the vadose zone: upper loess and lower fine sand. The loess layer is approximately 50 ft thick with a hydraulic conductivity, *K*, of approximately 0.005 feet per day (1.8×10^{-6} centimeters per second [cm/s]). The sand layer is approximately 15 ft thick, located between bottom of loess unit and water table with a hydraulic conductivity, *K*, of approximately 95 ft/day (3.3×10^{-2} cm/s).

4.3 CONTAMINANT DISTRIBUTION

Detected TCE concentrations in soil ranged from about 1 to 2,000 µg/kg based on the soil investigations conducted between 1999 and 2006. However, TCE concentrations were expected to be lower due to operation of the SVE system (Kemron, 2007). The majority of the remaining mass was believed to be located in the lower permeability loess unit, and concluded that removal by SVE from these lower-permeability zones was relatively inefficient.

The highest soil TCE concentration of 2,090 µg/kg was found at depth of 50 ft below ground surface (bgs) in boring LA10-SB06-103 at the northeast of the silo. Subsequently, the area around soil boring LA10- SB06-103 was further delineated to reveal an area of approximately 10,275 ft^2 that has TCE soil concentrations above the NDEQ remediation goal of 57.0 µg/kg. During the soil investigation, samples were collected at 20, 30, 40, and 50 ft below ground surface (bgs). A majority of the TCE soil exceedences were found in samples collected between 40 and 50 ft bgs, which is the transition zone between loess layers and the high permeability Grand Island formation.

Based on TCE and *cis*-1,2-DCE concentrations detected in soil during the 2006 investigation, two areas around the Silo were identified as potentially appropriate locations for further investigation: 1) at the east-northeast of the Silo (LA10-SB06-110, LA10-SB06-116, and LA10-SB06-122), and 2) around the southwest side of the Silo (SB05-33, SB05-34, and SB05-36).

Additional soil vapor monitoring and sampling programs were conducted on July 27 and August 30, 2010. On-site soil vapor monitoring consisted of recording oxygen, carbon dioxide, methane, and LEL readings. Off-site vapor analysis included VOC analysis using HAPSITE ER portable Gas Chromatograph/Mass Spectrometer (GC/MS). Samples were collected from all 39 SVE wells.

The data showed that:

- The highest soil vapor TCE concentrations were found at the east-northeast side of the silo (72,500 parts per billion by volume [ppbv] at SVE well LA10-SVE08-07);
- The highest soil vapor *cis*-1,2-DCE concentration were found at the east-northeast side of the silo (33,900 ppbv at SVE well LA10-SVE08-07); and
- Typical oxygen concentrations were lowest near the east-northeast side of the silo, and typically ranged from 8.4 to 18.8 % oxygen.

Analytical data for the samples collected during the August 2010 sampling program (35 days after the SVE system was shut off) generally showed increasing concentrations for TCE and *cis*-1,2-DCE concentrations in soil vapor relative to the July 2010 event (10 days after the SVE system was shut off). As expected, higher *cis*-1,2-DCE concentrations were observed in the same area where oxygen levels were relatively low (e.g., 10-15%). Based on the TCE and *cis*-1,2-DCE concentrations and lower oxygen levels at York site in the SVE wells on the east-northeastern side of the Silo (e.g., LA10-SVE08-07, LA10-SVE08-08, LA10-SVE08-11, LA10-SVE08-14, and LA10-SVE08-18), the area east-northeast of the Silo was selected as the location to perform H_2T pilot test.

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5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

With H_2T, a mixture of nitrogen gas and gaseous electron donors hydrogen, propane, and carbon dioxide was injected through a series of widely spaced injection points. The hydrogen drives in situ biodegradation by dechlorinating bacteria, transforming contaminants to innocuous daughter products such as ethene or ethane. An approximately 6-month bench-scale microcosm study was also conducted to better understand the extent to which reductive dechlorination of TCE would occur using the site vadose-zone soils and increase insight on the optimal gaseous electron donor mixture to be used in the demonstration.

Phase 1 involved the pre-treatment characterization using direct push techniques to evaluate the contaminant concentrations and soil characteristics. The baseline characterization activities included drilling 36 boreholes, collecting soil samples, and installing multi-level monitoring points.

Phase 2 involved the design and construction of gas mixture injection skid and underground piping. The injection skid consisted of piping, pressure and flow measurement gages, safety equipment, process control system, and gas cylinders that were connected to the piping manifold on the skid and injection wells at the site. Gas mixture was injected in a steady state mode with a constant low-flowrate gas stream (i.e., total flowrate <1 scfm). A tracer test was conducted in Phase 2 to verify injection and monitoring wells performances and to characterize gas transport in the vadose zone. The tracer gas was a mixture of 90% nitrogen and 10% helium gases.

Phase 3 involved an approximately 6-month operation and process monitoring period of the H_2T system. Monitoring of the influence of the hydrogen delivery approach on bioremediation processes relative to the control condition was achieved through the collection of soil vapor samples from all monitoring and injection wells. Sample analysis included concentrations of contaminants, daughter products, oxygen, and hydrogen.

Phase 4 consisted of post-treatment sampling, data analysis tasks, and writing the final project report. Soil samples were collected at the end of the treatment period (as determined based on process monitoring data), to compare to the soil concentrations measured in the pre-treatment (Phase 1) samples. Process monitoring data was evaluated in terms of the stated project objectives.

5.2 BASELINE CHARACTERIZATION ACTIVITIES

A total of nine injection points (i.e., three clusters of three holes at different depths) and 27 monitoring points (i.e., nine clusters of three holes at different depths) were installed and registered in the state of Nebraska. The three injection points in each cluster were equally spaced vertically in the vadose zone at depths of 20, 30 and 40 ft bgs. The three soil gas sampling points in each cluster were equally spaced vertically in the vadose zone at depths of 15, 30 and 45 ft bgs.

The deep soil gas injection and monitoring points in each cluster were logged in accordance with American Society for Testing and Materials (ASTM) D 2488 standard and Unified Soil Classification System (USCS) classification guidelines. Soil samples were collected from this borehole. Soil samples collected during monitoring point installation were representative of baseline conditions before gas injection. Soil samples from each of the 12 Geoprobe holes were collected at depths of approximately 10, 20, 30, and 40 ft bgs.

Soil concentrations ranged from <6.0 to 1,200 µg/kg for TCE and from <5.9 to 2,100 µg/kg for *cis*-1,2-DCE. Out of 48 soil samples (e.g., 12 points and 4 depths each), 26 samples have TCE concentrations above the NDEQ remediation goal of 57.0 µg/kg. Soil samples were also tested for *trans*-1,2-dichloroethene, vinyl chloride, and 1,1,1-trichloroethane (1,1,1-TCA). *trans*-1,2-DCE concentrations ranged from <5.9 to 73 µg/kg. Vinyl chloride and 1,1,1-TCA were not detected in any of the soil samples.

Vapor concentrations ranged from non-detect (ND) to 180.9 part per million by volume (ppmv) for TCE and from ND to 157.9 ppmv for *cis*-1,2-DCE. trans-1,2-DCE concentrations ranged between ND-8.6 ppmv. Vinyl chloride was not detected in any of the samples and 1,1,1-TCA was only found in MW-2D at a concentration of 0.006 ppmv.

5.3 DESIGN AND INSTALLATION OF GAS INJECTION SYSTEM

The injection skid consisted of piping, gauges, safety equipment, process control system, and gas cylinders that were connected to the piping manifold and injection wells at the site. Photos of the H_2T system configuration are shown in Figure 4. The gas injection system was designed to be operated without any electrical requirements because of the remoteness of the site and the safety concerns. Each gas flow was controlled using manual pressure regulators and flow control valves along with rotameters to measure flow and gauges to monitor pressure.

The piping from the skid to the injection wells wwa buried under ground to prevent damage during mowing. To comply with the required separation regulations in National Fire Protection Association (NFPA) 55, the propane tank was placed approximately 30 ft away from the hydrogen cylinders. Gas vendors replaced the gas supply containers (either compressed gas cylinders or liquid gases), as needed based on the readings during the weekly O&M, typically on the order of every week or every few weeks. Gas mixture was injected in a steady state mode at a flowrate of 0.28 scfm per injection point.

Leak tests were performed using soapy water at the end of the system installation. After the leak test of all gas lines, the excavated areas were filled using the excavated soil. Additionally, Hazard/Warning and NFPA decals were placed on the skid and propane lines to alert site vistors of potential hazards. The system leak test was performed once a week during the Weekly O&M. During the leak test, if any sign of bubbles were observed, the connection was re-tightened or re-connected using Teflon tape.

Figure 4. H_2T system.

5.4 FIELD TESTING

A tracer test was performed to verify injection and monitoring wells performances and to characterize gas transport in the vadose zone. The tracer test generated data that was used to demonstrate potential ROI without biological uptake, as well as to identify the presence of preferential pathways. The tracer gas was a mixture of 90% nitrogen and 10% helium. Helium and oxygen levels were monitored at both the injection and monitoring wells for a total of three events (Day 1, Day 4, and Day 7 of the tracer injection startup). The ROI for the tracer helium gas was estimated to be the distance from the injection well where 50% of the injected helium concentration was observed in the monitoring well.

Gas Mixture Injection and Process Monitoring: Over the 6-month gas injection operation and process monitoring period, a total of 830,000 standard cubic ft of gas was injected with the following average composition: 10% hydrogen, 79% nitrogen, 10% propane, and 1% carbon dioxide. The nitrogen and propane were added to help keep the system anaerobic from oxygen diffusing into the test zone. The carbon dioxide was added to ensure a carbon source for the dechlorinating bacteria. Weekly O&M was performed during H_2T system operation phase. The injection system was designed so that it did not need to be shut down for tank refill and cylinder replacements.

Based on the hydrogen concentrations at the monitoring points and the treatability test results, the total gas flow rate and hydrogen composition were doubled for the last month of the injection phase. The total gas flow rate was increased from 2.5 scfm to 5.0 scfm and hydrogen composition was increased from 10% to 20%. Flow and hydrogen composition were increased for the last month of the injection phase to evaluate whether increasing the flow rate would lower the oxygen levels in medium and deep zones.

Monitoring of the influence of the gas mixture delivery and the system performance during the gas injection phase was achieved through the collection of soil vapor samples from the monitoring points. Sample analysis included concentrations of VOCs, H_2, O_2, and CO_2. Soil gas was measured every two months to determine progress and to evaluate if modifications to the sampling frequency or an extension of this monitoring period would provide valuable performance data.

The collection of spatial and temporal data provided a means of evaluating the rate of the injected gas mixture transport and distribution within the treatment zone, as well as its effect on the rate of dechlorination. Data validation for the process monitoring sample set was provided by the inclusion of adequate controls in the design of the demonstration. The scattered placement of the monitoring served to minimize the contribution of small-scale heterogeneities on the performance of the technology.

Post-Bioremediation Characterization: The post-treatment characterization phase was similar to the pre-treatment characterization phase. The location of each soil sampling point was approximately 1-2 ft from the location of the deep well for each injection or monitoring points. In addition, soil samples were collected from four additional locations (i.e., 16 additional soil samples) around SVE wells SVE-7 and SVE-8 inside and outside the treatment area. The 16 additional samples were collected after it was noticed that some of the injected gas had entered

SVE wells 7 and 8 (i.e., high H_2 concentrations at these two wells), and the soil samples were collected from "inside" and "outside" of the treatment zone around SVE wells to show (if any) the difference in the TCE mass reduction.

The chlorinated solvent removal rate as well as the duration of the potential enhancement effect provided by the gas mixture was evaluated using the post-treatment characterization dataset. The latter was assessed through analyses of CVOC concentrations as well as by the abundance and/or increase/decrease in DHC species in the treatment zone.

Composite soil samples were collected from the excess soil collected during the well construction and confirmation boring drilling events, and sent to lab to determine if the soil concentrations are above or below the 80 µg/kg. In the state of Nebraska, any soils that are below the 80 µg/kg of TCE (i.e., Preliminary Remediation Goal) may be disposed directly on the surface. Since the TCE concentrations were below 80 µg/kg in all composite soil samples, the soils were emptied on site on the ground. Based on historic generator knowledge (previous analytical data), the soils were not hazardous waste (>10,000 µg/kg).

5.5 SAMPLING PLAN

The sampling plan including the number of samples collected and the analytical methods are provided in Table 2 and Table 3.

Table 2. Analytical methods used for sample analysis.

Matrix	Analyte	Method	Container	Preservative[1]	Holding Time
Soil	VOC[2]	SW8260	4 oz glass jar	None	14 days
	Moisture content	SW3550	4 oz glass jar	None	28 days
	DHC	In-house[3]	4 oz plastic jar	None	28 days
	Nutrients, pH, Organic carbon	In-house[4]	8 oz plastic jar	None	28 days
	Particle size	ASTM[5]	4 oz plastic jar	None	28 days
Soil gas	VOC[2]	In-house[6]	22 ml vial	None	72 hours
	VOCs screening	PID	NA	NA	NA
	Relative humidity	Field	NA	NA	NA
	Temperature	Field	NA	NA	NA
	Hydrogen	Field	NA	NA	NA
	Oxygen	Field	NA	NA	NA
	Carbon Dioxide	Field	NA	NA	NA
	Helium	Field	NA	NA	NA

[1] Preservatives were not required for these samples; however, all samples were stored and shipped at 4EC.
[2] Soil and vapor samples were tested for TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, Vinyl Chloride, 1,1,1-TCA, ethane, ethane, propane, and methane.
[3] Gene-Trac-Dhc and Gene-Trac Vinyl Chloride DNA tests were conducted using an in-house method at SiREM laboratory.
[4] Nutrient, pH, and organic carbon measurements were conducted using standard methods at Olsen laboratory.
[5] Particle size distribution analysis was conducted using ASTM D422/D4464M methodology.
[6] Soil vapor samples were collected using syringes in 22ml vials and analyzed using in-house method at Vaportech Services, Inc. laboratory.
PID = photoionization detector

Table 3. Total number and types of samples collected.

Component	Matrix	Number of Samples	Analyte	Location
Pre-demonstration sampling	Soil	48	VOC[2]	Deep borings at 10, 20, 30, and 40 ft bgs
	Soil	9	Physical/chemical parameters[1]	Three locations and three points at 10, 25, and 40 ft bgs
	Soil	9	Nutrients, pH, Organic carbon	Three locations and three points at 10, 25, and 40 ft bgs
	Soil	9	DHC	Three locations and three points at 10, 25, and 40 ft bgs
	Soil gas: Field measurement	Bi-monthly	H_2, O_2, CO_2, He, VOC[3]	All subsurface monitoring points
	Soil gas: Laboratory measurement	32	VOC[2], field blanks and duplicates	All subsurface monitoring points
Technology performance sampling	Soil gas: Field measurement	Bi-monthly	H_2, O_2, CO_2, VOC[3]	All subsurface monitoring points
	Soil gas: Laboratory measurement	96 (32 samples every 2 months)	VOC[2], field blanks and duplicates	Same subsurface monitoring wells selected for initial sampling
	Surface emissions	Bi-monthly	H_2, CO_2, VOC[3]	Ground surface and in the flush mounts at injection points
Post-demonstration sampling	Soil	48 (plus 16 samples from around SVE wells)	VOC[2]	Locations near Deep borings at 10, 20, 30, and 40 ft bgs
	Soil	9	Physical/chemical parameters[1]	Same as pre-demonstration sampling.
	Soil	9	Nutrients, pH, Organic carbon	Three locations and three points at 10, 25, and 40 ft-bgs
	Soil	9	DHC	Same as pre-demonstration sampling
	Soil gas: Field measurement	Bi-monthly	VOC[3]	Same subsurface monitoring points selected for initial sampling
	Soil gas: Laboratory measurement	32	VOC[2], field blanks and duplicates	All subsurface monitoring points

[1] Physical and chemical parameters measured included USCS soil classification, moisture content, particle size, moisture content, and pH.

[2] Soil and vapor samples were tested for TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, Vinyl Chloride, 1,1,1-TCA, ethene, ethane, propane, and methane.

[3] Soil gas and surface emission were screened for VOCs in the field using PID and LEL meter.

5.6 SAMPLING RESULTS

Comprehensive sampling results and analyses are provided in the ER-201027 final report (GSI, 2012). The results are summarized below.

Tracer Test: Helium gas reached the 10 ft distance monitoring wells (MW-5S, M, and D) after 16 hours. Traces of helium gas were observed at some of the shallow wells within 10-20 ft from the injection wells (e.g., MW-1S, MW-3S, and MW-4S). Also, a trace of helium gas was observed at MW-6M and MW-6D that can potentially be explained by the layers of fine to medium size sand observed during the logging of MW-6 in lower depths. Tracer gas reached the 15 ft distance monitoring wells (MW-3, and MW-6) at Day 4. After 4 and 7 days, helium was observed at almost all the monitoring wells, however, the levels of helium percentage were not high enough (i.e., 50% of injection helium concentration) to increase the ROI above approximately 15 ft.

The tracer test also generated data that demonstrate the presence of preferential pathways. For example, helium concentrations at MW-8 were higher than helium concentrations at MW-7 for both Day 4 and Day 7 of the test. Also, helium concentrations at MW-9, which is approximately 30 ft away from the closest injection well, were higher than most of the monitoring wells that are in the 15-20 ft distance from the injection wells (for example, compare helium percentages at MW-9 wells with MW-1, MW-2, and MW-7). After four days of tracer injection the helium concentrations at MW-3S reached 4.7% while maximum helium concentrations in the monitoring points MW-3M and MW-3D were 3.5% and 2.5%, respectively.

Vapor Sampling Results: Corrected injected gas flowrate over time for each injection points is shown in Figure 5. The lower flowrates in IW-1D and IW-2D injection points and higher flowrates at IW-3D were consistent with the lithology observations during soil logging and the pressure readings. An increase in hydrogen and propane concentrations and decrease in oxygen concentrations were observed at the monitoring points after increase in the flow rate and hydrogen composition.

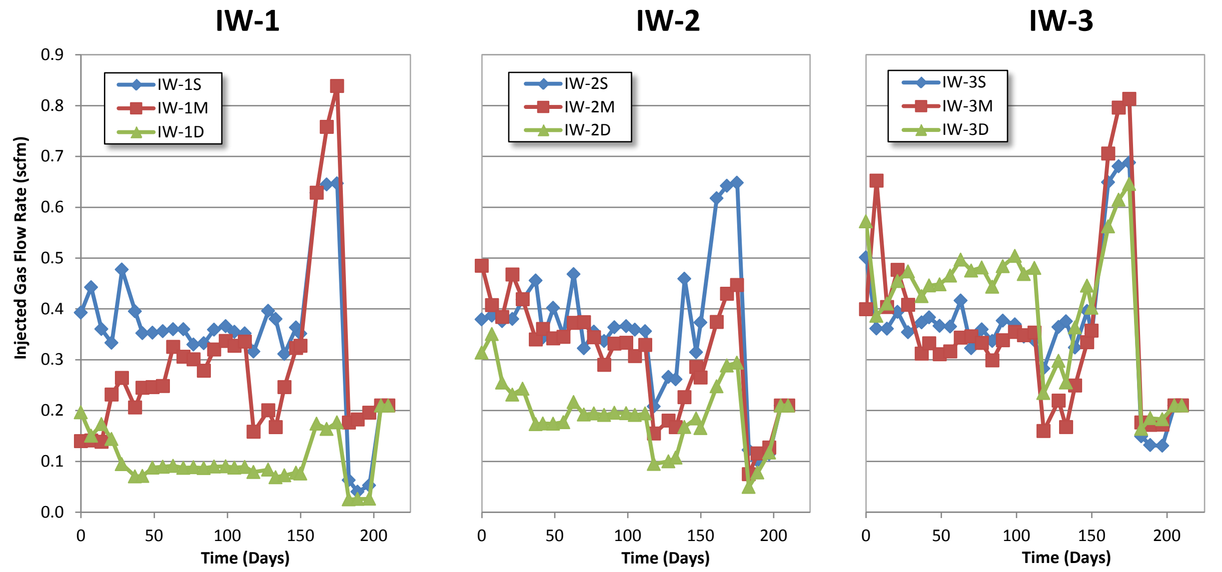

Figure 5. Corrected injected gas flowrates at three injection wells at different depths.

TCE concentrations ranged from <0.005 ppmv to 180.9 ppmv in May 2011, and from 0.005 ppmv to 78.5 ppmv in December 2011. The maximum TCE concentration in the vapor phase decreased by 57%. The median TCE concentration decreased by 78% from 4.47 ppmv to 1.00 ppmv. Concentrations of *cis*-1,2-DCE ranged from <0.01 ppmv to 157.9 ppmv in May 2011, and from <0.01 ppmv to 60.8 ppmv in December 2011. The maximum *cis*-TCE concentration in the vapor phase decreased by 62%. The median *cis*-TCE concentration decreased by 63% from 14.3 ppmv to 5.22 ppmv.

Before the gas mixture injection, measured oxygen concentrations ranged from 13.6% to 19.3% in the shallow monitoring points, from 13.2% to 19.4% in the medium monitoring points, and from 5.9% to 19.5% in the deep monitoring points. After gas mixture injection, measured oxygen concentrations ranged from 0.1% to 1.1% in the shallow monitoring points, from 0.1% to 10.7% in the medium monitoring points, and from 0.0% to 10.1% in the deep monitoring points.

The comparison of TCE and *cis*-1,2-DCE, and hydrogen and methane, in the H_2T monitoring wells before (i.e., pre-treatment characterization phase, May 2011) and after (i.e., post-treatment characterization phase, December 2011) gas injection phase are illustrated in Figure 6.

For the medium and deep monitoring points, oxygen concentrations increased significantly at around 15 ft distance from the point of injection. While deeply anaerobic conditions never reached at the medium and deep monitoring points, significant reduction in oxygen concentrations was attainable at the medium and deep monitoring intervals. Average oxygen concentrations were reduced from 16.1% to 0.4% in shallow, 16.8% to 5.7% in medium, and 16.3% to 5.7% in deep monitoring points. The low oxygen concentrations in the shallow monitoring points were observed at distances up to 40 ft away from the point of injection.

The hydrogen concentrations at different depths (i.e., shallow, medium, and deep) measured during and after the gas injection period are presented in Figure 7. Hydrogen concentrations before the gas injection were below the H_2 meter detection limit (i.e., 25 ppmv) at all monitoring points. Hydrogen concentrations never reached the injected concentration of 10%. The highest hydrogen concentrations were observed at the shallow depths (i.e., 15 ft bgs). Hydrogen concentrations decreased as the depth increased and as the distance from injection increased. Hydrogen was detectable at all depths and distances as far as 40 ft from the injection point exceeding the 15 ft target ROI.

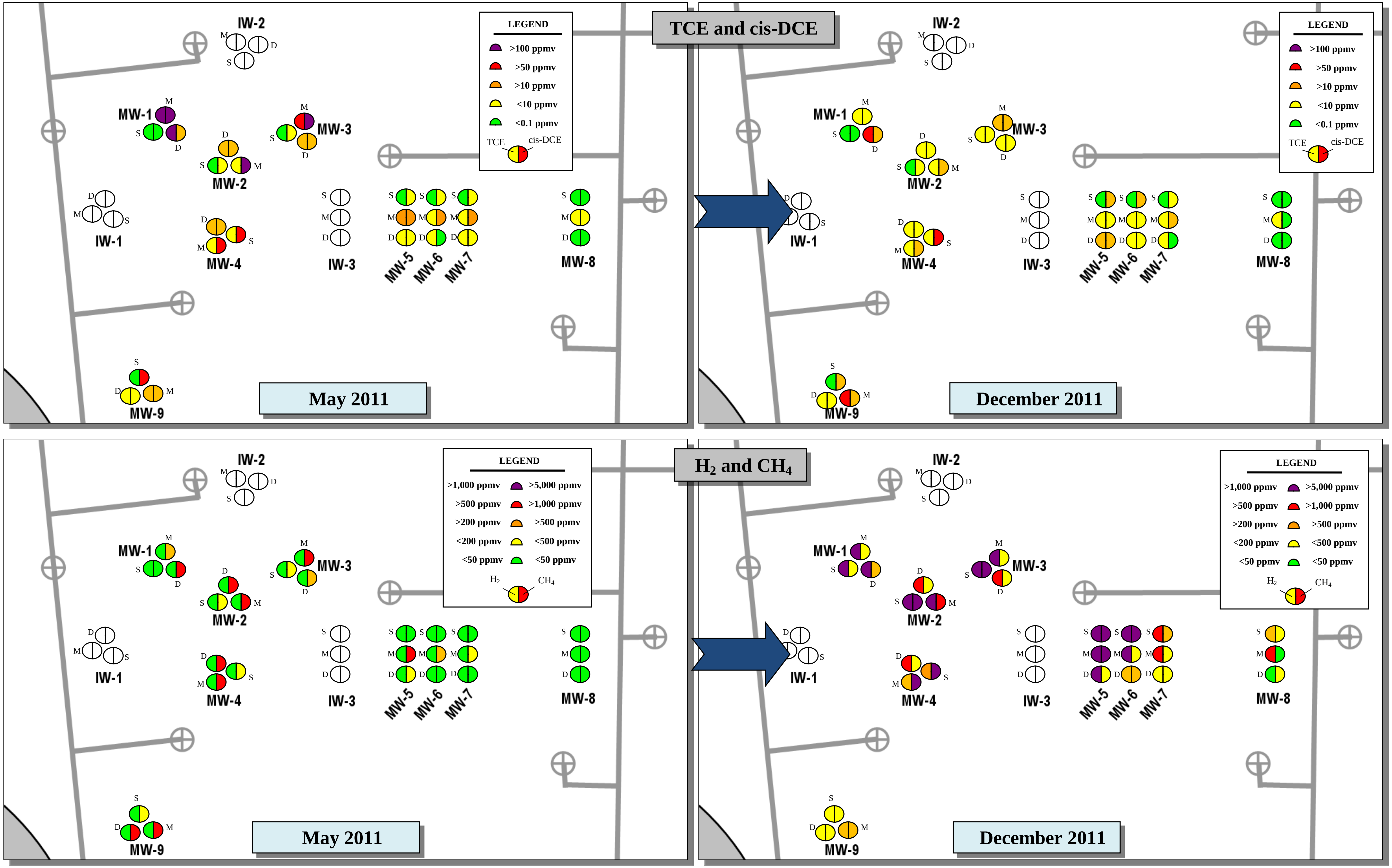

Figure 6. Soil vapor sampling results – pre-treatment characterization phase (May 2011) and post-treatment characterization phase (December 2011).

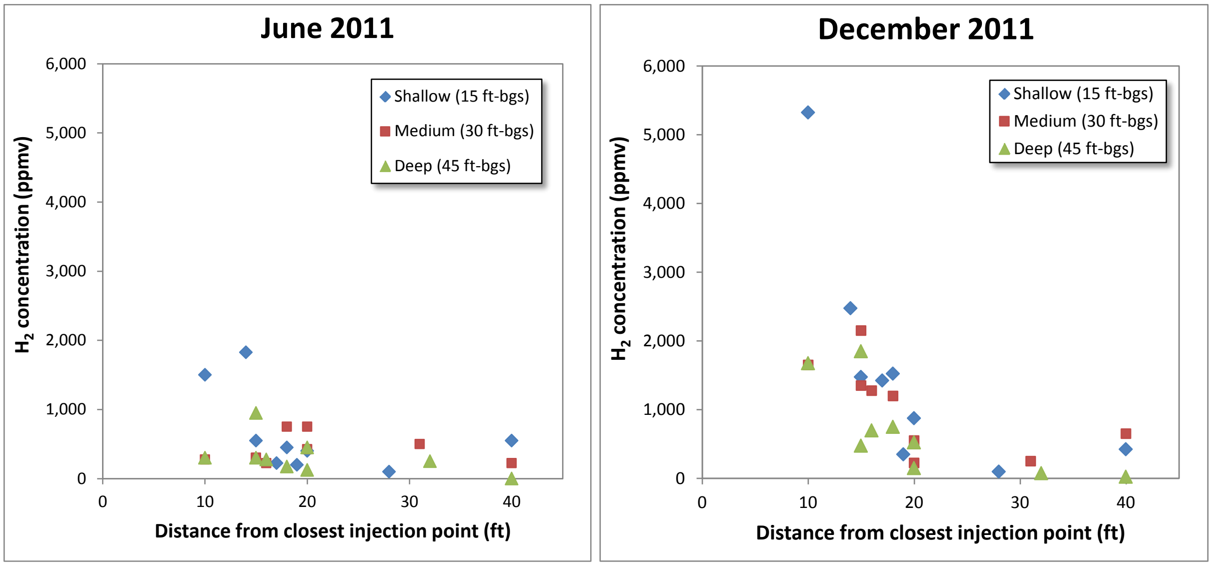

Figure 7. Hydrogen concentrations at different depths versus the distance from the closest injection point at first sampling event (left) **and after** (right) **gas injection.**

Soil Sampling during Post-Treatment Characterization: Soil sampling results from the post-treatment characterization phase and the comparison to the results from pre-treatment characterization phase are summarized in Table 4 and Table 5.

The t-test and Mann-Whitney analysis conducted on the 48-pair samples showed that by approximately 90% confidence the post-treatment TCE concentrations are smaller than the pre-treatment TCE concentrations. Similar analyses performed for *cis*-1,2-DCE showed that there is greater than a 90% but less than a 95% probability that the post-treatment *cis*-1,2-DCE soil concentrations are significantly greater than the pre-treatment *cis*-1,2-DCE soil concentrations.

Table 4. Statistics of 48 soil samples (pre- and post-treatment).

Median Concentration (µg/kg)	Pre	Post	% Change
TCE	7.85	3.95	-50%
cis-1,2-DCE	17	39.5	132%
trans-1,2-DCE	0.31	1.4	359%

Note: ND concentrations were assumed to be equal to 50% of Reporting Limit (RL).

The number of soil samples with TCE concentrations above 57 µg/kg, which is the NDEQ soil remediation goal, dropped from 13 samples in pre-treatment to five samples in post-treatment. The number of soil samples with *cis*-1,2-DCE concentrations above 400 µg/kg, which is the NDEQ soil remediation goal, dropped from 10 samples in pre-treatment to nine samples in post-treatment.

Table 5. Change in (a) the total VOC mass and (b) moles for all the samples.

(a)

Mass (g)	Pre	Post	% Change
TCE	289.0	127.2	-56%
cis-1,2-DCE	463.7	573.1	24%
trans-1,2-DCE	8.0	16.2	102%
Total	**760.7**	**716.6**	**-5.8%**

(b)

Moles	Pre	Post	% Change
TCE	2.2	1.0	-56%
cis-1,2-DCE	4.8	5.9	24%
trans-1,2-DCE	0.1	0.2	102%
Total	**7.06**	**7.05**	**-0.2%**

1) The concentrations of the ND samples were assumed to be equal to 50% of Reporting Limits (RL)
2) MW-9 was excluded for mass calculations

Additional soil samples (i.e., eight pairs) were collected from four additional locations (i.e., total of 16 additional soil samples) around SVE wells SVE-7 and SVE-8 inside and outside the treatment area. The t-test conducted on the 8-pair samples showed that by 92% confidence the inside-treatment area TCE concentrations are smaller than the outside-treatment area TCE concentrations. The number of samples was not enough to conduct Mann-Whitney test.

5.7 BENCH-SCALE TREATABILITY STUDY

In support of the H_2T demonstration in the field, a bench-scale treatability study of reductive dechlorination in unsaturated soil using several gaseous electron donor mixtures was conducted by Dr. Pat Evans' team at CDM Smith Environmental Treatability Laboratory. A summary of the bench-scale treatability study is described below.

The objectives of the bench-scale treatability study were to:

- Determine the extent to which reductive dechlorination of TCE occurs under unsaturated conditions in vadose-zone soil from the site.
- Identify the optimum gaseous electron donor mixture to be used in the demonstration, and investigate performance differences between propane and LPG.
- Evaluate the effects of soil moisture levels, gaseous electron donor mixtures, phosphorus addition, and bioaugmentation on reductive dechlorination of TCE and its daughter products.

TCE removals ranged from 35% to >99%, and a few conditions achieved full dechlorination to ethene. This demonstrates that complete reductive dechlorination was possible in this soil. Control bottles with neither gaseous electron donors nor bioaugmentation achieved 40% to 60% removal of TCE. Abiotic attenuation and sorption to the stoppers were probably the major sources of TCE removal in the un-bioaugmented controls.

TCE removal was consistently higher with bioaugmentation than without. No un-bioaugmented condition exceeded 70% TCE removal, whereas several of the bioaugmented conditions achieved >99% removal. Production of *cis*-1,2-DCE occurred in all of the bioaugmented conditions, indicating that part of the TCE loss was due to biodegradation.

Moisture level and electron donor concentration interacted to produce complex effects. With a high electron donor concentration, increased moisture was beneficial, whereas at a low electron donor concentration, increased moisture was detrimental. When high hydrogen concentrations, bioaugmentation, and LPG were used, TCE removal was not significantly affected by increased moisture levels. Increase in moisture had the opposite effect on TCE removal when the electron donor concentration was low (Figure 8).

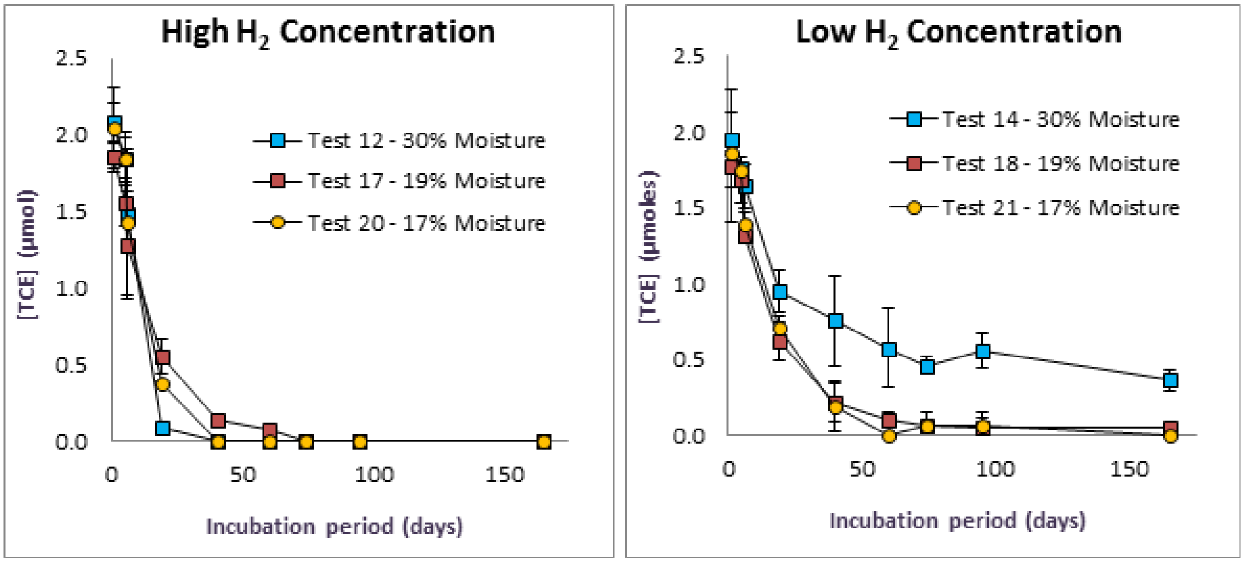

Figure 8. TCE concentrations with high (left) **and low** (right) **hydrogen concentration and LPG for varying moisture contents.**

Treatability Study Conclusions: The treatability study demonstrated that complete reductive dechlorination of TCE and its daughter products could occur in site soils with the addition of the gaseous electron donor hydrogen. However, several factors influenced the success of electron donor addition. Bioaugmentation with a commercially available culture containing *Dehalococcoides* had the greatest impact. All bioaugmented conditions rapidly achieved at least some transformation of TCE to *cis*-1,2-DCE, whereas none of the un-bioaugmented conditions did so until the last sampling point of the experiment. Complete dechlorination of TCE to ethene occurred only with bioaugmentation, and when moisture level and electron donor concentration were both high. For fastest bioremediation of Site vadose zone soil using this technology, a combination of bioaugmentation, high electron donor dosing, and moisture addition would be required.

However, the fact that some TCE transformation did occur in un-bioaugmented bottles after 100 days of incubation suggests that, given time, dechlorinator activity may increase at the site. Whether additional time would lead to complete reductive dechlorination is not known, but is not considered likely. Addition of the phosphorous nutrient triethyl phosphate did not appear to promote reductive dechlorination in un-bioaugmented microcosms, but may have initiated methanogenesis. LPG, which was added along with hydrogen, carbon dioxide, and nitrogen, was not inhibitory to reductive dechlorination when compared to pure propane gas. Because the LPG used in the bench-scale testing was not from the same source as the LPG used during the field demonstration, the lack of inhibition observed during the bench-scale testing does not unequivocally prove that the LPG used in the field was not inhibitory. It is possible that there could be differences in the concentrations of inhibitory minor constituents in LPG, from one refinery to another and also batch-to-batch differences. However, the observed increases in DCE during the field demonstration serve as one line-of-evidence indicating that the LPG used at the site did not appear to be inhibitory to reductive dechlorination.

A high moisture content (30%) promoted the most complete reductive dechlorination under conditions with high electron donor concentration (10%). Bioaugmentation interestingly, with lower moisture contents (17% to 19%) promoted reductive dechlorination of TCE to *cis*-1,2-DCE more effectively than a high moisture content (30%) when the electron donor concentration was low (1%). The reason appears to be competition for hydrogen since hydrogenotrophic methanogenesis led to rapid depletion of 1% hydrogen in the high moisture condition. This depletion may have resulted in hydrogen concentrations less than threshold requirements for reductive dechlorination. Thus use of low hydrogen concentrations in a field setting would require continuous injection to prevent depletion.

5.8 SUMMARY

The total estimated TCE mass in the treatment zone dropped from 289 grams during the pre-treatment characterization phase to 127 grams during the post-treatment characterization phase (i.e., 56% mass reduction). The total estimated *cis*-1,2-DCE mass increased from 464 grams during the pre-treatment characterization phase to 573 grams during the post-treatment characterization phase (i.e., 24% mass increase), for a total of 6% reduction in total chlorinated compounds. The molar mass of chlorinated compounds was unchanged (7.1 moles before versus 7.1 moles after). Therefore, while the system was successful at converting TCE, a "*cis*-DCE stall" condition at the site appeared to be present at the site.

Comparison of Field and Laboratory Test Results: H_2T demonstration at the site and the treatability tests in the laboratory were conducted in parallel. Key points from the field and laboratory tests are summarized below:

- The H_2T process removed half the TCE from the test zone that had been treated with soil vapor extraction for three years. This indicates the process may be effective for treating finer-grained units that are difficult to treat with SVE.
- In-test measurements of redox-related parameters (oxygen, methane) indicated that deeply anaerobic conditions were not achieved uniformly through the test zone, a likely contributing factor for the observed *cis*-DCE stall condition. For example, the average oxygen content in the treatment zone soils during test ranged from 0.1% to 11%.
- Lab microcosm work where the gas mixture was added to soil samples from the site indicated that samples that had been bioaugmented with dechlorinating bacteria performed much better than unamended soils, indicating a dechlorinating bacterial limitation at the site. The team strongly recommends that one should understand the bacterial limitation and issues involved with vadose zone bioaugmentation before attempting this technology.
- Redox-related parameters (oxygen, methane) measured in the field indicated that deeply anaerobic conditions were not achieved uniformly through the test zone, a likely contributing factor for the observed "*cis*-DCE stall" condition. The research team concluded that the system's inability to create deeply anaerobic conditions was likely a

major factor in the "*cis*-DCE stall" issue. The team recommends that one should understand the issues involved with creating and sustaining deeply reducing conditions before attempting this technology.

- Additional microcosm results indicated that low moisture may have been a contributing factor to this bacterial limitation. Lab microcosm work showed that a high moisture content (30%) promoted the most complete reductive dechlorination under conditions with high electron donor concentration (10%) and bioaugmentation. However, lower moisture contents (17% to 19%) promoted reductive dechlorination of TCE to *cis*-1,2-DCE more effectively than a high moisture content (30%) when the electron donor concentration was low (1%). The later condition for moisture content and electron donor concentration was similar to the condition observed in the field.
- It is possible to safely injection the hydrogen, nitrogen, propane, carbon dioxide gas mixture in the test zone. The radius of influence from the injection point was approximately 15 ft.
- In-test vapor VOC monitoring data were not very helpful in evaluating the progress of remediation.
- The H_2T system for this test was more successful than the existing SVE system at removing TCE from the fine-grained soils at this test site, but was not successful at removing a significant fraction of the *cis*-DCE. To help drive a full-scale H_2T drive test, treatment zone to deeply anaerobic conditions, some type of barriers over the top and around the sides of the treatment zone (even something as simple as adding water to reduce the gas permeability of the soils) might help break out of a *cis*-DCE stall condition.

Lessons Learned: A summary of the lessons learned during the H_2T implementation at the demonstration site is below:

- While *cis*-DCE was observed in the unsaturated zone, it still may be difficult to get to deeply anaerobic conditions. Future applications need to consider how to put in barriers to stop or reduce oxygen inward diffusion around outside of treatment zone, and potential caps or covers for top (we did not have a top diffusion problem at the demonstration site). One potential approach is wetting the soils around the perimeter of the treatment zone with soaker hoses or injection wells. It is likely that multi-level injection wells would be required to provide adequate distribution of water, around the perimeter, and across all the desired depth intervals.
- Extensive consideration was given near the last half of this test to see if some type of bioaugmentation could be performed. In the end the difficulties in distributing a liquid containing bacteria throughout this fine-grained unsaturated test zone was considered to be difficult.
- The H_2T process is best suited for fine-grained soils with a reasonable degree of pneumatic interconnectivity. The structure of silty, loess-like soil at the site may have included some micro-fractures, which probably conveyed the majority of the volume of gas around some areas within the treatment zone. It would follow that the postulated,

disconnected, zones of low permeability may have retained enough oxygen to inhibit reductive dechlorination within these zones. In a general sense, it is postulated that higher permeability soils (i.e., fine-grained sands) may allow for more uniform distribution of gasses, and more rapid displacement of oxygen; which could improve the effectiveness of the technology. However, one downside of trying to implement the technology in a higher permeability soils is that there would probably be a higher rate of gas consumption, which would impact costs. The research team concluded that the system's inability to create deeply anaerobic conditions was likely a major factor in the *cis*-DCE stall issue.

- Both microbial limitations and the inability to sustain highly reducing conditions throughout the treatment zone are important for vadose soils, especially after an SVE system has been in operation, because there are likely to be very low populations of DHC in aerobic media and even slow oxygen influx from the surface or perimeters could make it difficult to sustain sufficiently reducing conditions. Practitioners considering this technology should select sites with appropriate levels of anaerobic conditions and populations of DHC in the vadose zone.
- Implementation of H_2T is likely as or more expensive than SVE, but more effective for removing parent compounds. For the hypothetical full scale treatment, H_2T was at least half the cost of excavation.
- Extensive vapor sampling for chlorinated compounds during the test may not be that useful. Sampling for the injection gases and oxygen and methane was useful to the research team conducting this pilot test.
- For full scale systems, use of hydrogen generators has the potential to reduce gas costs by up to 50%. However, these generators need access to water and electrical power or a fuel such as methane or propane.

6.0 PERFORMANCE ASSESSMENT

Following completion of the sampling and analysis program, the data were reviewed to determine whether the success criteria for each performance objective had been met.

6.1 ACHIEVEMENT OF A GREATER ROI

Success Criteria Achieved? **YES**

Measurements of different gases at the monitoring points were used for this purpose. Monitoring points were located between 10 to 40 ft from the injection points. Success was defined as an ROI that is 50% greater compared to ROI of liquid addition to the unsaturated zone, estimated to be 5 to 10 ft. The ROI achievement was evaluated in two ways:

(1) Tracer test using helium/nitrogen tracer gas.

Helium gas reached the 10 ft distance monitoring wells at all depths (i.e., shallow, medium, and deep). Tracer gas reached almost all the monitoring wells including the 15 ft distance monitoring wells after Day 4. However, the levels of helium percentage were not high enough at the monitoring points farther than 15 ft from the injection points (i.e., 50% of the helium concentration in the injection gas) to confirm that the ROI extended beyond approximately 15 ft. The tracer test also generated data that demonstrated the presence of preferential pathways.

(2) Evaluating the ROI by looking at the concentrations of oxygen, hydrogen, and propane gases before, during, and after the gas injection phase.

Average oxygen concentrations were reduced from 16.1% to 0.4% in shallow, 16.8% to 5.7% in medium, and 16.3% to 5.7% in deep monitoring points. The low oxygen concentrations in the shallow monitoring points were observed at distances up to 40 ft away from the point of injection, while for the medium and deep monitoring points, oxygen concentrations increased significantly at around 15 ft distance from the point of injection. While anaerobic conditions never reached the medium and deep monitoring points, low oxygen concentrations were attainable at more shallow depths.

Hydrogen was detectable at all depths and distances as far as 40 ft from the injection point exceeding the 15 ft target ROI. Hydrogen concentrations never reached the injected concentration of 10%. The highest hydrogen concentrations were observed at the shallow depths (i.e., 15 ft bgs) and generally decreased as the depth increased and as the distance from injection point increased.

Propane was more easily distributed than hydrogen both with respect to distance from injection and depth. The detected propane concentration before gas injection (i.e., May 2011) ranged from <0.02 ppmv to 4.5 ppmv. Measured propane concentrations after gas injection (i.e., December 2011) ranged from 11.5 ppmv to 85,030 ppmv. Propane was easily distributed at significant distances from the point of injection at the 20, 30, and 40 ft bgs depths. For example, propane concentration of 16,397 ppmv was observed at MW-8D, which is 40 ft away from the injection point.

6.2 GREATER REDUCTION IN BASELINE MASS

Success Criteria Achieved? **YES FOR TCE, NO FOR DAUGHTER PRODUCTS**

The mass of TCE and its daughter products in soil was measured both before and after the demonstration was calculated. This analysis included the change in concentration and mass for 48 sample pairs collected from all of the injection and monitoring well locations during pre- and post-treatment characterization phases. Success was defined as 50% or greater reduction in baseline (no action) mass.

The median TCE concentrations of all 48 samples (i.e., 12 sampling locations and 4 depths) dropped from approximately 8 µg/kg during the pre-treatment characterization phase to 4 µg/kg during the post-treatment characterization phase. The median *cis*-1,2-DCE concentrations of all 48 samples (i.e., 12 sampling locations and 4 depths) increased from 17 µg/kg during the pre-treatment characterization phase to 40 µg/kg during the post-treatment characterization phase. The median TCE concentration decreased approximately 50% and median *cis*-1,2-DCE concentration increased approximately 123%.

The number of soil samples with TCE concentrations above 57 µg/kg, which is the NDEQ soil remediation goal, dropped from 13 samples in pre-treatment to five samples in post-treatment. The number of soil samples with *cis*-1,2-DCE concentrations above 400 µg/kg, which is the NDEQ soil remediation goal, dropped from 10 samples in pre-treatment to nine samples in post-treatment.

The total estimated TCE mass in the treatment zone—excluding results from MW-9, since this well is located outside the treatment area—dropped from 289 grams during the pre-treatment characterization phase to 127 grams during the post-treatment characterization phase. The total estimated *cis*-1,2-DCE mass increased from 464 grams during the pre-treatment characterization phase to 573 grams during the post-treatment characterization phase. The estimated mass showed that approximately 56% reduction in TCE mass and approximately 24% increase in *cis*-1,2-DCE mass were observed. An increase in the total mass of trans-1,2-DCE was also observed. The total molar mass of chlorinated compounds was unchanged (7.1 moles before and after). Therefore, while the system was successful at converting TCE, a "*cis*-DCE stall" condition at the site appeared to be present at the site.

Several t-test and Mann-Whitney analyses were performed to compare the means of the 48-pair TCE samples from pre- and post-treatment characterization phases. Average TCE concentration dropped from 166 µg/kg during the pre-treatment characterization phase to 74 µg/kg during the post-treatment characterization phase. The t-test conducted on the 48-pair samples resulted in p-value of 0.092 that corresponds to a 90.8% confidence in support of the hypothesis that the post-treatment TCE concentrations are smaller than the pre-treatment TCE concentrations. The Mann-Whitney analysis also resulted in a similar p-value of 0.104 that corresponds to a 89.6% confidence in support of the hypothesis that post-treatment TCE concentrations are significantly smaller than the pre-treatment TCE concentrations.

Both t-test and Mann-Whitney analyses show that there is approximately 90% confidence that the post-treatment TCE concentrations are significantly less than the pre-treatment TCE concentrations. The data sets are characterized by large variability (e.g., extreme positive outliers) and relatively large number of non-detects, which tends to adversely affects the power of statistical tests to detect differences. Similar analyses were performed for *cis*-1,2-DCE and the results show that there is greater than a 90% but less than a 95% probability that the post-treatment *cis*-1,2-DCE soil concentrations are significantly greater than the pre-treatment *cis*-1,2-DCE soil concentrations.

6.3 COST SAVINGS COMPARED TO CONTINUED SVE OPERATION

Success Criteria Achieved? **SOMETIMES**

The cost of H_2T application compared to SVE and soil excavation was calculated using the following cost drivers: the radius of influence to estimate the number of injection points, capital costs (injection skid; manifold system, wells), and O&M costs (delivered gas, operator cost). Three scenarios were considered and compared based on data collected during this H_2T demonstration. In each scenario, the H_2T system was compared with an alternative SVE system. All three scenarios represent the successful design used in the demonstration and had an ROI of 15 ft and a gas composition based on 20% hydrogen.

For all scenarios, the cost of H_2T was greater than SVE system operation. In Scenarios 1 and 2, the cost of H_2T system operation for two years based on the implemented demonstration design conditions was \$39/cy compared to the entire SVE system operation (i.e., \$37/cy) and soil excavation (i.e., \$97/cy). In Scenario 3, the cost of H_2T system operation based on the implemented demonstration design conditions was \$39/cy compared to the continuation of the existing SVE system operation (i.e., \$20/cy). Finally, in Scenario 4, the cost of H_2T system operation by using the existing SVE wells as gas injection wells was \$35/cy compared to the continuation of the existing SVE system operation (i.e., \$20/cy).

It must be noted that the de*cis*ion to switch to H_2T operation over an SVE system should be made based on the overall performance and not only on the cost assessments. For example, in the demonstration site where an SVE system was operating since 2008, the SVE system was not able to reduce the mass in the vadose zone due to the very low permeability soil (i.e., clayey silt loess material). Small molecules of hydrogen gas, on the other hand, were able to diffuse into the small pores of the low-permeability soil.

6.4 REDUCTION IN CARBON FOOTPRINT COMPARED TO SVE

Success Criteria Achieved? **MOSTLY YES**

The carbon footprint was estimated for two variations of H_2T (i.e., liquid nitrogen/hydrogen cylinder delivery versus on-site nitrogen and hydrogen generation) and compared to two variations of SVE system operation (i.e., continuous versus pulsed operation at 25% time). Success was defined as 50% reduction in the carbon footprint compared to SVE.

Using spreadsheet calculations (see Appendix G), the following values were calculated for the demonstration TCE site operating for a year (i.e., a treatment zone with dimensions of approximately 2,200 ft^2 area and 40 ft thickness). The most sensitive parameters included: 1) use of cylinders, gas in cryo-liquid form; tube trailers, or on-site nitrogen and/or hydrogen generators; 2) amount of electricity used by SVE system blower and gas generators; 3) amount of gas used in the direct hydrogen delivery process; and 4) number of trips required to deliver gas to the site. There were considerable uncertainties in the calculation. At some sites, use of SVE and activated carbon could result in a lower carbon footprint than the direct hydrogen injection process. Results from carbon footprint calculation are summarized in Table 6.

Table 6. Results of carbon footprint calculations.

Item	Amount (tons per year)	Source of Data	Item	Amount (tons per year)	Source of Data
High End Carbon Footprint Cases					
SVE + Granular Activated Carbon (GAC) Treatment Continuous Operation			Direct Hydrogen Delivery Process Liquid Nitrogen Delivery		
Electricity for Blower	19.0	SRT[1]	Producing H_2, LPG, and CO_2	5.4	assume 1% efficiency for H_2 consumption
Regenerating GAC	2.1	SRT	Producing N_2	0.6	from energy use calculations
Transporting GAC	0.3	SRT	Transporting gas to site	2.1	estimated trips + SRT
TOTAL	**21.4**		**TOTAL**	**8.1**	
Percent Reduction in carbon footprint compared to SVE+GAC: **62%**					
Low End Cases Carbon Footprint Cases					
SVE + GAC Treatment Pulsed Operation at 25% Time			On-Site Nitrogen and Hydrogen Generation		
Electricity for Blower	5.3	Tier 2 SRT[2]	Producing CO_2	0.6	assume 1% efficiency for H_2 consumption
Regenerating GAC	2.1	SRT	Producing H_2 and N_2 on-site	2.8	from energy use calculations
Transporting GAC	0.3	SRT	Transporting gas to site	1.0	estimated trips + SRT
TOTAL	**7.7**		**TOTAL**	**4.4**	
Percent Reduction in carbon footprint compared to SVE+GAC: **43%**					

[1] SRT Tier 1 typical value assumes system operates 90% of time

[2] Assumes system operates 25% of time

For the high end carbon footprint case, where a constant operation of SVE+GAC was compared with direct liquid nitrogen/hydrogen cylinder delivery, the carbon footprint was 21.4 tons of CO_2 for SVE+GAC versus 8.1 tons of CO_2 for the H_2T system. For the high end case, the carbon footprint of H_2T system operation is approximately 62% less than SVE system operation. For the low end case, where a pulsed operation of SVE+GAC was compared with on-site nitrogen and hydrogen generation, the carbon footprint was 7.7 tons of CO_2 for SVE+GAC versus 4.4 tons of CO_2 for the H_2T system. For the low end case, the carbon footprint of H_2T system operation is approximately 43% less than SVE system operation. Note that the high-end hydrogen case has approximately the same footprint as the low-end SVE case. In the carbon footprint calculations, it was assumed that the generated methane stays in the vadose zone and the amount is negligible compared to other contributors to the carbon footprint. Therefore, methane generation and its potential emission were not included in the carbon footprint calculations.

6.5 SAFETY

Success Criteria Achieved? **YES**

One of the potential risks associated with field implementation of the H_2T system is the use of gases (i.e., H_2 and LPG) that are explosive under certain conditions. Although the concentration of the explosive gases in the gas mixture is 20% by volume, it was expected that the H_2T process was considered safe because the flammable gases disperse quite readily in the atmosphere and no detections of flammable gases above ground were observed. It is also expected that the oxygen levels at the injection points below ground surface are close to zero. Nevertheless, standard engineering practices can be used to provide a safe system. As part of H_2T performance objective the concentrations of H_2 and propane were monitored at the surface to maintain levels below the LELs at the surface. The effectiveness was a function of satisfying all of the compressed gas safety codes (i.e., NFPA50A, NFPA55). As part of H_2T performance objective the LEL of H_2 and propane were monitored at the surface to maintain levels below the LEL at the surface.

The objective was considered to be met if flammable gas concentrations of less than 10% of the LEL at surface are achieved. In order to evaluate the safety concerns associated with the technology, flammability relative to explosivity limits were assessed along with H_2 air emissions. Soil gas monitoring included explosivity measurements using an explosivity meter.

No health and safety incidents occurred during the demonstration and flammable gas concentrations above the ground surface were not detectable. It should be noted that hydrogen and propane concentrations exceeded the LELs at some points below ground surface, but there was not enough oxygen available at those points to make the system potentially explosive. While concerns regarding safety of hydrogen and propane injections are reasonable, the results of this demonstration indicate the technology can be implemented safely.

6.6 EASE OF USE

Success Criteria Achieved? **YES**

The effectiveness of the technology is also related to the relatively easy implementation of the H_2T system compared to other technologies such as SVE. It was anticipated that the ease of permitting (no air permits were required) and the ease of operation make the implementation of this technology quick and easy. Success criteria for this performance objective were evaluated qualitatively. It should be noted that a site-specific comparison of H_2T versus SVE operation should be implemented because the ease of use also depends whether engineering controls for safety is implemented for H_2T or vapor-phase emissions control system is needed for SVE.

Required operator manpower was evaluated for both the existing SVE system and for H_2T system. Feedback from field personnel regarding ease of use of H_2T compared to SVE was also used. The metric for this performance objective was the frequency at which an operator needed to visit the site. The reasons for site visitation during normal operations included gas cylinder change-outs, system leak test, pressure and flow readings, and monitoring. This occurred once per week (i.e., weekly O&M) or every few weeks (i.e., tank re-fill or cylinder replacement), which was considered reasonable.

7.0 COST ASSESSMENT

The H_2T demonstration site (former Atlas Missile site) was used as a basis for developing the cost estimates. Four different scenarios were developed for in situ treatment of TCE in the unsaturated zone at this site. These scenarios were developed to compare actual demonstration design and operating conditions to likely full-scale design and operating conditions.

As part of the demonstration, the cost of implementing the field demonstration program was carefully tracked and this cost data was used to estimate the expected cost of implementing the H_2T system at other sites. In addition, the cost of potential bioaugmentation and barrier measures including capping or wetting the margins to prevent oxygen intrusion were roughly estimated. Bioaugmentation costs were included as a contingency (assuming bioaugmentation can be done effectively at some sites) to achieve complete dechlorination.

7.1 COST MODEL

A cost evaluation assuming full-scale treatment of affected soils at the former Atlas Missile Site was performed. This treatment zone represented approximately 46,000 cy of soil. All costs associated with the field validation/demonstration of the H_2T system were tracked in an Excel spreadsheet. The site-specific conditions must be considered in the design when the cost analysis calculations in this cost model are transferred to other sites. Three scenarios were considered and compared in this cost assessment based on data collected during this H_2T demonstration. In each scenario the H_2T system was compared with an alternative SVE system. All scenarios represent the successful H_2T design used in the demonstration except for the nitrogen and hydrogen generators and have an ROI of 15 ft and a gas composition based on 20% hydrogen.

There are 39 SVE wells at the site in the area that TCE soil concentration had initially exceeded the NDEQ soil remediation goal of 57 µg/kg before the start of SVE system operation in 2008 (i.e., approximately 27,500 ft^2 or 0.6 acre). For the purpose of this study, a cost assessment for a similar SVE system was performed (i.e., number of wells, flow rates, on-site treatment system, treatment area, etc.).

SVE Scenario 1: H_2T versus new SVE System. This scenario represents the comparison of costs associated with the H_2T system with the costs associated with setting up and operating an entire SVE system including the capital cost of well installation and GAC treatment system or soil excavation. Scenario 1 represents the design used in the demonstration where gas injection wells were installed for the H_2T system and the SVE wells were shut down and were not used as gas injection wells.

Excavation Scenario 2: H_2T versus Soil Excavation. This scenario represents the comparison of costs associated with the H_2T system with the costs associated with soil excavation. Similar to Scenario 1, Scenario 2 represents the design used in the demonstration where gas injection wells were installed for the H_2T system.

SVE Scenario 3: H_2T with New Gas Injection Wells versus Continuing Operation of an Existing SVE System. This scenario represents the comparison of costs associated with the H_2T system with the costs associated with continuing an existing SVE system operation. Similar to Scenarios

1 and 2, Scenario 3 represents the design used in the demonstration where gas injection wells were installed for the H_2T system and the SVE wells were shut down and were not used as gas injection wells.

SVE Scenario 4: H_2T with Existing SVE Wells versus Continuing Operation of an Existing SVE System. In Scenario 3, the existing SVE wells were used as the gas injection wells for the H_2T system. Scenario 4 represents the conditions where the screen intervals are not very long and the site managers decide to use the existing SVE wells as H_2T gas injection wells.

7.1.1 Assumptions

The assumptions made during this cost assessment are summarized below:

- Pre- and post-project site characterization activities are similar for the H_2T and SVE systems.
- For scenarios where injection and monitoring well installation is required, one monitoring point will be installed for every five injection points. The designs of injection and monitoring wells were different.
- The total area of TCE contamination at the demonstration site is based on the TCE soil concentrations above 57µg/kg is the same in all depths from 0 to 60 ft bgs and was estimated based on the data presented in the Site Investigation Report (Kemron, 2007).
- ROI was 15 ft for both the SVE and H_2T systems in all scenarios. ROI was approximately 15 ft for the SVE system based on the placement of the existing SVE wells.
- Soil type in the treatment area allows the uniform distribution of both injected gas for H_2T system and extracted air for the SVE system.
- Labor unit costs for site characterization activities, well installation, O&M, and system performance monitoring are similar for the H_2T and SVE systems.
- The whole project will take two years.
- Because of the large injected gas volume, nitrogen and hydrogen gases are produced using generators. Vendor quotes were used for the capital costs and power consumption of the generators.
- Gas unit costs do not change over the course of the project.
- LPG was replaced by hydrogen and the total hydrogen composition in the injected gas mixture is increased to 20% for all flowrates.
- Water barrier wells were installed at the treatment zone perimeter using 74 temporary holes (i.e., assuming 5 ft ROI). It was assumed that water would be injected at an injection rate of 5 gallons per minute (gpm) per well.
- Bioaugmentation was implemented to the entire treatment zone area with 10 ft ROI. It was assumed that the bioaugmentation was performed in 88 wells (i.e., assuming 10 ft ROI) at an injection rate of 10 gpm per well was assumed.

The specific elements of the cost model unique to the implementation of the H_2T system are described below.

7.1.2 Cost Elements

No rigorous cost model has been developed for anaerobic bioventing. However, the costs should be similar to aerobic bioventing with the following additional costs: field treatability and tracer tests; gas mixture additions; and additional soil and gas analyses.

Gas Mixture Injection Skid: Application of the H_2T system requires construction of the gas mixture injection skid. The design, labor, and material costs associated with construction of the gas mixture injection skid were tracked in the Excel spreadsheet.

Consumable Gases (i.e., H_2, N_2, LPG, and CO_2): Application of the H_2T system requires hydrogen and nitrogen gases as the major components of the gas mixture. These gases will be provided either by a vendor in the form of compressed gas or liquid, or by using generators. For the demonstration, material costs associated with preparation of the gas mixture were tracked in an Excel spreadsheet. For the demonstration, hydrogen gas was provided in cylinders and nitrogen was provided in liquid form in a tube trailers. No vaporizer was needed for nitrogen.

It should be noted that the cost of nitrogen and hydrogen generators should be included in the cost estimate for large scale H_2T system where large amount of nitrogen and hydrogen required. When high volume of nitrogen and hydrogen needed for injection, it is more economical to purchase a generator and produce nitrogen and/or hydrogen on-site than to buy these gases in cylinders, tube trailers or liquid nitrogen tanks. If H_2T is applied at a small site, it is possible that purchasing compressed or liquid nitrogen or hydrogen cylinders is more cost effective. Because the volume of gas needed is site-specific, when estimating H_2T implementation costs at another site, a cost comparison is needed to decide whether a nitrogen or hydrogen generators should be used.

Installation of Injection and Monitoring Points: Application of the H_2T system requires installation of injection and monitoring points, such that the labor and material costs associated with installation of these points was tracked.

Treatability and Tracer Studies: A H_2T treatability study to determine the site-specific requirements for implementation of the technology may be useful at some sites. The field treatability study involves one or both of the following elements: 1) injection of air into a single well at various flow rates to characterize gas permeability and pneumatic radius of influence in the vadose zone, and 2) tracer tests to determine the rate of consumption of oxygen and influence of oxygen diffusion from the surface. During the tracer test, H_2 and helium are injected together and H_2 and O_2 consumption is monitored in comparison with helium as the conservative tracer.

Cost data that was tracked included the following cost parameters: labor, materials, and analytical testing. Labor was tracked according to the type of personnel required to conduct the treatability study (field technician, engineer, program manager, etc.) and their associated labor hours.

Bioaugmentation and Water Barrier Installation: Successful application of the H_2T technology at some or many sites (such as this site) may require bioaugmentation in the vadose zone and/or installation of barriers, such as capping or wetting the margins to prevent oxygen intrusion. Costs associated with this step were estimated based on the required labor time and material.

Soil and Soil Vapor Sample Collection and Analysis: Application of the H_2T system requires measurement of CVOC concentrations in soil and soil vapor, oxygen levels throughout the study area (zone of influence), and soil moisture in different soil layers (alternatively, soil moisture can be estimated based on field observations and knowledge of local climate). For the demonstration, costs associated with collection and analysis of soil and soil vapor samples were tracked.

Data Evaluation: Application of the H_2T system requires review of the soil boring logs, CVOC soil and soil vapor concentrations, and other site data to evaluate the performance of the H_2T system at the site. Costs associated with this step were estimated based on the field demonstration as well as experience with application of other bioventing systems at other sites.

O&M: Application of the H_2T system requires O&M that includes delivered gas and operator costs. These labor and material costs were tracked as part of the demonstration.

7.2 COST ANALYSIS

This section provides a cost comparison of each of the scenarios. The cost inputs for this estimate were based on demonstration data, vendor quotes, or the Remedial Action Cost Engineering and Requirements (RACER) software (RACER, Version 10.4). Drillers and certified analytical laboratories that were part of the H_2T demonstration were used to estimate drilling and analytical costs. The cost breakdown for each scenario is presented in Table 7.

The cost model was provided to estimate the H_2T implementation cost for the following cases:

1) H_2T as a replacement for traditional soil treatment technologies (e.g., SVE, excavation, or liquid-based biodegradation) at sites where no treatment has yet occurred (Scenarios 1 and 2); and
2) H_2T as a cheaper polishing step to replace expensive SVE systems that are no longer removing large amounts of contaminant mass (Scenarios 3 and 4).

All performance data was normalized to the volume of bulk treated soil for evaluating the cost benefit. Cost calculations were performed so that the cost of the H_2T technology can be compared to the competing technology, SVE or excavation. Four scenarios were considered and compared in this cost assessment based on data collected during this H_2T demonstration. The cost assessment was performed for the implementation and/or continuation of a system similar to the existing SVE system at the site.

Table 7. Project implementation costs at former Atlas Missile Site for different designs.

		SCENARIO 1		SCENARIO 2		SCENARIO 3		SCENARIO 4	
		H_2T	SVE	H_2T	EXCAVATION	H_2T	SVE	H_2T	SVE
COST ELEMENT	**DATA TRACKED**	(entire system)	(entire system)	(entire system)	(entire system)	(entire system)	(existing system)	(use SVE wells)	(existing system)
TASK 1. Treatability Study and Site Characterization (i.e., Soil concentration, permeability test, microcosm study, qPCR testing, etc.)									
Project management	Labor (Sr. Technical), 50 hrs	$7,500	$7,500	$7,500	$7,500	$7,500	$0	$7,500	$0
Travel to the site	Airfare, per diem, etc.	$10,000	$10,000	$10,000	$10,000	$10,000	$0	$10,000	$0
Drilling	Drilling subcontractor	$25,000	$25,000	$25,000	$25,000	$25,000	$0	$25,000	$0
Soil sample collection and shipping	Labor time and material	$6,000	$6,000	$6,000	$6,000	$6,000	$0	$6,000	$0
Analytical laboratory	Lab fee	$10,000	$10,000	$10,000	$10,000	$10,000	$0	$10,000	$0
Waste disposal	Permitting, labor and material	$6,000	$6,000	$6,000	$0	$6,000	$0	$6,000	$0
Microcosm study	Laboratory fees	$40,000	$0	$40,000	$0	$40,000	$0	$40,000	$0
Data review and analysis	Sr. Technical, 50 hrs	$7,500	$7,500	$7,500	$7,500	$7,500	$0	$7,500	$0
Miscellaneous costs	-	$10,000	$10,000	$10,000	$10,000	$10,000	$0	$10,000	$0
Task 1 Total		**$122,000**	**$82,000**	**$122,000**	**$76,000**	**$122,000**	**$0**	**$122,000**	**$0**
TASK 2. Engineering Design, Construction (i.e., Gas Injection Skid, SVE System, Gas Distribution System, etc.)									
Project management	Labor (Sr. Technical), 80 hrs	$12,000	$12,000	$12,000	$6,000	$12,000	$6,000	$12,000	$6,000
Travel to the site	Airfare, per diem, etc.	$10,000	$10,000	$10,000	$0	$10,000	$0	$10,000	$0
System Design	Sr. Technical / Subcontractor	$40,000	$65,000	$40,000	$0	$40,000	$0	$40,000	$0
System Construction	Subcontractor	$80,000	$300,000	$80,000	$0	$80,000	$0	$80,000	$0
Shipping	Shipping to the site	$2,000	$2,000	$2,000	$0	$2,000	$0	$2,000	$0
Bioaugmentation	Labor time and material	$310,000	$0	$310,000	$0	$310,000	$0	$310,000	$0
Barrier implementation: capping and/or wetting the margins	Labor time and material	$120,000	$0	$120,000	$0	$120,000	$0	$120,000	$0
Miscellaneous costs	-	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000
TASK 2 Total		**$584,000**	**$399,000**	**$584,000**	**$16,000**	**$584,000**	**$16,000**	**$584,000**	**$16,000**
TASK 3. Installation									
Project management	Labor (Sr. Technical), 40 hrs	$6,000	$12,000	$6,000	$0	$6,000	$12,000	$6,000	$12,000
Travel to the site	Airfare, per diem, etc.	$20,000	$20,000	$20,000	$0	$20,000	$20,000	$20,000	$20,000
Drilling	Drilling subcontractor	$125,000	$125,000	$125,000	$0	$125,000	$0	$0	$0
System Installation (e.g., piping, trenching, etc.)	Labor time and material	$45,000	$65,000	$45,000	$0	$45,000	$0	$30,000	$0
Leak test, Tracer test	Labor time and material	$5,000	$5,000	$5,000	$0	$5,000	$0	$5,000	$0
Miscellaneous costs	-	$25,000	$25,000	$25,000	$0	$25,000	$25,000	$25,000	$25,000
TASK 3 Total		**$226,000**	**$252,000**	**$226,000**	**$0**	**$226,000**	**$57,000**	**$86,000**	**$57,000**
TASK 4. System Operation (i.e., O&M, Monitoring, etc.)									
Project management	Labor (Sr. Technical), 200 hrs	$30,000	$30,000	$30,000	$20,000	$30,000	$30,000	$30,000	$30,000
Travel to the site	Airfare, per diem, etc.	$35,000	$35,000	$35,000	$35,000	$35,000	$35,000	$35,000	$35,000
Sample collection and shipping	Labor time and material	$60,000	$50,000	$60,000	$30,000	$60,000	$50,000	$60,000	$50,000
Analytical laboratory	Lab fee	$80,000	$50,000	$80,000	$50,000	$80,000	$50,000	$80,000	$50,000
Gas	Material and delivery	$476,000	$0	$476,000	$0	$476,000	$0	$476,000	$0
Electricity	Power to run SVE system	$0	$70,000	$0	$0	$0	$70,000	$0	$70,000
On-site vapor treatment system	Material and maintenance	$0	$150,000	$0	$0	$0	$150,000	$0	$150,000
Weekly O&M	Technician, 800 hrs	$65,000	$65,000	$65,000	$8,000	$65,000	$65,000	$65,000	$65,000
Vapor monitoring (field)	Labor time and material	$45,000	$25,000	$45,000	$25,000	$45,000	$25,000	$45,000	$25,000
Soil excavation	Labor time and material	$0	$0	$0	$870,000	$0	$0	$0	$0
Off-site transportation and waste disposal	Labor time and material	$0	$0	$0	$2,500,000	$0	$0	$0	$0
Miscellaneous costs	-	$30,000	$30,000	$30,000	$30,000	$30,000	$30,000	$30,000	$30,000
TASK 4 Total		**$821,000**	**$505,000**	**$821,000**	**$3,568,000**	**$821,000**	**$505,000**	**$821,000**	**$505,000**
TASK 5. Post-Remediation Site Characterization									
Project management	Labor (Sr. Technical), 50 hrs	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500
Travel to the site	Airfare, per diem, etc.	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000
Drilling	Drilling subcontractor	$25,000	$25,000	$25,000	$25,000	$25,000	$25,000	$25,000	$25,000
Soil sample collection and shipping	Labor time and material	$6,000	$6,000	$6,000	$6,000	$6,000	$6,000	$6,000	$6,000
Waste disposal	Permitting, labor and material	$6,000	$6,000	$6,000	$6,000	$6,000	$6,000	$6,000	$6,000
Analytical laboratory	Laboratory fees	$40,000	$40,000	$40,000	$40,000	$40,000	$40,000	$40,000	$40,000
Data review and analysis	Labor (Sr. Technical), 50 hrs	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500
Miscellaneous costs	-	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000	$10,000
Task 5 Total		**$112,000**	**$112,000**	**$112,000**	**$112,000**	**$112,000**	**$112,000**	**$112,000**	**$112,000**
TASK 6. Final Report and Demobilization									
Prepare Draft Technical Report	Labor (Sr. Technical), 200 hrs	$30,000	$30,000	$30,000	$30,000	$30,000	$30,000	$30,000	$30,000
Review Draft Technical Report	Labor (Sr. Technical), 50 hrs	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500	$7,500
Prepare Final Technical Report	Labor (Sr. Technical), 150 hrs	$22,500	$22,500	$22,500	$22,500	$22,500	$22,500	$22,500	$22,500
Prinicipal Oversight/Review	Labor (Sr. Technical), 40 hrs	$15,000	$15,000	$15,000	$15,000	$15,000	$15,000	$15,000	$15,000
Demobilization	-	$35,000	$35,000	$35,000	$35,000	$35,000	$35,000	$35,000	$35,000
Task 6 Total		**$110,000**	**$110,000**	**$110,000**	**$110,000**	**$110,000**	**$110,000**	**$110,000**	**$110,000**
CONTINGENCY	15%	$296,250	$219,000	$296,250	$582,300	$296,250	$120,000	$275,250	$120,000
TOTAL COST		$2,271,250	$1,679,000	$2,271,250	$4,464,300	$2,271,250	$920,000	$2,110,250	$920,000
COST PER CUBIC YARD	Total volume = 46,000 cy	$49	$37	$49	$97	$49	$20	$46	$20

In Scenarios 1 and 2, the cost of H_2T system operation for two years based on the implemented demonstration design conditions was $49/cy compared to the entire SVE system operation (i.e., $37/cy) and soil excavation (i.e., $97/cy). In Scenario 3, the cost of H_2T system operation based on the implemented demonstration design conditions was $49/cy compared to the continuation of the existing SVE system operation (i.e., $20/cy). Finally, in Scenario 4, the cost of H_2T system operation by using the existing SVE wells as gas injection wells was $46/cy compared to the continuation of the existing SVE system operation (i.e., $20/cy).

For all the cost analysis scenarios, the cost of using gas generators was used. Because of the high volume of nitrogen and hydrogen needed for injection, it is more economical to purchase a generator and produce nitrogen and/or hydrogen on-site than to buy these gases in tube trailers, liquid nitrogen tanks or pressurized cylinders. Approximately 42% of the total cost of the H_2T system is the cost of gas if the gas is purchased and delivered to the site as liquid nitrogen and compressed hydrogen cylinders. When nitrogen and hydrogen generators are used, only 22% of the total cost of the H_2T system is the cost of gas and the unit cost of H_2T is reduced by approximately 31%, from $71/cy to $49/cy.

For all scenarios, the cost of H_2T was greater than SVE system operation. However, it is expected that for cases where larger contaminated areas are being treated for longer treatment periods, the H_2T system is more economical than SVE or excavation. It must be noted that the de*cis*ion to switch to H_2T operation over an SVE system should be made based on the overall performance and not only on the cost assessments. For example, in the demonstration site where an SVE system was operating since 2008, the SVE system was not able to reduce the mass in the vadose zone due to the very low permeability soil (i.e., clayey silt loess material), likely due to preferential removal from a high-permeability layer at the bottom of the treatment interval. Small molecules of hydrogen gas, on the other hand, were able to diffuse into the small pores of the low-permeability soil.

When comparing each task across the different scenarios, the costs of the treatability study, gas permeability test, engineering design, and project management are similar under different scenarios. For the excavation it was assumed that 40% of the excavated soil would be re-packed in-place and only 60% of the contaminated excavated soil will be transported off-site and disposed as waste.

For this demonstration, propane was cheaper than hydrogen and therefore was used as 10% of the gas mixture to deplete oxygen. However in large-scale projects where a hydrogen generator will be used, it is more economical to eliminate propane gas and inject 20% hydrogen gas instead.

It should be noted that for the demonstration site where bulk nitrogen and hydrogen gases where purchased and delivered to the site, the gas cost was approximately $3 per cy/month at the original flowrate, and approximately $7 per cy/month for the last month after doubling the flowrate and hydrogen gas composition.

7.3 COST DRIVERS

The total costs of implementing H_2T are mainly driven by gas-related costs as presented in Table 7. Sensitivity analyses were performed to evaluate the effects of gas flowrate and ROI on the unit cost of H_2T implementation.

7.3.1 Sensitivity to Gas Flowrate

As mentioned in the Cost Analysis section, for higher gas flowrates where large volumes of nitrogen and hydrogen needed for injection, it is more economical to purchase nitrogen and hydrogen generators and generate these gases on-site than to buy these gases in tube trailers, liquid nitrogen tanks or pressurized cylinders. In this section, the cost calculations are performed based on gas costs using nitrogen and hydrogen generators. It was also assumed that the ROI is 15 ft for all different gas flowrates. All of the cost calculations are for a two-year H_2T system operation.

Gas-related costs included gas generators, compressed gases (i.e., CO_2 and helium), and electricity consumption. The purpose of using LPG during the demonstration was to reduce the gas cost since LPG is a cheaper gas compared to hydrogen gas when hydrogen is provided in compressed cylinders. Because a hydrogen generator was used for the cost calculations in this section, LPG was replaced by hydrogen and the total hydrogen composition in the injected gas mixture was increased to 20% for all flowrates. Therefore, LPG cost is excluded from the cost analysis.

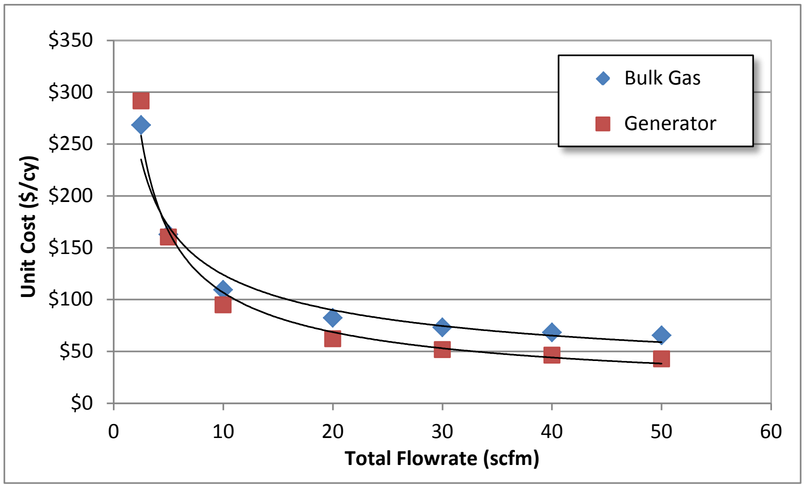

Figure 9. Sensitivity of H_2T costs to total gas flowrate.

It should be noted that the total cost of the H_2T system could be decreased if the oxygen infiltration from above, bottom and/or sides is prevented or reduced. The oxygen infiltration from above could be prevented or reduced if a surface cover (i.e., plastic or concrete) is used in the treatment area. It is, however, more difficult to prevent or reduce the oxygen infiltration from the sides or bottom. Two possible ways to reduce lateral oxygen infiltration from sides are to use a closed loop of gas injection wells and/or to use water barriers on the perimeter of the treatment zone. The effect of total gas flowrate on the unit cost of H_2T are presented in Figure 9. Site-specific pilot studies must be conducted to determine the optimum gas flowrate required to keep the treatment zone anaerobic.

At a gas injection flowrate of approximately 5 scfm the gas cost using bulk gas versus an on-site generator was similar. For total gas flowrates higher than 5 scfm the use of nitrogen and hydrogen generators are more economical. These cost calculations are for a two-year H_2T system operation. If the H_2T system operation is longer than two years, the cost savings by using gas generators will be increased.

7.3.2 Sensitivity to ROI

ROI can affect both the number of injection wells and the total gas flowrate. A main advantage of using H_2T over SVE is that the small hydrogen molecules diffuse into the low-permeability soil (i.e., silt and clay) more easily, thereby increasing the radius of influence. This makes the H_2T technology a good alternative to the SVE system when SVE operation is not effective in low-permeability soils.

The ROI is related to several factors including soil lithology and heterogeneity, gas flow rate and composition, well design, and superposition. In this demonstration three injection locations and three depths at each location were used. In large scale H_2T implementation where multiple injection wells are installed in a grid pattern, the ROI is expected to increase compare to this demonstration and lesser gas is expected to be used as a result of superposition. Site-specific pilot studies and tracer tests should be conducted to determine the ROI required to keep the treatment zone anaerobic.

The effect of ROI on the unit cost of H_2T is presented in Figure 10. Sensitivity analysis was performed for ROI values from 5 to 25 ft in a treatment area of 27,500 ft^2. The number of injection wells was increased dramatically from 15 to 350 when the ROI is decreased from 25 ft to 5 ft. By increasing the ROI from 10 ft to 15 ft, the total cost of H_2T operation is reduced by approximately 23% (i.e., \$64/cy to \$49/cy). Conversely, increasing the ROI from 15 ft to 20 ft, the total cost of H_2T operation is reduced by approximately 10% (i.e., \$49/cy to \$44/cy). It was assumed that the total number of pore volumes injected within two years of H_2T operation was similar for all the ROI values and therefore, the gas cost for all different ROI values were the same. The analysis shows that the effect of ROI on the total H_2T cost is significant and an accurate estimate of site ROI is needed.

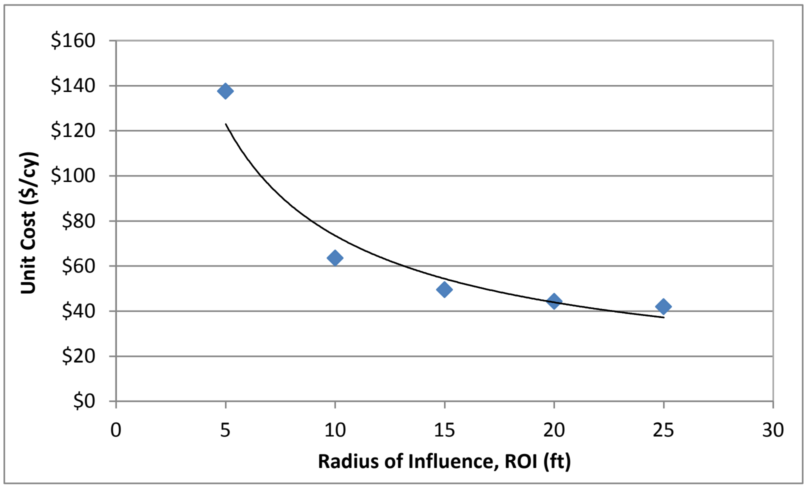

Figure 10. Sensitivity of H_2T costs to ROI.

8.0 IMPLEMENTATION ISSUES

Key H_2T implementation issues are summarized below.

- Specific permits for H_2T may be required by local codes and will include drilling, well installation permits, and hazardous materials storage permits. Other permits may be necessary and will be dependent on local codes.
- One of the main safety concerns associated with H_2T application is the flammability of hydrogen and LPG and the potential production of methane gas. It was shown in this demonstration that the safety concerns could be addressed easily by following the safety codes (e.g., NFPA50A, NFPA55, etc.).
- Soil permeability and heterogeneity, soil moisture, etc., can greatly affect the performance of H_2T system.
- A suitable population of dechlorinating organisms (DHC) is needed to ensure complete conversion of PCE or TCE to non-toxic products (e.g., ethane).
- In-test measurements of redox-related parameters (oxygen, methane) indicated that deeply anaerobic conditions were not achieved uniformly through the test zone, a likely contributing factor for the observed *cis*-DCE stall condition. The research team concluded that the system's inability to create deeply anaerobic conditions was likely a major factor in the *cis*-DCE stall issue.
- Lab microcosm work indicated that samples that had been bioaugmented with dechlorinating bacteria performed much better than unamended soils, indicating a dechlorinating bacterial limitation at the site. The team strongly recommends that future practitioners considering this alternative should first conduct lab testing with and without bioaugmentation long enough to be sure whether there is a microbial limitation, and then measure the electron acceptor influxes to estimate initial and sustained hydrogen demand, before designing and implementing a field test.
- Additional microcosm results indicated that low moisture may have been a contributing factor to this bacterial limitation. Lab microcosm work showed that high moisture content (30%) promoted the most complete reductive dechlorination under conditions with high electron donor concentration (10%) and bioaugmentation. However, lower moisture contents (17% to 19%) promoted reductive dechlorination of TCE to *cis*-1,2-DCE more effectively than a high moisture content (30%) when the electron donor concentration was low (1%). The later condition for moisture content and electron donor concentration was similar to the condition observed in the field.
- When liquid nitrogen was supplied in a commercially available trailer approximately 20-30% of the liquid nitrogen was wasted due to ventilation to the atmosphere. The lost volume of nitrogen from tube trailers should be considered when the de*cis*ion for using tube trailers versus nitrogen generator is being made.
- If generators are to be used at a site, whether the generators are powered by fuel or electricity, the safety concerns must be addressed with regard to the placement of the generators and their proximity to the treatment area.

- Using both hydrogen and LPG at the site increases safety concerns, and relevant safety codes must be followed for the distance between LPG tank and the hydrogen cylinders (i.e., 30 ft for this demonstration). For large-scale projects where an on-site hydrogen generator is used, it is more economical to replace LPG by hydrogen gas.

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APPENDIX A

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