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Use of Comatabolic Air Sparging to Remediate Chloroethene-Contaminated Groundwater Aquifers

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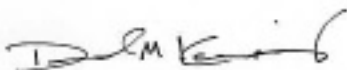
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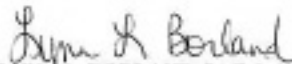
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Final Report

Use of Cometabolic Air Sparging to Remediate Chloroethene-Contaminated Groundwater Aquifers

by

**Battelle
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July 31, 2001



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ABBREVIATIONS AND ACRONYMS

AFRL/MLQ	Air Expeditionary Forces Technology Division
AS	air sparging
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
CAH	chlorinated aliphatic hydrocarbon
CAS	cometabolic air sparging
c-DCE	<i>cis</i> -1,2-dichloroethene
CF	chloroform
cfm	cubic feet per minute
CO ₂	carbon dioxide
1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
DCA	dichloroethane
DCE	dichloroethene
DO	dissolved oxygen
DoD	Department of Defense
DRE	destruction and removal efficiency
ESTCP	Environmental Security Technology Certification Program
FID	flame ionization detector
GAC	granular activated carbon
GC	gas chromatograph
H ₂ SO ₄	sulfuric acid
HCl	hydrochloric acid
hp	horsepower
HP	Hewlett Packard
I.D.	inside diameter
IRP	Installation Restoration Program
LFL	lower flammable limit
LNAPL	light, nonaqueous-phase liquid
McAFB	McClellan Air Force Base
MCLs	maximum contaminant levels
MP	monitoring point
MW	monitoring wells

NA	not analyzed
ND	not detected
NH ₄	ammonia
NO ₃	nitrate
NRMRL	National Risk Management Research Laboratory
O ₂	oxygen
O&M	Operation and Maintenance
OSU	Oregon State University
OU	Operable Unit
P&T	pump and treat
PCE	tetrachloroethene
	perchloroethene
PID	photoionization detector
ppmv	parts per million by volume
psi	pounds per square inch
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
scfm	standard cubic feet per minute
SF ₆	sulfur hexafluoride
SLPM	Standard liters per minute
SOP	Standard Operating Procedure
SVE	soil vapor extraction
TCA	trichloroethane
TCE	trichloroethene
TKN	total Kjeldahl nitrogen
USAF	United States Air Force
U.S. EPA	United States Environmental Protection Agency
VC	vinyl chloride
VOA	volatile organic analysis
VOC	volatile organic compounds

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During Phase 1 of the study (April through December 1999), Adisorn Tovanabootr (an OSU student) led the field demonstration effort, which was to form a major portion of his doctoral studies at OSU. Unfortunately, shortly following Phase 1, Mr. Tovanabootr was diagnosed with Leukemia. After approximately 10 months of struggling with Leukemia, Adisorn passed away in December 2000. Adisorn's contribution to the study was invaluable and he was missed during the Phase 2 studies. He was deeply devoted to this project. This report is dedicated to his memory.

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Final Report

Battelle

July 31, 2001

1. Introduction

1.1 Background Information

The Department of Defense (DoD) is faced with the task of remediating many sites contaminated with a variety of compounds, including chlorinated aliphatic hydrocarbon (CAH) compounds. When a contaminant release occurs, these compounds may be present in the geologic media in any or all of three phases: adsorbed to soils, in free-phase form, or dissolved in groundwater. Of the three phases, dissolved contaminants in the groundwater are considered to be of greatest concern because of the risk of human exposure through drinking water; primary concerns for sorbed and free-phase contaminants often reside with their potential impact to groundwater. CAHs, used for years as industrial cleaners and degreasers, comprise some of the most common groundwater contaminants found at federal installations. Among the most common solvents are the chloroethenes and chloroethanes. The United States Air Force (USAF) uses more than 900 sites that are contaminated with chlorinated solvents in excess of drinking-water standards and that may require cleanup. Similar cleanup situations are faced by industry, other government agencies, and up to 85% of Superfund sites (United States Environmental Protection Agency [U.S. EPA] and USAF, 1993).

The Environmental Security Technology Certification Program (ESTCP) supported an 18-month field study to investigate the cometabolic air sparging (CAS) process at McClellan Air Force Base (McAFB), California. MCAF B was selected as the demonstration site for a variety of reasons: 1) MCAF B has significant CAH groundwater contamination; 2) previous studies supported by the Air Force Research Laboratory (AFRL/MLQ), Tyndall AFB, Florida demonstrated that indigenous bacteria at MCAF B could utilize propane as a growth substrate and support cometabolic CAH degradation; and 3) MCAF B is a member of the SERDP National Environmental Technologies Test Site program (NETTS) and expressed interest in supporting this unique technology.

The following text provides a layout of this report. Section 1 of this report provides an introduction to the technology including background information, official DoD requirements statements, objectives, regulatory drivers, and previous testing of the technology. Section 2 describes the technology, the biological process, strengths and weaknesses of the technology, and major factors influence cost and performance. Section 3 describes the test site and facilities. The demonstration approach, sampling and monitoring methods, and field and analytical methods are described in Section 4. The performance assessment is described in Section 5, which provides an interpretation of the results of the demonstration. The cost assessment is included in Section 6 and implementation issues, such as cost and performance observations, lessons learned, and approaches to regulatory compliance and acceptance are discussed in Section 7. References are included in Section 8. The report also has 7 appendices, labeled Appendix A through G. Appendix A provides points of contact for the study, and Appendix B provides a schedule of operating conditions and field observations. Appendix C shows all groundwater monitoring data and Appendix D shows all data from all soil gas monitoring points. The data in Appendices C and D are organized chronologically by groundwater or soil gas monitoring point. Historical figures for groundwater and soil gas monitoring points are shown in Appendices E and F; here, TCE, *c*-DCE, propane, oxygen (% in the vadose zone), and methane concentrations are plotted over time for the duration of the Phase 1 and Phase 2 field demonstrations. Lastly, Appendix G provides backup tables used to develop the costs for the cost assessment in Section 6.

1.2 Official DoD Requirements Statements

The following ten DoD needs have been identified as being applicable to this study:

1. U.S. Air Force ESDH Need No. USAF 817, Technology to Remediate Trichloroethene (TCE) and Other Chlorinated Organic Compounds in Soil and Groundwater
2. U.S. Air Force ESDH Need No. USAF 2008, Methods and Remedial Techniques are Needed to More Effectively Treat Groundwater Contaminated with Chlorinated Solvents Such as TCE, Trichloroethane (TCA), and Perchloroethene (PCE)
3. U.S. Air Force ESDH Need No. USAF 552, Develop a Method for In Situ Remediation of Soil and Groundwater Contaminated with TCE and Other Chlorinated Solvents
4. U.S. Air Force ESDH Need No. USAF 701, In Situ Treatment for Dense, Nonaqueous-Phase Layers
5. U.S. Air Force ESDH Need No. USAF 574, Remediation of Groundwater Contaminated with Other Chlorinated Solvents
6. U.S. Air Force ESDH Need No. USAF 1611, Treatment of Chlorinated Hydrocarbons

7. U.S. Air Force ESDH Need No. USAF 242, Hazardous Waste Treatment Technologies for Installation Restoration Program (IRP) Site Remediation of the Source of Chlorinated Organic Compounds
8. U.S. Air Force ESDH Need No. USAF 281, Hazardous Waste Treatment Technologies for IRP Site Remediation of the Plume of Chlorinated Organic Compounds
9. U.S. Army Need No. A(1.2.f), Alternatives to Pump and Treat
10. U.S. Army Need No. A(1.2.c), Solvents in Groundwater

The needs listed above are connected to the need to develop in situ technologies capable of remediating chlorinated solvents and other contaminants in groundwater. While previous work on air sparging has focused on its application to petroleum hydrocarbon contamination, this study focused on its application to the remediation of chlorinated solvent contamination.

1.3 Objectives of the Demonstration

The purpose of this demonstration was to evaluate the effectiveness of and costs associated with CAS for removal of CAHs from groundwater. The demonstration will serve to disseminate new information about air sparging to assist DoD environmental managers with the task of evaluating remedial proposals for CAH contaminants. The following lists specific objectives that were identified in the Demonstration Plan:

- Evaluation of oxygen and growth substrate (i.e., propane or methane) distribution in the subsurface
- Determination of growth substrate acclimation requirements
- Determination of growth substrate and oxygen uptake rates, after acclimation
- Evaluation of the ability of indigenous microorganisms to degrade different CAH compounds
- Prediction of long-term process stability
- Estimation of costs for CAS and comparison of costs for CAS to the cost of traditional air sparging or pump and treat (P&T) technologies

1.4 Regulatory Drivers

The target CAH compounds for the CAS technology include a variety of chlorinated solvents, including TCE, dichloroethene (DCE) isomers, vinyl chloride (VC), and TCA and lower chlorinated ethane isomers. The regulatory drivers for these environmental contaminants are

maximum contaminant levels (MCLs) (Table 1), governed under the Safe Drinking Water Act (42 U.S.C. s/s 300f et seq., 1974).

1.5 Previous Testing of the Technology

Travis and Rosenberg (1997) reported on the in situ bioremediation of TCE at Savannah River using cometabolism with methane as the primary growth substrate. Modeling results showed that bioremediation resulted in a 25% increase of TCE degradation over air-stripping alone. Horizontal wells for methane, air, and nutrient injection and extraction were used at the Savannah River Site (Hazen et al., 1994). Cometabolic CAH degradation by propane-degrading bacteria is unique to this study.

Table 1. Regulatory Drivers for CAS Target Contaminants

Organic Chemical	MCL (mg/L)	Potential Health Effects from Ingestion of Water
Tetrachloroethene	0.005	Liver problems; increased risk of cancer
Trichloroethene	0.005	Liver problems; increased risk of cancer
1,1-Dichloroethene	0.007	Liver problems
<i>cis</i> -1,2-Dichloroethene	0.07	Liver problems
<i>trans</i> -1,2-Dichloroethene	0.1	Liver problems
Vinyl chloride	0.002	Increased risk of cancer
1,1,1-Trichloroethane	0.2	Liver, nervous system, or circulatory problems
1,1,2-Trichloroethane	0.005	Liver, kidney, or immune system problems
1,2-Dichloroethane	0.005	Increased risk of cancer

Source: <http://www.epa.gov/safewater/mcl.html#3> (accessed December 2000).

2. Technology Description

2.1 Description

Air sparging is the process of injecting clean air directly into an aquifer for remediation of contaminated groundwater. In situ air sparging remediates groundwater through a combination of volatilization and enhanced biodegradation of contaminants. The induced air transport through the groundwater removes the more volatile and less soluble contaminants by physical stripping, and increased oxygen availability in the groundwater stimulates increased biological activity. Soil vapor extraction (SVE) may be combined with air sparging to control vapors emitted during the sparging process, particularly for CAH-contaminated sites.

CAS is an innovative form of conventional air sparging designed to remediate CAH-contaminated groundwater and to reduce off-gas CAH emissions. As with traditional air sparging, CAS also involves air injection directly into the aquifer. However, CAS is unique in that it also includes the addition into the aquifer of a gaseous organic growth substrate (growth substrate) to promote the in situ cometabolic degradation of CAH compounds. A cometabolic air sparging system is expected to be significantly lower in cost and duration than a comparable pump-and-treat system.

2.1.1 Technology Background, Development, Function, and Intended Use. CAS was developed as an extension of conventional air sparging to remediate groundwater contaminated with chlorinated solvents that are otherwise recalcitrant to aerobic degradation. Numerous studies have shown that various chlorinated solvents can be degraded cometabolically under aerobic conditions, by propane-, butane-, or methane-degrading bacteria. The CAS concept combined the knowledge of cometabolic degradation using bacteria that grow on these gaseous substrates with the more conventional air sparging approach.

The CAS technology is applicable to sites where groundwater is contaminated with chlorinated solvents that are known to be degraded cometabolically using butane, propane, or methane as primary growth substrates. The technology is limited to sites where air sparging would otherwise be considered an acceptable approach, but whose contaminants cannot be degraded as primary growth substrates and can only be degraded cometabolically. Target contaminants would include lower chlorinated ethenes (TCE, DCE isomers, and VC) and lower chlorinated ethanes (TCA and dichloroethane [DCA] isomers). The technology is not applicable to sites contaminated with aerobically and cometabolically recalcitrant compounds such as PCE.

2.1.2 Theory of Operation. CAS removes contaminants from saturated soil sediments through three primary removal mechanisms:

1. Increased dissolved oxygen (DO) plus propane introduction supports propane degradation, growth of indigenous propane-degrading bacteria, and the subsequent cometabolic degradation of CAHs by the propane-degrading bacteria.

2. Increased DO enhances in situ biodegradation by indigenous microbes of contaminants that can be used as substrates for energy and growth. Such contaminants include VC and DCE, which may be degraded as primary growth substrates or cometabolically.

3. Volatile organic compounds (VOCs) partition into the vapor phase and are transported to the vadose zone in the air stream where they may be degraded, captured by an SVE system, or released to the atmosphere, depending on the system design and the contaminant. Significant VOC degradation in the vadose zone may occur for VOCs that can oxidized aerobically, such as benzene, toluene, ethylbenzene, and xylenes (BTEX). Cometabolic degradation of VOCs also may occur if sufficient growth substrate is present in the vadose zone to support cometabolism, and if the growth substrate itself degrades in the vadose zone.

The relative contribution of each of these removal mechanisms is dependent on site characteristics, contaminant type and concentration, system design, and operational parameters. Table 2 lists general parameters that affect the design, operation, and performance of air sparging and CAS systems.

Table 2. Key Parameters that May Affect the Performance of Air Sparging Systems

Site Characteristics	Contaminant Characteristics	Operation Criteria
Soil heterogeneity and presence of low-permeability soils	Contaminant type	Contaminant removal rates
Hydraulic conductivity, gradient and direction	Henry's constant	Air distribution
Depth to water table and water table fluctuations	Vapor pressure	Air injection pressure and flowrate
Volume and extent of Contamination	Density	DO measurements
Aquifer permeability	Solubility in water	Saturated and unsaturated zone pressure measurements
Potential aboveground receptors	Octanol/water partition coefficient	Contaminant of sparged air
Presence of free-phase non-aqueous-phase liquids	Biodegradation potential	
Groundwater chemistry		

The ability of the vadose zone to degrade residual vapors (i.e., its biodegradation capacity) is dependent on the type and availability of indigenous soil microbes that can degrade the growth substrate and can cometabolically degrade the contaminant of interest; the contaminant type and concentration, and its degradation requirements; and the physical characteristics of the vadose zone soils (depth, porosity, specific surface area, heterogeneity, and anisotropy). If conditions in

the vadose zone soils can be optimized to destroy the residual sparging or CAS vapor stream, no vapor collection and treatment system is required.

SVE systems are commonly coupled to air sparging systems where the biodegradation capacity of the vadose zone is inadequate or unknown, or where the contaminants of concern are known to be recalcitrant to aerobic biodegradation. In some cases, SVE systems are installed for safety reasons to minimize the potential for uncontrolled vapor migration to subsurface structures or human receptors.

2.2 Process Description

Conceptually, CAS is a simple process of injecting a gaseous substrate such as propane with air beneath a groundwater table. Like conventional air sparging, CAS uses conventional installation techniques and common equipment such as air compressors, piping, and wells. The major components of a typical cometabolic air sparging system are shown in Figure 1, including an air injection well, an air compressor or blower to supply air, monitoring points and wells, and an optional SVE system.

The air injection wells generally are vertical and are screened at depths located below the contamination level. The wells are grouted to depths below the water table to prevent short-circuiting of air through a sand pack into the vadose zone. If the medium is homogenous sand, the airflow will be relatively uniform around the air injection well, resulting in good mass transfer. In contrast, a heterogeneous medium may result in non-uniform and confining airflow thus reducing air sparging effectiveness. In practice, all sites have some degree of soil heterogeneity and non-uniform airflow is common. The practitioner must ensure that the non-uniformity of airflow is acknowledged and accounted for in the system design.

Compressors or blowers are needed to supply air to the injection wells. The selection of a compressor or blower depends upon site-specific characteristics that dictate airflow and pressure requirements. The monitoring points and related equipment are needed to provide information on compressor air flowrates and pressure, and contaminant concentrations in the groundwater, soil, and effluent air stream to analyze the progress of the remediation. In some air sparging systems, an optional vapor extraction well is installed to transfer contaminated vapor from the vadose zone for treatment. Blowers require approximately 30% less energy than compressors and result in approximately 50% less noise. However, blowers have much less capacity than compressors to overcome strong hydrostatic pressures. Consequently, compressors are more suited to greater depths and tighter formations than blowers.

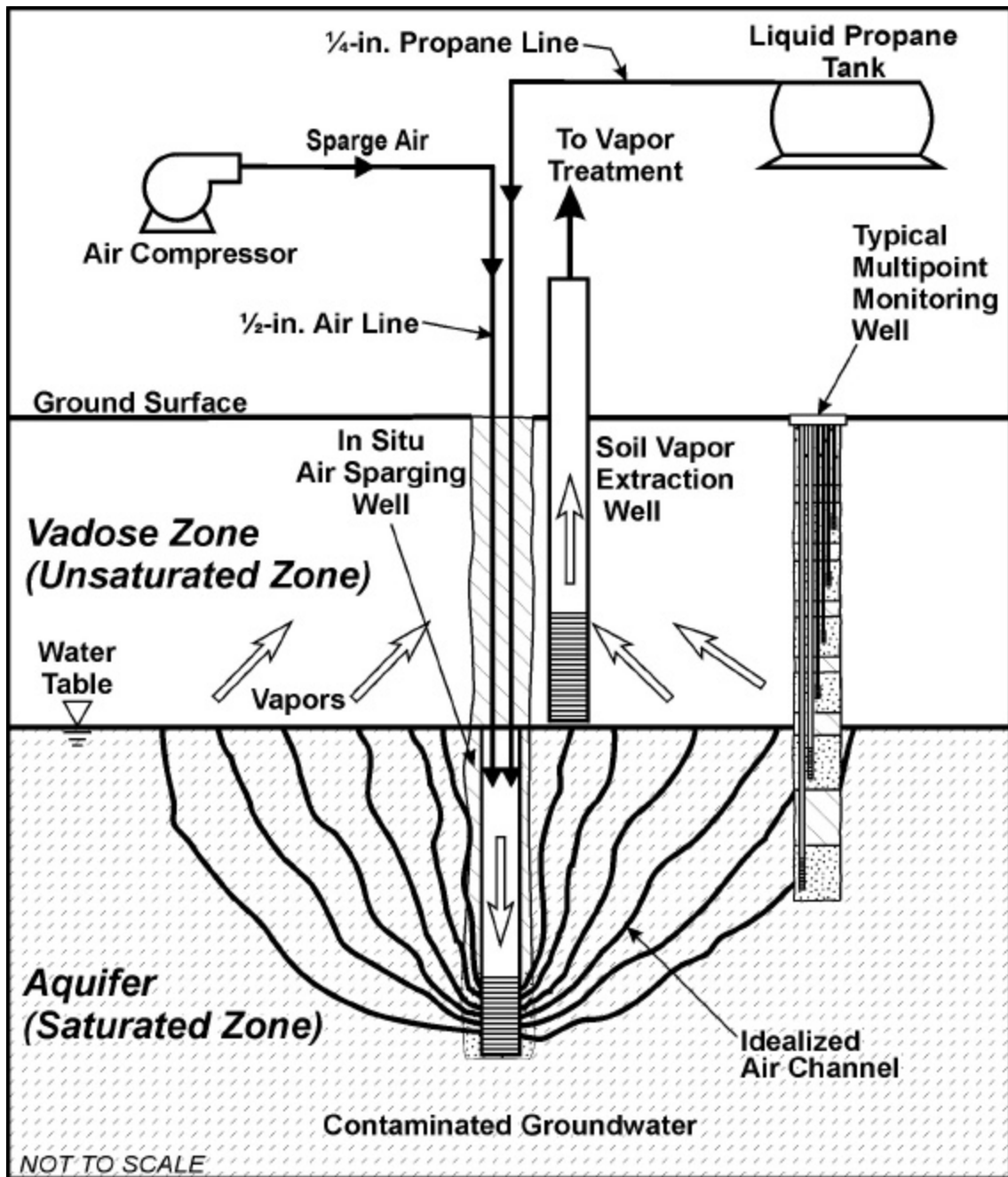


Figure 1. Conceptual Cometabolic Air Sparging Process Diagram

Air sparging has been demonstrated to be very effective at contaminant reduction, both for petroleum hydrocarbons and chlorinated solvents. A combination of volatilization and biodegradation allow for removal of many compounds to below detection limits. Historically, many sites have shown significant rebound of contaminant concentration after conducting air sparging. The cause of this appears to be primarily due to poor initial monitoring techniques that indicated the site was clean. Improved monitoring techniques such as discrete sampling from

groundwater monitoring points should alleviate this problem; however, it is recommended that sites continue to be sampled for at least one year after discontinuing cometabolic air sparging.

2.2.1 Key Design Criteria. Key design criteria include well spacing, injection rates, propane consumption, monitoring requirements, equipment sizing, and treatment duration. The criteria below are described for a system utilizing propane as the carbon source and should be adjusted accordingly if either butane or methane gas is used as the primary growth substrate.

- Well spacing should be based on the USAF Air Sparging Design Paradigm (Leeson et al., 2000).
- Injection rates, injection frequency, and propane requirements should be based on site-specific pilot studies and will depend on the rate of biological propane consumption. Unlike conventional air sparging, the primary goal of CAS is not to strip contaminants to the vadose zone; rather it is to promote propane and contaminant degradation in the saturated zone.
 - Injection rates should be as low as possible, while maintaining a reasonable zone of influence. Typical air sparging injection rates range from 5 to 20 standard cubic feet per minute (scfm). Air injection rates for cometabolic air sparging may be lower, to minimize contaminant volatilization.
 - Sparging with propane should be conducted intermittently to allow depletion of propane in groundwater between sparge events.
 - Propane should be added at a concentration of 1 to 4% in the injection air, depending on propane utilization rates. The stoichiometric equivalent propane concentration to 20% air is 4% propane. Thus, 4% is the maximum proposed propane concentration to prevent anaerobic conditions. However, lower concentrations are recommended, to minimize microbial competition between propane and the contaminant of interest.
 - Post treatment monitoring is required to assess the potential for contaminant rebound.
- Equipment such as air compressors, flow meters, and pressure gages should be sized according to site-specific sparge requirements.
- Monitoring should be conducted biweekly to monthly for the first six months to verify in situ degradation of the primary growth substrate and cometabolic CAH degradation. Thereafter, monitoring may be conducted on a quarterly basis to verify the biologically active system.

2.2.2 Performance Criteria. Technology performance is based on achievement of site-specific cleanup goals in groundwater. In the case of this study, the performance goal was to achieve MCLs for groundwater contaminants.

2.3 Strengths, Advantages, and Weaknesses of the Technology

CAS has several advantages over conventional remediation technologies, combining the benefits of conventional air sparging with the added value of cometabolic activity. Specific advantages are described in the following paragraphs.

- Air sparging is an aggressive process that can remove contaminants at a much faster rate than can standard pump-and-treat systems. Groundwater pumping with ex-situ treatment relies on dissolution of sorbed contaminants into the aquifer. Because many contaminants have low solubilities, the process of contaminant desorption and dissolution can limit the rate of effective removal in site-specific process designs. Therefore, conventional pump-and-treat systems sometimes require prohibitively long pumping durations to remove the pore volumes necessary to achieve site remediation. Alternatively, air sparging of CAHs, involving volatilization of dissolved and sorbed contaminants beneath the water table into the injected air, can lead to much higher contaminant removal rates than groundwater pumping alone.
- The cometabolic component of CAS allows for enhanced biodegradation of CAHs in groundwater to accelerate their removal, reduce vapor emissions, and increase the degree of remediation attainable. This component of CAS also results in mineralization of the CAHs to CO₂, H₂O, and chloride, which is preferable to transfer of the contaminants to another matrix.
- Conceptually, CAS is a simple process that uses commercial, off-the-shelf equipment. The air sparging component of CAS requires standard air compressors or blowers that can deliver air to the subsurface efficiently and at relatively low flowrates. To enhance cometabolism, CAS requires the addition of a gaseous growth substrate (such as propane, butane, or methane), which is widely available.

Disadvantages of CAS do exist and require thorough evaluation prior to implementation of the technology. Some uncertainties about long-term effectiveness will remain, as is the case with any innovative technology, but proper monitoring and evaluation can mitigate these uncertainties. Specific disadvantages include the following:

- Similar to most remedial technologies, the effectiveness of air sparging can be limited by soil heterogeneities at a site (i.e., differing permeabilities). In fact, minimal differences in soil permeabilities may

result in non-uniform distribution of injected air. This non-uniform distribution may lead to areas within a site that are not treated directly.

- At very large or very deep sites, air sparging costs may become prohibitive as a result of the relatively small zone of influence of the injected air. While the vertical column of air sparging may be relatively large, 15 ft is used as a common rule of thumb for the sparging radius of influence.
- CAS relies on the degradation of the primary growth substrate and cometabolic CAH transformation in the saturated zone and in the vadose zone for volatilized contaminants. Thus, microorganisms that can catalyze these reactions must be present in both the saturated and vadose zones. While methanotrophs are extremely common, propane- and butane-degrading microorganisms may not be present at every site. If degradation in the vadose zone is not achieved, soil vapor extraction of sparging off-gas may be required.
- If bacteria are not available, bioaugmentation may be a necessary step. However, to date there are no reports of in situ bioaugmentation for cometabolic degradation of environmental contaminants, making this an untested approach.
- CAS relies on cometabolic CAH degradation in both the saturated and vadose zones. In some cases, CAH cometabolism in the vadose zone may play a larger role than degradation in the saturated zone, and may be critical to the efficacy of CAS, due to the ease of CAH stripping from the saturated zone.

CAS is a new and innovative technology that uses air sparging principles but attempts to optimize in situ contaminant degradation by adding a growth substrate to the vapor stream. Because CAS is in a relatively young stage of development, the effectiveness of growth substrate addition and its potential to result in cost savings by reducing above ground vapor treatment were subjects of this study.

2.4 Factors Influencing Cost and Performance

When comparing CAS with alternative technologies, the cost and performance of CAS should be comparable to air sparging/stripping combined with SVE and above-ground treatment of off-gases. The primary difference between CAS and air sparging/SVE treatment is that the CAS process would avoid the SVE requirement and the collection and treatment of the off gas stream. Performance should be enhanced because bacteria would be expected to achieve equal or lower concentrations in groundwater than stripping alone. Cost would be reduced because the cost of propane would be considered small compared to the cost of an SVE system and the extended operation and maintenance costs of an off-gas treatment system (see Section 6).

Thus, major factors that will influence the performance and cost of this technology are: (1) the relative cost of SVE and above ground off-gas treatment, compared to propane requirements (refer to Section 6 and the *CAS Cost and Performance Report* [Battelle, 2001]); (2) the regulatory requirement for off-gas treatment (no off-gas treatment would make CAS much less expensive); and (3) the cometabolic performance in the vadose zone.

3. Site/Facility Description

3.1 Background and Test Site Selection

The McAFB site has relatively high TCE concentrations and a wide distribution of CAH compounds. This study was conducted at Operating Unit A (OU A). Upon first inspection, OU A appeared to have relatively permeable zones and to be geologically suitable for air sparging. Figure 2 shows the geologic cross-section of the site used to make this assessment. The site also was remotely located at the southern end of the base in an area of low vehicular traffic and minimal aboveground obstructions. However, drilling at the site revealed a heterogeneous aquifer with some relatively low permeable zones where sparging was hindered (see Section 5).

Oregon State University performed microcosm studies with soil collected from Operable Unit (OU) A before installation of the system. The results showed that propane-degrading bacteria are present at the site, indicating that propane would be a suitable primary growth substrate to promote in situ CAH cometabolism.

3.2 Site/Facility Characteristics

McAFB is located approximately 7 miles north of Sacramento, CA. In July 1987, the base was placed on the U.S. EPA's National Priorities List. In 1993, McAFB was designated a SERDP National Test Site. McAFB is divided into 11 operable units, designated as OUs A through H, OU B1, OU MW-C1, and OU GW. The CAS demonstration was conducted at OU A. The TCE plume in this area is shown in Figure 3. The site has TCE concentrations in excess of 500 µg/L.

OU A is the location of a former demolition and scrap material burning and burial pit that was operational from 1964 to 1969. Materials that were burned or buried include residues, scrap material, fuels and oils, solvents, semivolatile organic compounds, and volatile organic compounds. Around 1969, the activities ceased and the pit was filled. From 1953 to 1964, the site was used to store miscellaneous materials. Before 1953, the site was undeveloped grassland.

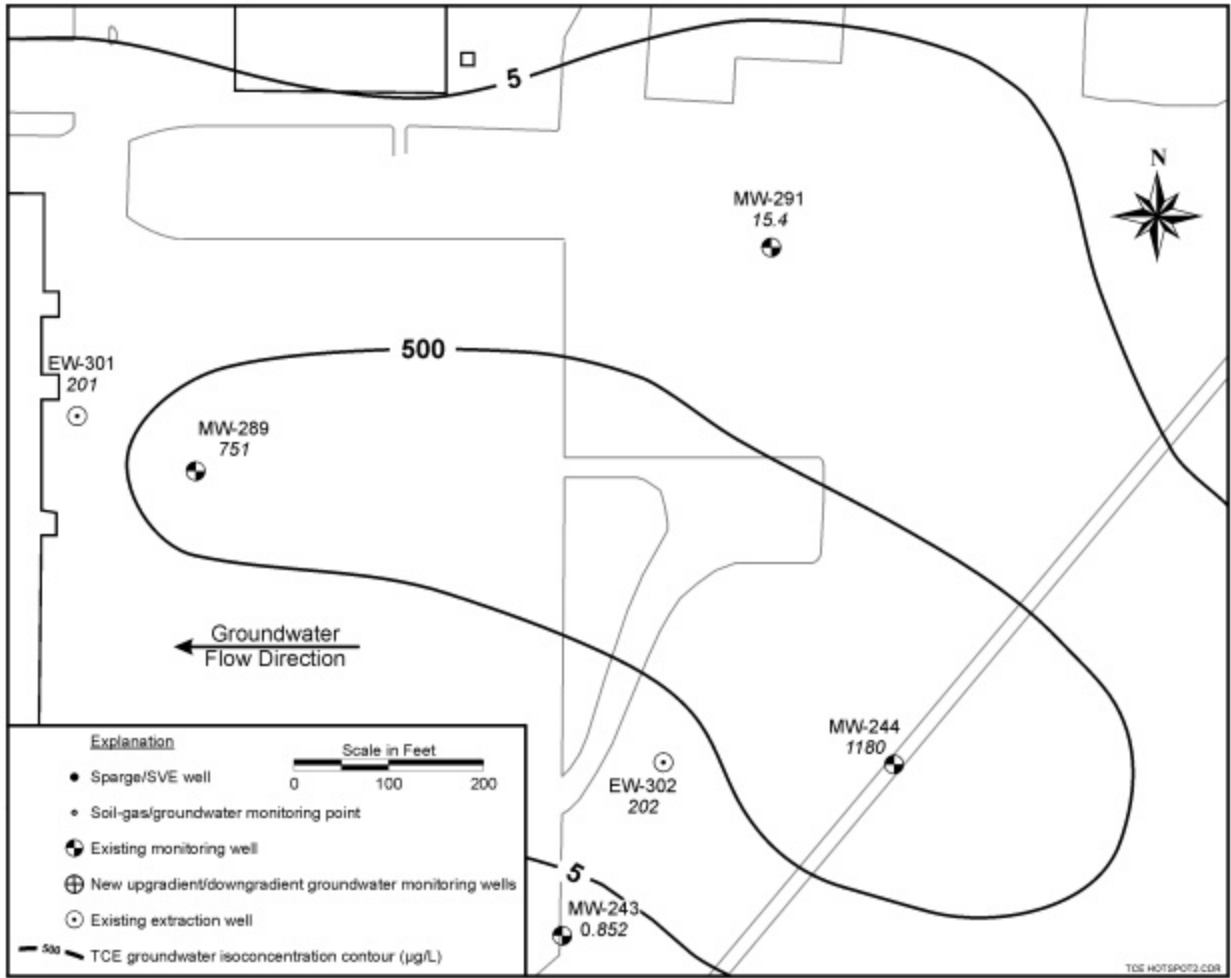


Figure 3. TCE Plume Contours at OU A

4. Demonstration Approach

4.1 Performance Objectives

The primary performance objective for this study was to conduct cometabolic air sparging at McAFB. The goal was not to remediate the site below regulatory levels, but rather to determine whether CAS is effective and whether employed monitoring techniques adequately predict performance. Other specific objectives included the following:

- Comparing air sparging effectiveness with and without the propane growth substrate, using one control sparge well and one propane-fed sparge well
- Monitoring propane degradation rates
- Establishing the effective zone of influence for oxygen and propane
- Establishing CAH concentration reductions resulting from CAS, and the relative contributions to site remediation of CAH stripping and cometabolic CAH degradation
- Conduct an economic analysis of cost and performance of CAS.

4.2 Physical Set-Up and Operation

Two test plots were installed at OU A: Zone C (propane and air injection or active test plot) and Zone A (air injection only or control test plot). Installations and operation activities were identical between the two test plots and are described in more detail in the following sections.

4.2.1 System Equipment. Each test plot contained one central sparge well, a soil vapor extraction well, six multi-level monitoring points, and two groundwater monitoring wells. In addition, one air injection system and one SVE system were used for both test plots. The propane injection system was connected to the active test plot only. These installations are shown in Figure 4 and described in the following sections.

McAFB installed all wells according to the requirements of McClellan Standard Operating Procedure (SOP) McAFB-004 for groundwater wells and SOP McAFB-006 for soil-gas monitoring points (McClellan, 1997). A Battelle staff member was on site to provide technical input and supervision. McAFB initiated dig and well permits, selected a drilling contractor, and scheduled the drilling.

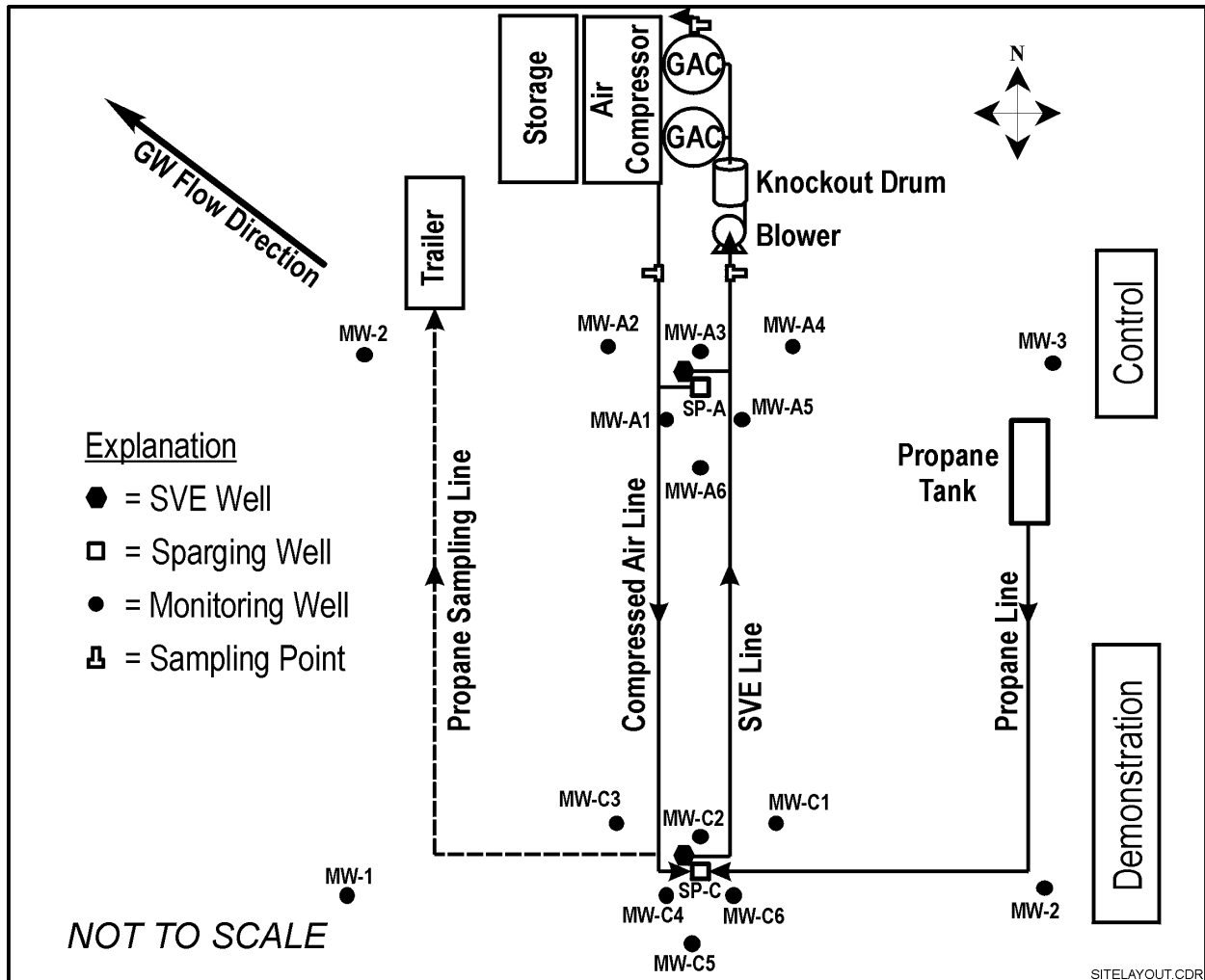


Figure 4. CAS Site Layout at McAFB

4.2.1.1 Sparge Wells. The primary design objective for the sparge wells was the effective distribution of compressed air into the subsurface. The sparge wells were designed to accommodate the required airflow and delivery pressure for the design objectives. Each sparge well was designed for flexible operation, enabling injection of a range of flowrates under a range of pressures. This flexibility was required to construct a system that was capable of varying operational parameters in response to varying field conditions.

One sparge well was installed into each test plot to compare air sparging with and without a growth substrate. One sparge well received air only (sparge well SP-A located in the control test plot), and one received propane plus air (sparge well SP-C located in the active test plot). Construction details were the same for both sparge wells to ensure similar performance during operation and to increase flexibility for future experiments.

The sparge wells were located approximately 100 ft apart. The 100-ft distance between sparge wells provided adequate distance to prevent the commingling of groundwater sparge effects (i.e.,

commingling of air bubbles or propane). As much as possible, the sparge wells were oriented perpendicular to the direction of groundwater flow, so that the effects of an upgradient well could not impact a downgradient well. Minor commingling was observed in the vadose zone, where propane was detected at very low concentrations in the vadose zone above the control well that did not receive propane.

Sparge well construction details are shown in Figure 5. The sparge well assembly was completed aboveground and consisted of a 17.5-ft-long, 2-inch inside diameter (I.D.) stainless steel pipe casing connected to 2.5-ft-long, 2-inch-diameter, 20-slot stainless steel screen. Three lengths of 3/8-inch stainless steel tubing were connected to the top of the casing: one tube was for propane injection, one tube was for air injection, and the third tube was utilized as a sample line. The tubing for propane and air injection extended into the casing approximately 8 inches while the sample line extended into the casing for approximately 2 inches. The purpose of this configuration was to enhance safety by reducing the volume of pipe that will contain a potentially explosive air/propane mixture.

When drilling was completed to the desired sparge well depth, the sparge well assembly was placed in the borehole through the center of a rig-mounted hollow-stem auger. The bottom of the sparge well assembly was located at 120 ft below ground surface (bgs). Sand (14 × 40 mesh) was added to the borehole (116 to 120 ft bgs) and the auger was gradually lifted until sand surrounded the well to approximately 1 ft above the screened interval. A bentonite seal (see Table 7 of SOP McAFB-004 for allowable materials) was added to the borehole and the auger was lifted gradually until the bentonite occupied the borehole up to 2 ft above the water table (approximately 98 to 116 ft bgs). Borings were grouted to a depth of 1 ft bgs according to SOP McAFB-004. Gravel or rock chips were added up to 6 inches bgs as a support for the concrete surface completion. The sparge well installation was completed with a 0.5-ft-thick, sloped concrete pad finished at grade around the air, propane, and sample lines, with the lines encased in polyvinyl chloride (PVC) pipe extending to the surface. All of the well surface completions were done by the McAFB drilling contractor and met the base requirements for being left in place following the study. The sparge wells were connected to the propane tank and air compressor via separate 2-inch-I.D. steel pipe.

The driller developed the new sparge wells. Development included removing sediment from inside the well casings and flushing fines from the portion of the formation adjacent to the well screens. Development continued until a minimum of five casing volumes of water had been removed from the sparge wells and until the pH, temperature, and conductivity stabilized in the pump effluent.

4.2.1.2 Soil Vapor Extraction System. A single SVE well was constructed adjacent to each sparge well. The SVE wells were used as a safety precaution in the event that the aboveground vapor CAH concentrations exceeded McAFB requirements. This did not occur throughout the demonstration, so the SVE system was not used.

The SVE wells were installed with a hollow stem auger and were screened from 90 ft bgs to the lowest recorded water table depth (approximately 111 ft bgs) using 20-slot, 2-inch-diameter, schedule 40 PVC. The casing extended from the ground surface to 90 ft bgs, and consisted of 2-

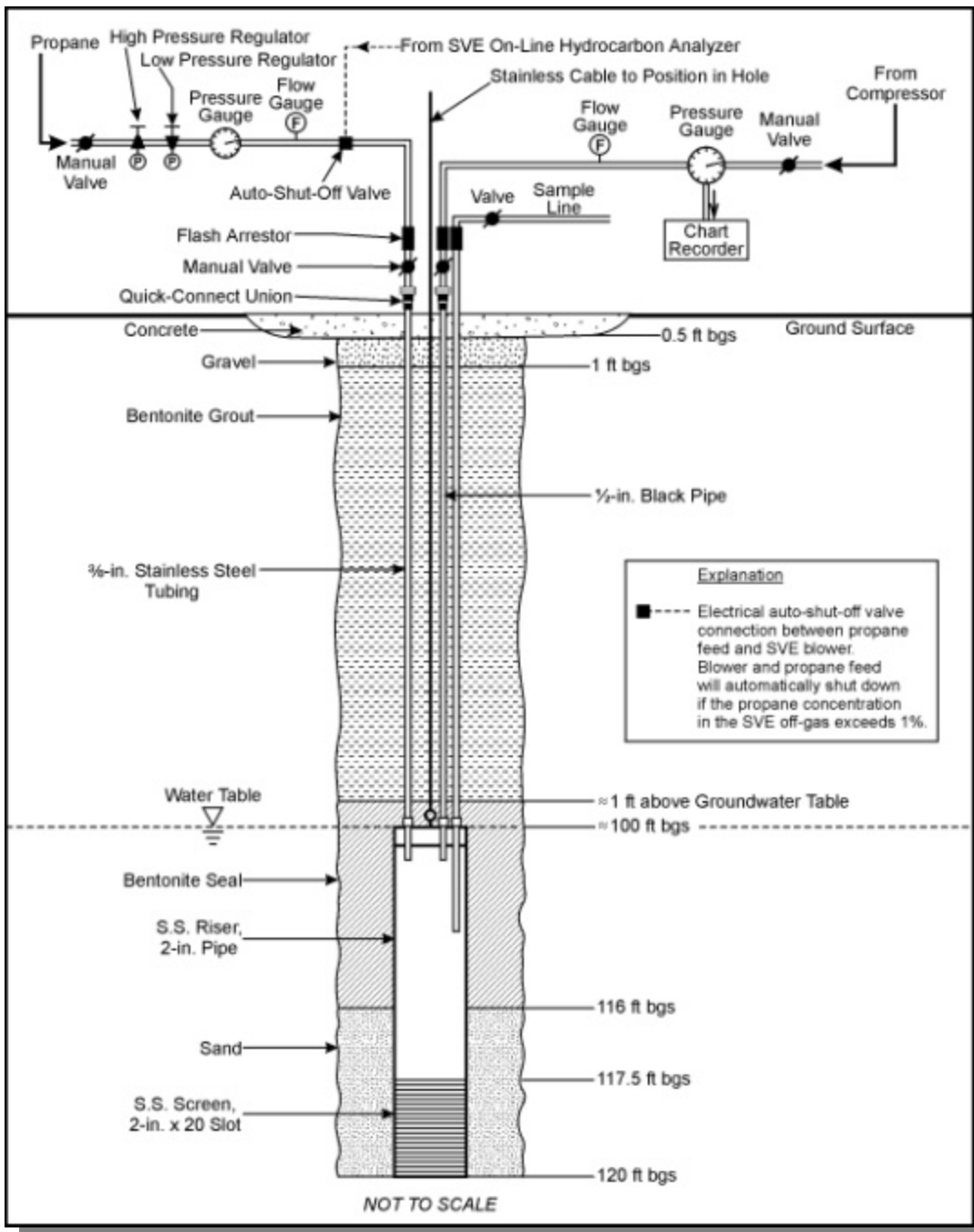


Figure 5. As Built Sparge Well Configuration

inch-diameter schedule 40 PVC pipe. Sand was added to the borehole until it covered the entire screened interval of the SVE well plus an additional 2 ft (approximately 88 ft bgs) as specified in SOP McAFB-006. The annular space was filled with bentonite chips that were thoroughly hydrated before completing the well construction followed by grout to a depth of 1 ft bgs as

specified in SOP McAFB-006. Gravel or rock chips were added from 1 ft to 6 inches bgs to provide support for the concrete surface completion. A 6-inch concrete pad was poured around the SVE well casing. Wells had riser completion as specified in SOP McAFB-006. All of the well surface completions were done by the McAFB drilling contractor and met the base requirements for being left in place following the study.

A 6-horsepower (hp), multi-speed blower, capable of operation at two to three speeds, was used for vapor extraction from the SVE wells. The SVE wells were manifolded to a feeder pipe that conducted the vapor through the extraction blower. A detachable water knockout vessel was placed in line to remove any gross moisture from the extracted vapor stream prior to the blower. The vapor was then forced through dual granular activated carbon (GAC) canisters for treatment prior to discharge to meet McAFB's 95% destruction and removal efficiency (DRE) requirement for extracted vapors. Each pipe leading from an SVE well was fitted with a flowmeter and a sampling port to facilitate monitoring of extracted vapor concentrations and flowrates.

For safety, the blower was built with explosion-proof electrical (i.e., Class 1, Div 1) and mechanical components. An ambient air bypass valve was installed that could dilute the SVE off-gas with ambient air for additional safety.

The SVE system was designed to extract 45 cfm per well, which is three times the maximum injection rate of 15 cfm. This would dilute the maximum applied concentration of propane in the extracted vapor stream to below the lower flammable limit (LFL) of 2.1%, providing an additional margin of safety. The only mechanical equipment downstream of the SVE well was the extraction blower. In addition to these safety precautions, the SVE blower system also was equipped with an LFL monitor located upstream of the blowers. The system was wired to shut down automatically if the propane concentration in the off-gas exceeded 50% of the propane LFL. The system was wired to stop propane injection if the blowers failed. This never occurred.

4.2.1.3 Groundwater and Soil-Gas Multi-Level Monitoring Points. Six monitoring points were installed surrounding each sparge well in a manner that allowed for the collection of soil gas and groundwater from a single sampling location at discrete depths (Figure 6). The soil-gas monitoring points were used to monitor soil-gas concentrations of carbon dioxide, oxygen, propane, and CAHs. The groundwater monitoring points were used to collect groundwater samples for DO, propane, and CAHs. The multi-level monitoring points consisted of two groundwater monitoring points screened at 113 and 117 ft bgs (bottom of screens), and four soil-gas monitoring points screened at 30, 85, 95, and 105 ft bgs.

Monitoring points in the vadose zone consisted of ¼-inch-diameter nylon tubing to their specified depths. They terminated with 6-inch-long and 1-inch-diameter 20-slot screens of PVC or stainless steel. Installation of vadose zone monitoring clusters conformed to the requirements of the SOP "Installation of Modified Soil Vapor Piezometer Nests" (McClellan AFB, 1999).

Groundwater monitoring points consisted of 2-inch-diameter PVC pipe, with 10-slot, 1.0-ft-long screens. The upper groundwater monitoring points were screened from 112 to 113 ft bgs, while the lower groundwater monitoring points were screened from 116 to 117 ft bgs. Submersible

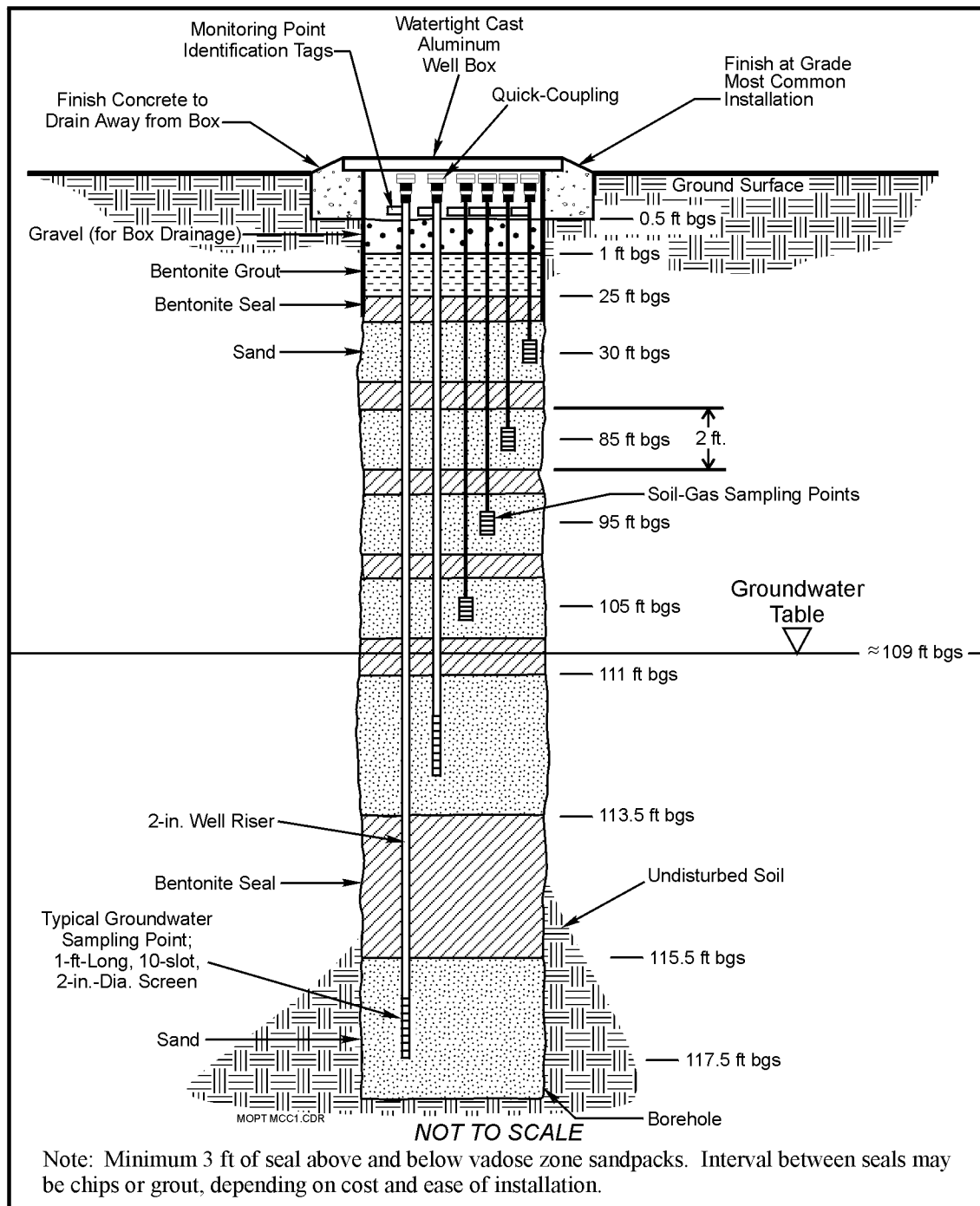


Figure 6. As Built Layout for Multi-level Soil Gas and Groundwater Monitoring Points

pneumatic bladder pumps were installed at the screened intervals to collect groundwater samples. The rigid PVC casing served as support when lowering the monitoring device into the boreholes. A pneumatic bladder pump was dedicated to each groundwater monitoring point. As-built depths of screened sections were confirmed by measuring the length of the casing

installed in the borehole. Groundwater monitoring points were constructed according to the requirements of SOP McAFB-004 (McClellan AFB, 1999).

All tubing from each vadose zone monitoring point was finished with quick-connect couplings and was labeled twice. The tubing was labeled with a firmly attached metal tag, marked by direct engraving. The labels were placed close to the ground so that if the tube was damaged, the labels would survive. The top of the casing for each saturated zone monitoring point also was clearly identified. The top of each monitoring point was labeled to be visible from above, by painting labels on the concrete pad and well casing.

The following nomenclature was used to identify the monitoring assembly. Monitoring points in the control test plot were labeled A and those in the active test plot were labeled C. The groundwater monitoring locations are represented by their depth 113 ft and 117 ft bgs, respectively (i.e., groundwater monitoring points at the 113 ft bgs level were labeled as MW-A1-113 through MW-A6-113 and MW-C1-113 through MW-C6-113).

Soil gas points were labeled according to their depth in the vadose zone; they were installed at 30-, 85-, 95-, and 105-ft bgs, respectively. For example, soil gas points at the well C1 are labeled as SG-C1-30, -85, -95, or -105, depending on the depth of the soil gas point.

4.2.1.4 Groundwater Monitoring Wells. For each sparge well, one upgradient and one downgradient monitoring well was installed. Each monitoring well was located 50 ft from the sparge well and was screened from 110 to 120 ft bgs. These four groundwater monitoring wells consisted of 2-inch PVC piping with 10-slot 10-ft-long well screens. A sand filter pack (14 × 40 mesh) was installed surrounding the screened interval (see SOP McAFB-004; McClellan AFB, 1999). A bentonite seal was placed between the top of the filter pack of the lower screened interval to approximately ½-ft below the bottom of the upper-screened interval. A sand filter pack was installed surrounding the upper screened interval, according to McAFB-004. A bentonite seal was placed from the top of the upper sand filter pack to above the static water table (McAFB-004).

4.2.1.5 Air Injection System. The air compressor supplied airflow and pressure to produce 25 pounds per square inch (psi) delivery air pressure and 15 cubic feet per minute (cfm) (maximum) air flowrate to each sparge well. The compressor was selected to provide durable, low-maintenance, and continuous heavy-duty air delivery for the project duration. For this purpose, a Quincy QRDS-15T120, 15-hp, 208V three-phase, oilless air compressor was installed at the site. This compressor was capable of supplying air continuously at 75-psi and 60-cfm.

For safety purposes, the compressor was located a minimum of 50 ft from the propane storage tank and propane gas lines, which is twice the required distance of 25 ft.

Operators adjusted the flowrate into the sparge wells with the system controls to attain the target flowrate of approximately 5 cfm in each well. Once the system was installed, the delivery pressures and flowrates were adjusted to establish similar flowrates in each sparge well.

4.2.1.6 Propane Gas Storage and Injection System. The propane gas growth substrate was delivered by a certified provider (Kamps, Manteca, CA), and stored on site in a 1,000-gallon tank. The propane injection system was constructed with in-line propane sensors and shutdown switches that would shut the system down if propane concentrations in the SVE lines reached 50% of the LFL (i.e., 1%), or if the air injection or vapor extraction systems failed. All sensors and alarms were explosion proof, as required, if they were likely to come into contact with propane.

The demonstration was conducted using 95% grade propane, which was a higher grade than commercial propane (generally 80 to 90% propane). Special measures were taken to make the propane odor-free, because of concern that the methyl mercaptain compounds added to commercial propane mixtures for odor could be harmful to the propane-degrading bacteria. The use of odor-free propane created other risks, particularly a risk of an unknown leak that would not be detected by smell. For this reason, all propane gas lines were monitored for leaks on a weekly basis. This resulted in increased monitoring costs. Costs also were impacted slightly by requiring a more expensive grade of propane than commercial grade.

The propane was injected into sparge well SP-C via a separate gas injection line. The propane was mixed with air in the sparge well at a depth of approximately 115 ft bgs. The maximum atmospheric concentration of propane introduced with air into the sparge well was approximately 4%, to provide a 5:1 oxygen:propane ratio. This ratio is calculated from the stoichiometry of propane and oxygen consumption shown in Equation 1:



The 4% propane concentration was the *maximum* target concentration of growth substrate that was employed during CAH testing. However, generally propane was added at lower concentrations, ranging from 1 to 4%.

Because the LFL of propane is an atmospheric concentration of 2.1%, the uppermost soil-gas points were monitored for propane concentrations, to protect against surface propane emissions from exceeding the LFL. The uppermost soil gas points never achieved the 2.1% propane concentration over the project duration.

Propane and DO levels were measured in the groundwater to determine not only whether there was residual propane in the groundwater but also whether the groundwater remained aerobic. If residual propane was measured or the aquifer DO dropped below 1 mg/L, the propane feed was decreased or terminated until propane disappeared and oxygen levels could rebound. Pulsing of propane was conducted to maintain low residual propane levels and to promote greater CAH degradation. All changes in air or propane flowrates were recorded and dated in a field-dedicated logbook.

4.2.1.7 Field Analytical Trailer. An Air Force field analytical trailer provided workspace for data analysis and other field tasks. The trailer belongs to AFRL/MLQ. The field gas chromatograph (GC), test kits, reagents, and analytical gases for the field demonstration were housed within the existing AFRL/MLQ laboratory trailer for the duration of the field

demonstration. The trailer was equipped with a Hewlett Packard (HP) GC, Model 5890, with a flame ionization detector (FID) and photoionization detector (PID), and a purge-and-trap sampler with 16 auto sample ports. The GC was set up, calibrated, and operated by Battelle. The GC was fitted with a GSQ-PLOT column (J&W Scientific, Folsom, CA).

For safety, the trailer and associated electrical equipment was located a minimum of 50 ft from the propane storage tank, which is twice the minimum required distance (25 ft) for standard equipment.

4.2.2 System Operation. The CAS field demonstration was conducted for 540 days at McAFB and was divided into two phases. Phase 1 focused on the groundwater remediation and propane degradation along with CAH dechlorination. Phase 2 of the demonstration focused on propane degradation and CAH remediation in the unsaturated zone. Table 3 shows the schedule for Phases 1 and 2, the number of days of operation for each phase, and startup periods for each phase.

To minimize stripping and maximize biodegradation, particularly during startup, sparging was conducted intermittently. Intermittent sparging involved sparging for 4 hours to saturate the formation with propane and oxygen, and turning off the sparge well for a predetermined period (generally one week). The length of time between intermittent sparging depended on the rate of groundwater flow and the rate of propane degradation. This was determined by monitoring of groundwater for DO and propane. The control well (without propane) was operated under the same conditions as the propane-fed well for comparison between the wells. A detailed schedule of operating conditions and field observations is provided in Appendix B.

4.3 Sampling, Monitoring, and Analytical Procedures

This section describes preliminary testing and system monitoring procedures.

4.3.1 System Testing. In most cases, system testing was conducted prior to initiation of propane injection. The exception is the sulfur hexafluoride (SF₆) tracer test that was conducted during Phase 2. The following activities were conducted as part of the system testing:

- Equipment shakedown
- Baseline testing
- Helium tracer testing
- Pressure transducer testing
- SF₆ tracer testing

4.3.1.1 Equipment Shakedown. A shakedown of all purchased equipment, including the equipment in the Air Force Trailer, was conducted to ensure that the equipment was in proper working condition and met the specifications identified when purchased. All purchased equipment, including major equipment such as the air compressor, SVE blower, groundwater monitoring point diaphragm pumps and controllers, and minor equipment such as valves and pressure gauges, operated satisfactorily upon receipt. The in-well diaphragm pumps caused some difficulty because of their very slow operating flowrates. Because of the slow flowrates,

Table 3. Schedule of Operation for Phases 1 and 2

Day	Task
<i>Construction and Mobilization</i>	
-65 to -42	Drilling and CAS installation
-44 to -40	Refurbishment of onsite GC
-51 to -47	10-h sparge test (air only)
-30 to -1	Develop analytical QA/QC
0 ¹	Initiation of air sparging (air only)
<i>Start-Up and Phase 1</i>	
0-36	Establish background CAH levels; air distribution tests
36	Propane injection initiated at 2% in air
37-79	Monitored propane concentrations in saturated and vadose zones in both test plots. No air sparging.
81-124	Weekly propane injection (4 h at 4% propane).
125-170	Propane injections increased to twice weekly (4 h at 2% propane) to accelerate TCE/c-DCE bioremediation
170-187	No propane or air added so that propane oxidation rates could be verified and compared to earlier rates to see if remediation would continue without additional propane.
188-243	Ammonia to active and control test plots (with propane & air in active test plot, air only in control test plot) at 0.01%, due to potential nitrogen limitation in the treatment zone.
244-392	Propane concentrations in the saturated and vadose zones were monitored. No air sparging.
<i>Phase 2</i>	
393-394	SF ₆ and pressure transducer tests conducted for Multi-Site ESTCP study; sparged at 10 scfm (air only) for 1 day.
398-401	Post-sparge baseline, beginning of Phase 2.
404-427	Weekly propane injection (4 h, 1% propane in air)
431-435	Conducted nitrogen push-pull tests in the vadose zone to see if vadose zone is nitrogen limited.
440-450	Weekly propane injections (4 h, 1% propane in air)
454-478	Weekly propane injections (4 h, 2% propane in air)
482	Sparged for 4 h at 4% propane. Increased sampling frequency to measure degradation kinetics.
485-503	Bi-weekly injection of 4% propane and 0.1% ethylene.
504-511	Ethylene monitoring in vadose & saturated zones, no sparging.
512-526	Weekly sparging with methane at 7.9 standard liters per minute (SLPM)
527-545	Methane monitoring in vadose and saturated zones, no sparging
546	Methane injection at 7.9 SLPM
588	Final groundwater and vadose zone sampling event

¹Day 0 is May 12, 1999.

well development at each sampling event required approximately four hours. However, this obstacle was overcome by on-site staff that initiated well development in the morning on sampling days and conducted alternate tasks during development process.

The AFRL/MLQ trailer analytical equipment required rehabilitation and repair, due mostly to disuse prior to this study. Besides requiring a new column, the manufacturer conducted an on-site shakedown of the GC and Purge and Trap plumbing and temperature controls. In addition, an updated ChemStation (Agilent, 2000; Palo Alto, California) data integration program was purchased to operate the GC and Purge and Trap and to integrate the chromatograms. The new ChemStation software required a computer of greater capacity than the computer housed in the trailer. Battelle provided a computer at no additional charge for use during the study.

4.3.1.2 Baseline Monitoring. Groundwater samples were collected from the discrete groundwater sampling points to monitor DO concentrations in response to gas sparging using a water quality meter (Horiba U-10). Baseline monitoring included the collection of groundwater and soil gas CAH and oxygen concentrations. Baseline monitoring was conducted over a 40-day period, after the helium and pressure transducer tests and before the onset of propane sparging. Groundwater quality parameters including pH and conductivity also were measured using a water quality meter (Horiba U-10). Temperature could not be measured from the surface, due to the 100-ft travel distance for the groundwater samples to travel, and thermocouples were not installed in the wells. The groundwater samples were collected using the U.S. EPA Low-Flow Groundwater Sampling Procedures with the use of pneumatic bladder peristaltic pumps. Groundwater samples were analyzed on site for VOCs using the AFRL/MLQ trailer GC-FID/PID.

The following CAH compounds were targeted for the baseline sampling effort: PCE; TCE; *cis*-dichloroethene (*c*-DCE); 1,1-dichloroethene (1,1-DCE); chloroform (CF); and 1,1-dichloroethene (1,1-DCA). The selection of these compounds was based on the range of contaminants detected at OU A.

Soil gas parameters during background sampling included CAH concentrations and oxygen. Soil gas was extracted from the vadose zone with a ¼-hp diaphragm pump. A sufficient amount of soil gas was purged before sample collection and field parameters were measured. The diaphragm pump was run for 10 minutes to flush out the lines. A Tedlar™ bag was purged three times with the soil-gas before collection.

4.3.1.3 Helium Tracer Testing. The helium tracer test was conducted to measure the recovery of helium by the SVE system. Helium recovery by the SVE system would determine whether the majority of helium was recoverable (i.e. distributed within a workable radius of influence).

Helium was measured with a Marks Helium Detector Model 9821 which has a minimum sensitivity of 100 parts per million by volume (ppmv) (0.01%). The helium detector is factory calibrated and cannot be calibrated in the field; however, proper operation is checked with a helium standard. Helium standards commonly contain 100 ppmv (0.01%), 5,000 ppmv (0.5%), or 10,000 ppmv (1%) He.

4.3.1.4 Pressure Transducer Test. Pressure transducer measurements allow for monitoring of pressure changes in the groundwater at the initiation of air injection. These pressure changes may be correlated to a zone of influence of the air sparging system. The response of pressure transducers in nearby groundwater monitoring points was recorded during system startup for approximately 90 hours. Ashcroft pressure transducers (Model 2KC1) were attached to a data logger, which recorded measurements during testing.

4.3.1.5 SF₆ Tracer Testing . During Phase II, a sulfur hexafluoride (SF₆) tracer test was conducted by blending SF₆ with the air injection stream from the in situ air sparging compressor. SF₆ was injected continuously at a known mass rate for approximately 24 hours, at which time groundwater samples were collected to assess air distribution within the aquifer. The groundwater samples were collected from the discrete groundwater monitoring points. The concentration of SF₆ in the injected air was determined in the field. Based on the injection concentration, a theoretical solubility in the groundwater was calculated using a dimensionless Henry's law gas constant for SF₆ of 150.

The SF₆ data do not give a direct measure of air saturation. Instead, the SF₆ data indicate where sparge air has been present in the groundwater zone during the period of its injection. In general, it can be assumed that SF₆ concentrations measured near saturation indicate that air pathways were near the sampling point; zero or near-zero percent saturation indicates that air has not been in the vicinity of the sampling point.

There were no attempts to recover SF₆ within the air sparging system, because both proposed test areas are situated such that existing McAFB groundwater extraction wells would eventually capture and remove 100% of the SF₆ tracer.

4.3.2 System Monitoring. The site was staffed 75% to 100% of the time during system operation. The on-site staff checked the mechanical equipment daily (Monday through Friday), including blowers, compressors, flow meters, and pressure meters, according to manufacturer requirements. Air flow meters, pressure gauges, and other monitoring equipment were adjusted when used and recorded in a field-dedicated logbook. Adjustments to the operating flowrates or pressures for sparged air or sparged propane were made if they deviated by more than $\pm 10\%$ of their target values.

4.3.2.1 Groundwater Sampling. Groundwater samples were collected during air sparging with air only, followed by weekly collection (approximately) after initiation of propane injection. Parameters measured included groundwater quality parameters, contaminant concentrations, dissolved oxygen, and propane. Sample collection included quality assurance/quality control (QA/QC) samples, which included a check standard and a duplicate sample for every batch of 12 groundwater or soil gas samples. Prior to sampling, sampling point identification was checked and recorded along with the date and time in the field logbook. Groundwater samples were collected using in-well pneumatic bladder peristaltic pumps.

Some flexibility was maintained for field sampling frequency for each analytical constituent. For example, during Phases I and II, the soil-gas monitoring points at the 95 ft depth points were monitored at greater frequency to identify propane degradation and/or CAH cometabolism than

the remaining soil gas points. The remaining points were monitored approximately monthly so their results could be compared with those of the 95 ft depth. Similarly, during Phase II, because most of the observed activity occurred in only six of the twelve groundwater monitoring points in the active test plot, only these six monitoring points were sampled regularly. The remaining points were sampled approximately monthly. Furthermore, the active test plot was sampled at a higher frequency (weekly) than the control test plot (weekly during Phase I and monthly during Phase II). These approaches to sampling provided sufficient data to monitor and assess process performance while minimizing analytical time and operating costs.

During Phase II, the active test plot monitoring points that were sampled with the highest frequency were monitoring points MW-C2, MW-C3, and MW-C4 at the 117-ft depth interval. These monitoring points demonstrated the highest levels of propane-degrading and CAH cometabolic activities. Between Phases I and II, all monitoring points at the 113-ft depth interval ran dry and were unable to be sampled for groundwater. Although unexpected, this was not necessarily surprising, because the groundwater in the Sacramento area is reported to drop as much as 1 ft per year. For this reason, the 113-ft interval groundwater monitoring points were not sampled during Phase II.

Groundwater Quality Parameters. Groundwater quality parameters included redox, temperature, pH, turbidity, alkalinity, nitrate (NO_3^- -N), ammonia (NH_4^+ -N), and total Kjeldahl nitrogen (TKN). Samples were measured for DO, redox, pH, conductivity, turbidity, and temperature under continuous flow using a water quality meter (Horiba Model U-10). To minimize sample aeration, a continuous flow-through cell was used to provide a sampling chamber for the meter. A sufficient volume of water from the well or groundwater sampling point was purged before sample collection to ensure that a sample representative of the formation was obtained. Purged volume equaled three times the well volume or the volume required to establish stable DO, redox, pH, conductivity, turbidity, and temperature readings. A minimum of one well volume was purged for each sample event.

Contaminant Measurements. During Phase 1, groundwater samples were analyzed for VOCs in the field using the USAF laboratory GC-FID/PID. During Phase 2, groundwater samples were sent to the OSU laboratory for analysis, also using a GC-FID/PID. Analytical methods, sampling frequency, and requirements for VOCs in groundwater are listed in Table 4.

Groundwater samples for on- and off-site contaminant analyses were collected in 40 mL volatile organic analysis (VOA) vials with Teflon™-coated septa-lined caps. The pH of the aqueous effluent samples was adjusted to a value of <2 with hydrochloric acid (HCl) to stabilize the organic species, and the samples were stored at 4°C until analysis. During Phase II of the demonstration, when HCl in the samples was observed to have interfered with nitrate/nitrite analyses, duplicate samples were taken at each monitoring point; one sample was preserved with HCl and the other with sulfuric acid (H_2SO_4). Sulfuric acid did not appear to hinder $\text{NO}_3^-/\text{NO}_2^-$ analyses. The VOA vials were stored at 4°C until analysis.

Table 4. Analytical Methods and Sampling Frequency/Requirements for VOCs in Groundwater and Soil Gas

Analyte	Sample Location (Matrix)	On- or Off-Site Analysis	Frequency	Method or Instrumentation	Container Type	Container Size	Preservative	Holding Time
O ₂ /CO ₂	SGMP (vapor)	On	Weekly	GT 205	None	NA	NA	NA
Temp/dew point/relative humidity	SGMP (vapor)	On	Weekly	Hygrometer/ Thermometer Model 35519-041 (Control Corp)	None	NA	NA	NA
CAHs	SGMP (vapor)	On	Weekly	8021BM; HP GC Model 5890	Tedlar™	1 L	None	Same day
Propane/Methane/Ethylene	SGMP (vapor)	On	Weekly	8021BM; HP GC Model 5890	Tedlar™	1 L	None	Same day
DO/pH/Temp/Turbidity/Conductivity	GWMP (liquid)	On	Weekly	Horiba Model U-10	None	NA	NA	NA
CAHs	GWMP (liquid)	Phase 1: On Phase 2: Off	Weekly	SW 9-846 802BM; HP GC Model 5890	VOA vial	40-mL	Phase 1: 4°C Phase 2: one vial HCl, second vial H ₂ SO ₄	14 days
Propane/Methane/Ethylene	GWMP (liquid)	Phase 1: On Phase 2: Off	Weekly	SW 846 802BM; HP GC Model 5890	VOA vial	40-mL	Phase 1: 4°C Phase 2: one vial HCl, second vial H ₂ SO ₄	14 days
NO ₂ /NO ₃ /SO ₄	GWMP (liquid)	Phase 2: Off	Weekly	IC	VOA vial	40-mL	Phase 1: 4°C Phase 2: one vial HCl, second vial H ₂ SO ₄	14 days
Propane	Sparge well (vapor)	On	Continuous	Series 8800 Continuous Analyzer (Baseline Industries)	None	NA	NA	NA

SGMP = soil gas monitoring point

GWMP = groundwater monitoring point

The following analytes were targeted for the on-site analyses: PCE; TCE; c-DCE; 1,1-DCE; CF; and 1,1-DCA. The selection of these compounds was based on the range of contaminants detected at OU A. Intermediate breakdown products, such as TCE epoxides, are highly unstable and will not remain in the groundwater long enough to be measured. Therefore, finding and measuring these breakdown products in groundwater and soil gas was not included in the scope of this study.

Samples measured in the field were analyzed using a purge-and-trap GC method. Samples were identified and quantified against known standards. Liquid standards were prepared gravimetrically in an off-site laboratory and shipped to the site. These standards were stored at 4°C until use. They were diluted volumetrically on site using deionized water and were injected manually into the purge-and-trap for GC analysis. A minimum of one check standard was analyzed for every set of 15 purge and trap samples.

4.3.2.2 Soil Gas Sampling. Soil gas samples were collected once during air sparging with air only, followed by weekly collection (approximately) after initiation of propane injection. Parameters measured included contaminant concentrations, oxygen, carbon dioxide, and propane. Sample collection included QA/QC samples. When propane uptake was measurable, soil gas monitoring points that showed maximum activity were sampled more frequently, while those that did not show significant activity were monitored less frequently. During Phase 1, the soil gas monitoring points at the 85-ft and 95-ft depth were monitored weekly (approximately) in the active test plot. The 85-ft and 95-ft depth monitoring points in the control test plot were monitored approximately every two to three weeks, because much less activity was expected in the control test plot. Monitoring points in both test plots at the 30-ft depth and the 105-ft depth were monitored approximately every two to four weeks. During Phase 2, the sampling frequency was reduced to monthly for all monitoring points except the 95-ft-depth monitoring points in the active test plot.

Soil gas was extracted from the vadose zone with a ¼-hp diaphragm pump. A sufficient amount of soil gas was purged before sample collection and field parameters were measured. The diaphragm pump was run for 10 minutes to flush out the lines. A Tedlar™ bag was purged three times with the soil-gas before collection.

During Phase 2, at every sampling event, the temperature, dew point, and relative humidity of the soil gas were analyzed using a Control Company Digital Hygrometer/Thermometer Model 35519-041. During Phase 1, these measurements were not taken. They were included in Phase 2 due to a concern that low moisture content was inhibiting propane degradation in the vadose zone. A digital display showed the measurements within the sample instantaneously. The probe of the hygrometer/thermometer was placed in a stilling chamber comprised of a six-inch piece of SCH 40 PVC. The readings were taken after 10 minutes of purging the stilling chamber with fresh soil gas.

Contaminant Concentrations. Analytical methods and sampling frequency/requirements for VOCs in soil gas are listed in Table 4. Soil gas was also analyzed for VOCs using the GC-FID/PID in the USAF analytical trailer; target soil-gas VOCs were TCE, c-DCE, 1,1-DCE, 1,1-DCA, and CF. VOCs were identified and quantified against a standard mixture. Gas samples

were analyzed using the purge-and-trap GC method. Detection limits for chlorinated compounds were as follows:

<u>Compound</u>	<u>Water</u>	<u>Soil Gas</u>
▪ 1,1-DCE	0.27 ppb	62 ppbv
▪ 1,1-DCA	0.204 ppb	55 ppbv
▪ cis-DCE	0.278 ppb	100 ppbv
▪ chloroform	0.284 ppb	55 ppbv
▪ TCE	0.424 ppb	93 ppbv
▪ PCE	0.292 ppb	99 ppbv

Oxygen and Carbon Dioxide Concentrations. Gaseous concentrations of carbon dioxide and oxygen were analyzed using a GasTech series gas monitor Model 205, equipped with a digital display that shows continuous soil-gas concentrations. A digital display shows the soil gas concentrations of carbon dioxide and oxygen within the sample instantaneously. The battery charge level on the GT205 was checked to ensure proper operation. The air filters were checked and, if necessary, were cleaned or replaced before the sample started. The instrument was turned on and equilibrated for at least 10 minutes before conducting calibration checks. The instrument was checked using 10% oxygen standard, 5% carbon dioxide standard, and an ambient air sample before each day of measurements. If the instrument did not measure the calibration check correctly, the instrument was then sent back to the manufacturer for a maintenance and calibration. The sampling pump of the instrument was checked to ensure that it was functioning.

Propane Concentration. Propane concentrations in soil gas were measured using the on-site GC-FID/PID in the USAF trailer (Hewlett Packard, Model 5890 Series II). The GC was calibrated against propane standards, which were taken from a specialty gas cylinder provided for the project (Scott Specialty Gases, Plumsteadville, PA). Samples were collected using Tedlar™ bags, which were carried to the field trailer for analysis. Samples were drawn from the bags using a hand-held syringe and were hand injected into the purge-and-trap autosampler for analysis.

4.3.2.3 Depth to Groundwater. The depth to groundwater in groundwater monitoring points was measured with a water-level probe (Solinst, Model 101 with P4 probe). The probe lead was a 200-ft measuring tape marked with 0.01-ft increments. The probe gives a tone when it encounters water. Light, nonaqueous-phase liquid (LNAPL) was not encountered at the site, so an oil-water interface probe was not required. Water-level measurements were recorded in the field notebook. The probe was decontaminated between wells.

5. Performance Assessment

For the purposes of this report, and to maintain brevity, Section 5 focuses on selected groundwater monitoring points at the active and control test plots that represent the typical activity observed during the experimental operating period. Data for all the groundwater and soil-gas monitoring points are located in Appendices C and D, respectively. Historical figures for the groundwater and soil-gas monitoring points are presented in Appendices E and F, respectively. A discussion of the air distribution evaluation testing conducted at the site is first discussed to provide an understanding of the subsurface environment (Section 5.1). A summary of the study results from both phases is presented in Section 5.2, followed by a data assessment presented in Section 5.3, and a technology comparison in Section 5.4.

5.1 Air Distribution Evaluation

Three diagnostic tests were conducted to evaluate the air distribution at the test site: helium tracer testing, pressure testing, and sulfur hexafluoride (SF₆) tracer testing. Results from these tests are discussed in the following sections.

5.1.1 Helium Tracer Testing. A helium tracer test was performed to determine the capture effectiveness of the SVE system (Figure 7). The percent of the injected air that is captured was calculated by a simple steady-state mass balance. The SVE flowrate is multiplied by the asymptotic helium concentration (expressed as a helium volume/total volume percentage) and then it is divided by the helium injection rate times 100% as shown below.

$$\% \text{ recovery} = \frac{Q_{\text{SVE}} \times C_{\text{Off-gas}}}{Q_{\text{Helium}} \times C_{\text{gas tank}}} \quad (2)$$

Where Q_{SVE} = the SVE flowrate; $C_{\text{off-gas}}$ = the tracer concentration in the SVE off-gas; Q_{helium} = the helium flowrate; and $C_{\text{gas tank}}$ = the helium concentration in the gas tank.

Greater than 80% of the injected helium was recovered in the SVE wells in both the active and control test plots. However, vapor extraction rates in the active test plot were much higher than in the control test plot; vapor extraction rates exceeded 45 scfm in the active test plot compared to a maximum extraction rate of 20 scfm in the control test plot. This greater vapor recovery in the active test plot was due to greater permeability and not to mechanical differences. The vacuum measured in both test plots exceeded 100 inches of mercury.

5.1.2 Pressure Transducer Testing. Pressure transducer tests were performed to determine if subsurface confining layers existed that would act as a barrier to vertical air flow. Pressure transducer test results indicated that vapor breakthrough was achieved in both systems within a reasonable time period (Figure 8). However, longer recovery periods and erratic behavior observed at the active test plot suggested that some subsurface stratification existed in this area that impacted air distribution. Propane distribution results discussed in Section 5.2 support this conclusion, since some monitoring points had measurable propane concentrations while others did not.

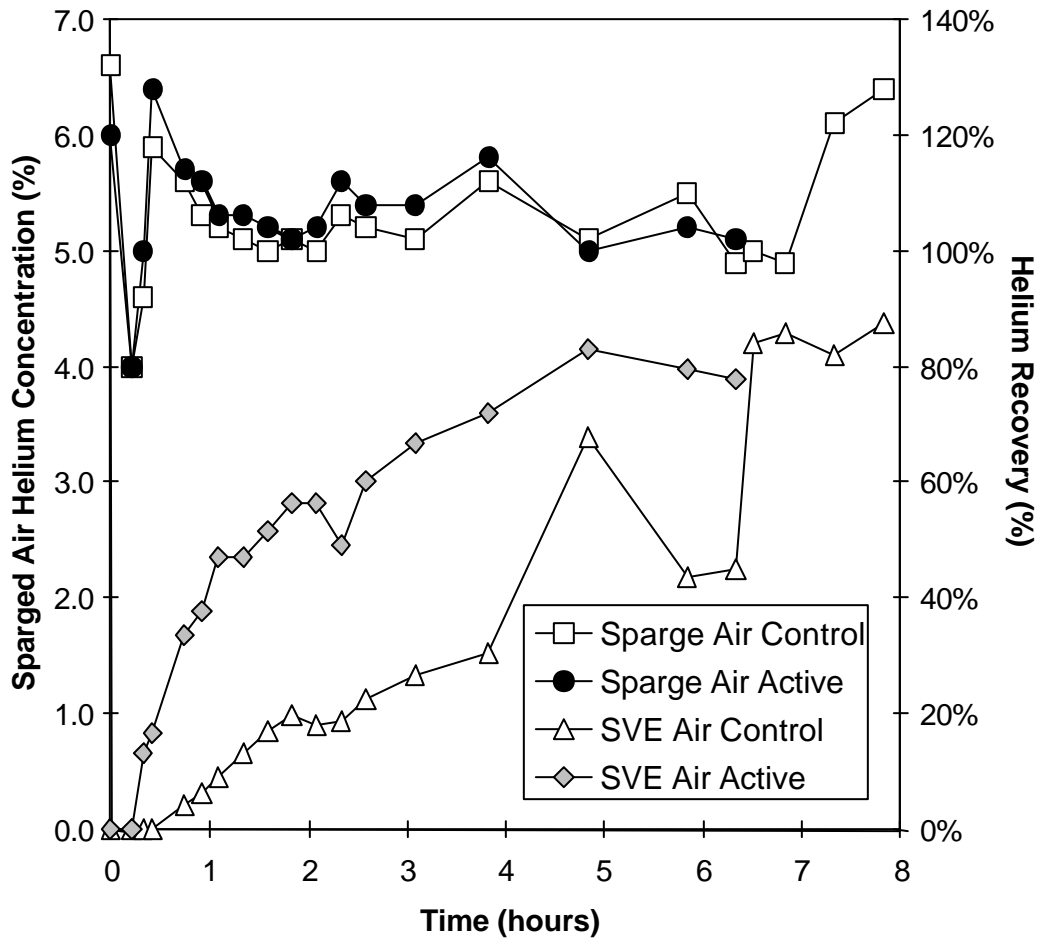


Figure 7. Helium Tracer Test Results from the Control Test Plot and the Active Test Plot

5.1.3 SF₆ Tracer Testing. In addition to the helium tracer and pressure transducer tests, an SF₆ test was conducted at the McAFB site as part of the Multi-Site Air Sparging program, funded by ESTCP. Results of the SF₆ tracer testing were reported in the Final Report of the Multi-Site Air Sparging Study and are included below (Leeson et al., 2001).

A second pressure transducer test was conducted as part of the Multi-Site Air Sparging study as well as an SF₆ tracer test. The tests were conducted at both the active and control test plots.

Injection pressure for the active test plot was significantly higher than for the control test plot (>20 psi versus 10 psi) at a nominal 10 cfm flowrate. Pressure responses in the monitoring wells were similar at both test plots. In general terms, the responses were fairly large (>1 m of water in several cases) and the pressure changes persisted for hours. This would suggest that stratification was playing a role in the air distribution at both test plots. At the control test plot, the pressure change during startup was approximately 120 cm. The behavior of the pressure after approximately 2.5 hours is unusual in our experience. It suggests that there was some fairly steady increase in the volume of trapped air over the duration of the test (Figure 9). The

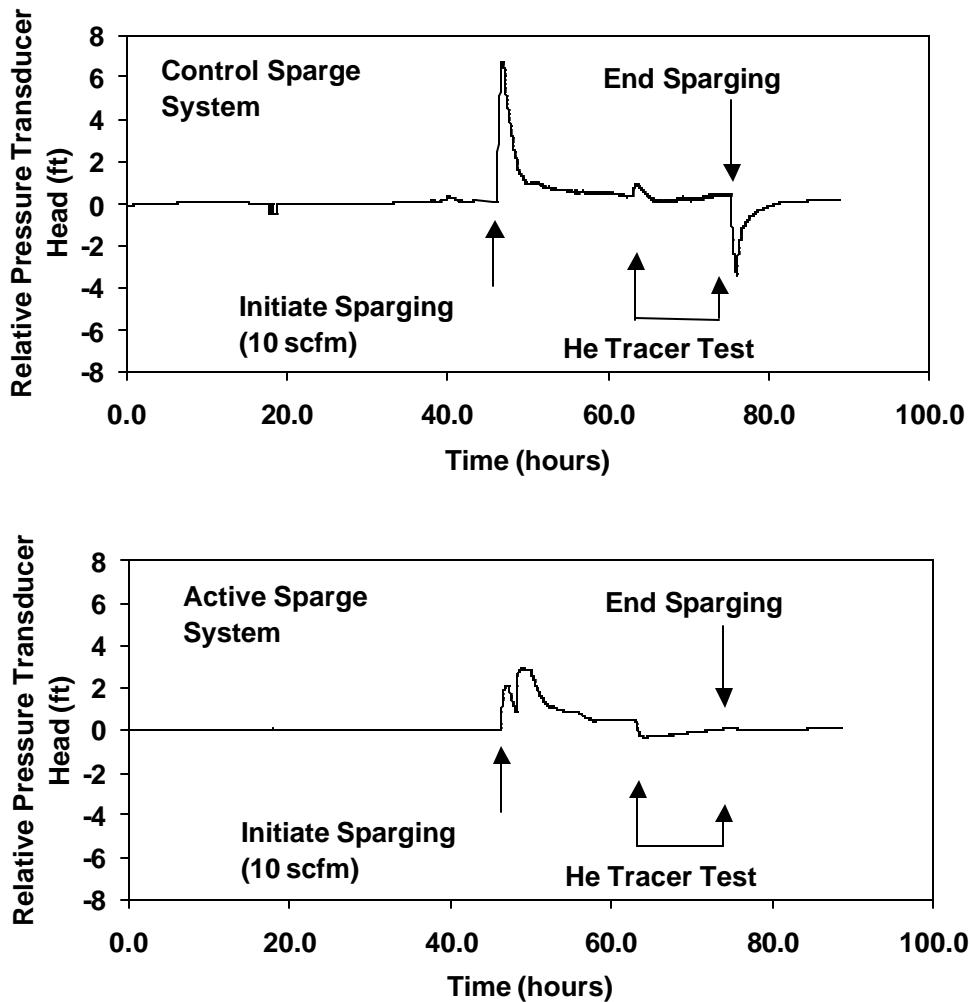


Figure 8. Pressure Response versus Time in the Active and Control Test Plots

shutdown data would appear to be consistent in that there is an extended period during which the pressure remains below hydrostatic pressure (Figure 10).

Data for the active test plot are similar; however, due to operational constraints, the tests were not run as long as at the control test plot (Figures 11 and 12). In addition, system shutdown at the active test plot was initiated before the system had time to come to equilibrium. That is the reason the pressure at the beginning of shutdown of the active test plot is above hydrostatic. In both cases the transducer readings were not adjusted after initial startup.

During the SF₆ tracer test, SF₆ was injected simultaneously into the two test plots for a period of approximately 2 hours. Following that time, the system was shut down and water samples were collected from all of the groundwater monitoring points. Concentrations of SF₆ in the groundwater (expressed as percent of saturation with respect to the injection concentration) are shown in Figures 13 and 14, for the control and active test plots, respectively. The distributions

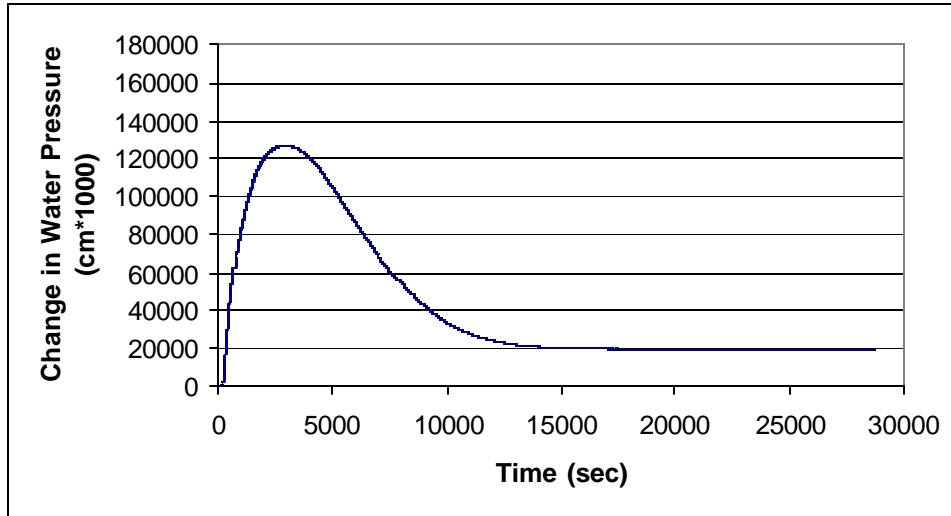


Figure 9. Water Pressure Change at MWA1 During Startup at the Control Test Plot

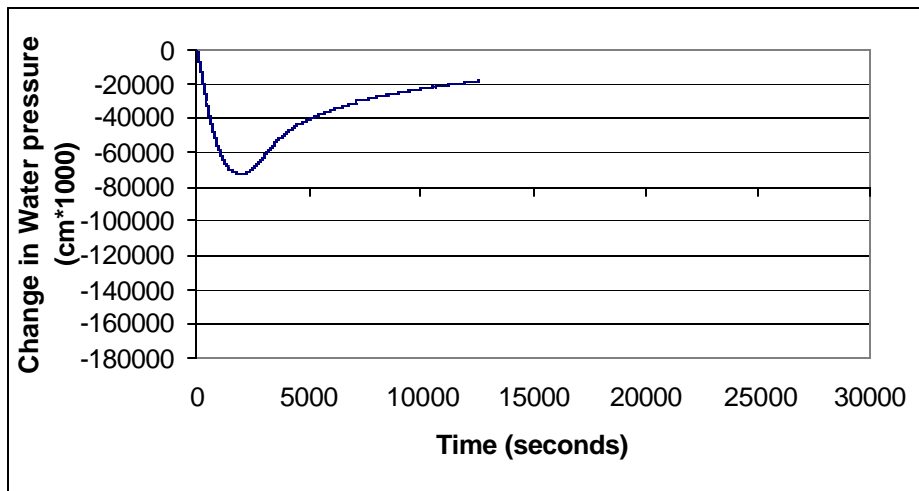


Figure 10. Water Pressure Change at MWA1 During Shutdown at the Control Test Plot

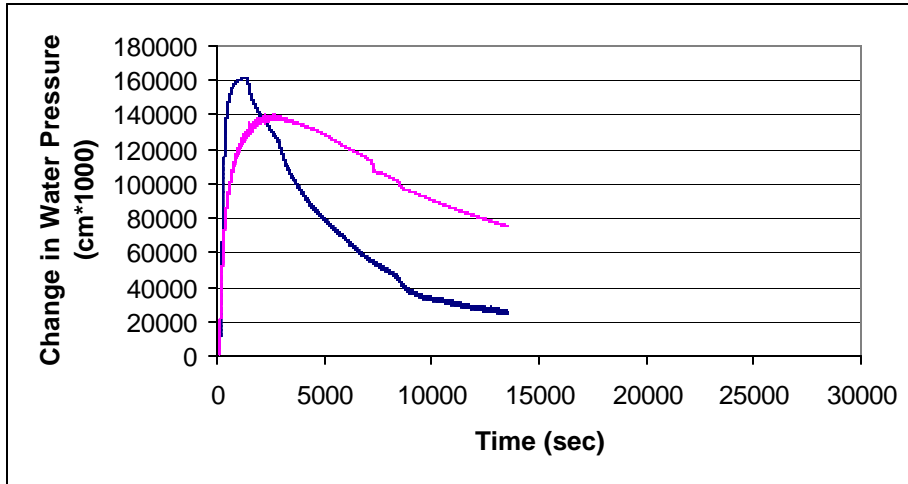


Figure 11. Water Pressure Change at MWC3 and MWC4 During Start-Up at the Active Test Plot

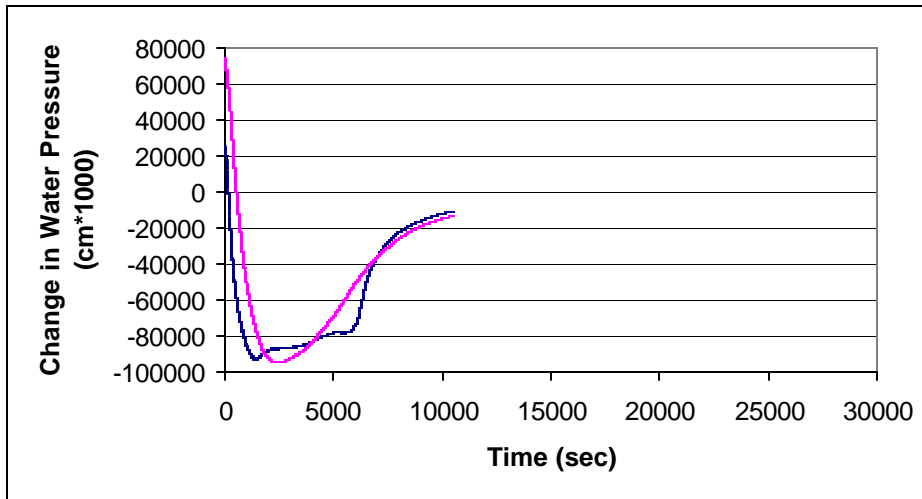


Figure 12. Water Pressure Change at MWC3 and MWC4 During Shutdown at the Active Test Plot



Figure 13. SF₆ Data Expresses as Percent Saturation With Respect to the Input Concentration at the Control Test Plot

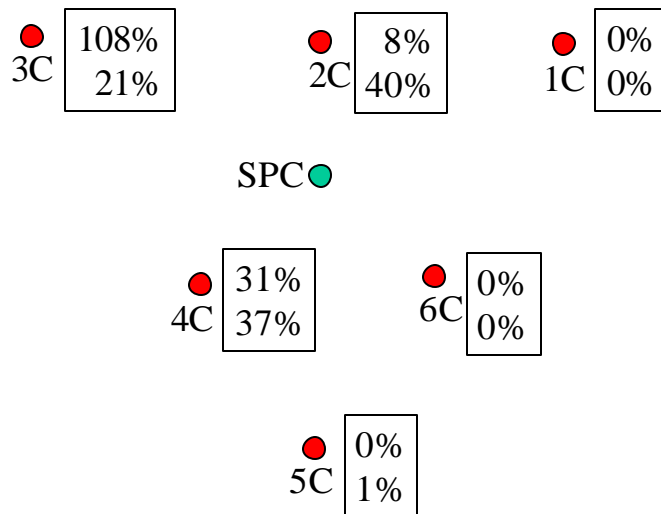


Figure 14. SF₆ Data Expresses as Percent Saturation With Respect to the Input Concentration at the Active Test Plot

for the two test plots are significantly different. At the control test plot, there was essentially no SF₆ observed at the 117-ft depth, while at the 113-ft depth, significant concentrations were observed at all monitoring points from which samples were collected (i.e., all except monitoring point 3). In contrast, at the active test plot (Figure 14), SF₆ was observed at both levels in monitoring points 2, 3, and 4, but no SF₆ was observed at either level in monitoring points 1, 5, and 6. These results are consistent with the propane injection results, where elevated propane concentrations could be measured in monitoring points 2, 3, and 4, but only trace to no propane was observed in monitoring points 1, 5, and 6 at the active test plot.

Based on the results from the tracer studies, monitoring during the Phase 2 studies focused only on the active test plot monitoring points where sparging was most effective. Monitoring of inactive monitoring points was minimized to reduce project costs. Furthermore, results presented in Section 5.2 focus primarily on the most active monitoring points where propane degradation and CAH cometabolism was measured.

5.2 CAS Study Results

Section 5.2 is divided into two primary subsections to discuss Phase 1 (Section 5.2.1) and Phase 2 (Section 5.2.2) of the CAS demonstration.

5.2.1 Phase 1 Demonstration. The Phase 1 operating period was performed in a series of steps as shown in Table 3. Unless noted, activities were conducted in both test plots.

5.2.1.1 Groundwater Results. Propane, contaminant, and dissolved oxygen concentrations are shown in Figures 15 through 20 for selected monitoring points. The following subsections discuss propane uptake, c-DCE, and TCE cometabolism, and nitrate limitations observed during Phase I of the study.

5.2.1.1.1 Propane Uptake. Propane sparging was initiated on day 36. A fairly long lag period of about 50 days (Days 36 to 86) occurred before propane utilization was evident in the saturated zone; this is most evident in monitoring point MW-C4-113 (Figure 15), but also is seen in monitoring points MW-C3-113 and MW-C3-117 (Figures 16 and 17, respectively).

Dissolved propane and oxygen concentrations and corresponding propane degradation rates in the saturated zone varied greatly, indicating some areas were more effectively sparged than others. For example, monitoring points MW-C4-113 (Figure 15) and MW-C3-113 (Figure 16) showed relatively high dissolved propane concentrations after each sparge event, between 1 and 3 mg/L. Much lower concentrations were measured in MW-C3-117 (approximately 1 mg/L or less) (Figure 17) and only trace concentrations of propane were measured in MW-C1-113 (Figure 18). The SF₆ data demonstrated similar results, where virtually no SF₆ was measured at monitoring points MW-C1-113/117, MW-C5-113/117, and MW-C6-113/117, and relatively low SF₆ concentrations were measured in MW-C2-113. Thus, it appears that the propane sparging did not reach every groundwater monitoring point, most likely due to soil heterogeneities.

With successive propane additions, the rate of propane utilization increased as the microbial population was stimulated (Figures 15 through 17). DO concentrations closely matched these

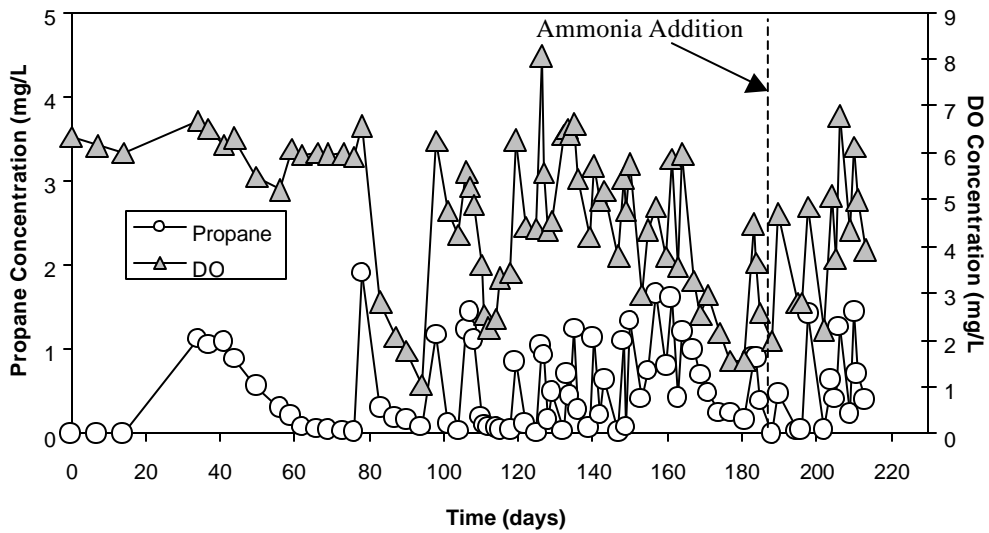
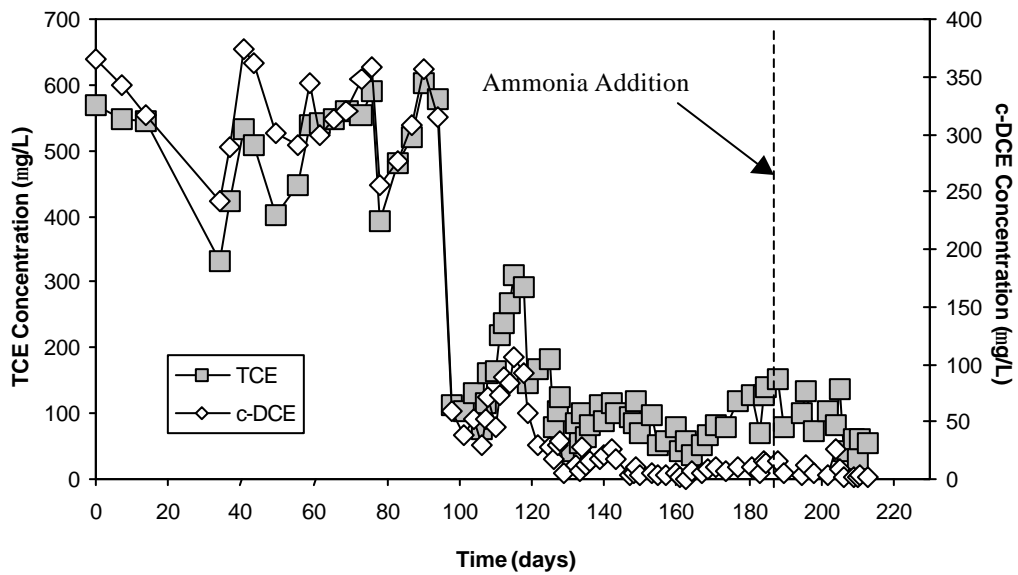


Figure 15. Groundwater Monitoring Point MW-C4-113 in the Active Test Plot

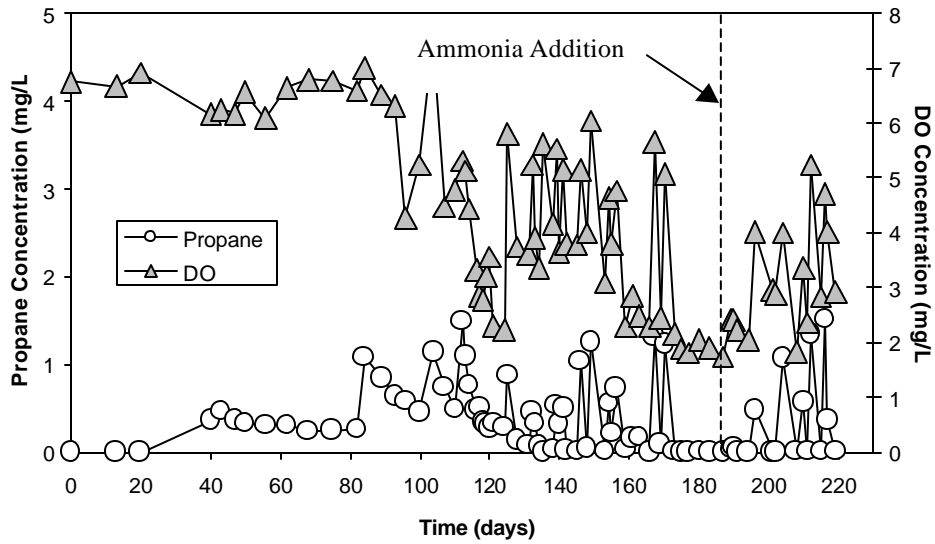
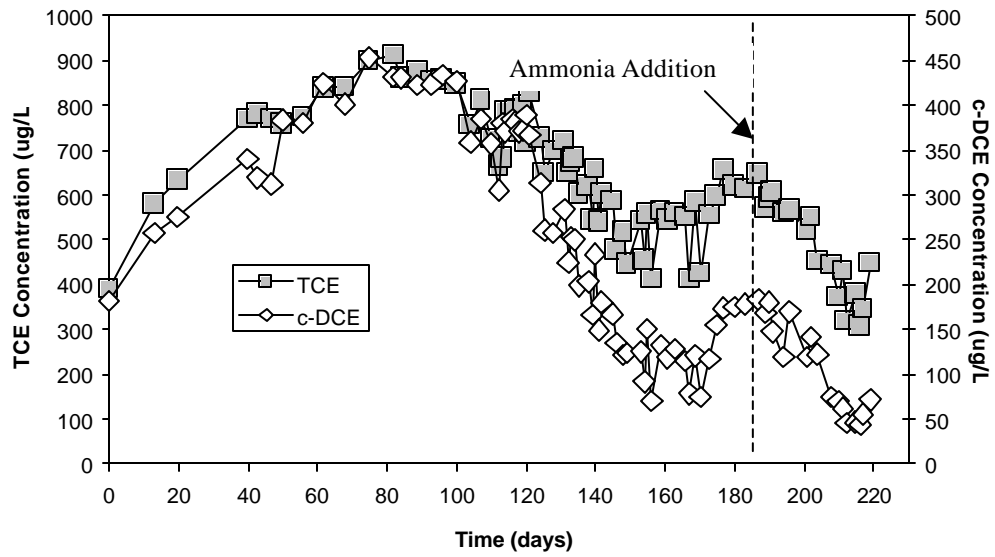


Figure 16. Groundwater Monitoring Point MW-C3-113 in the Active Test Plot

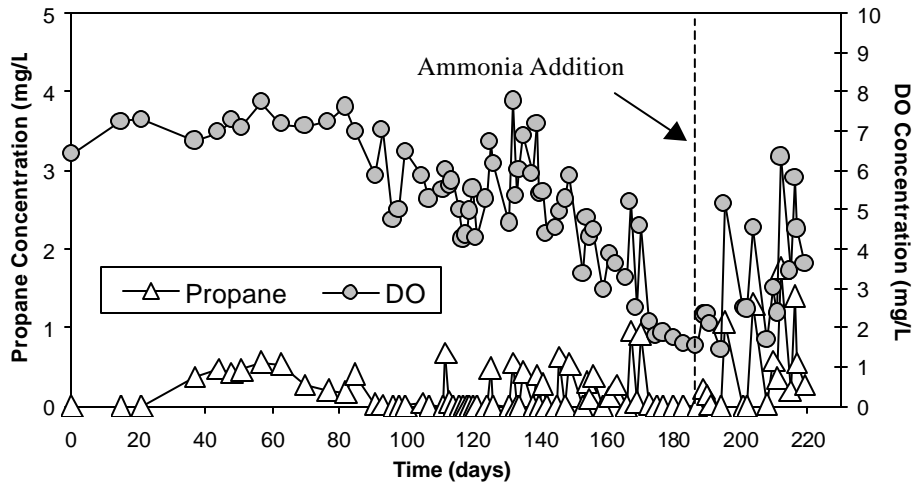
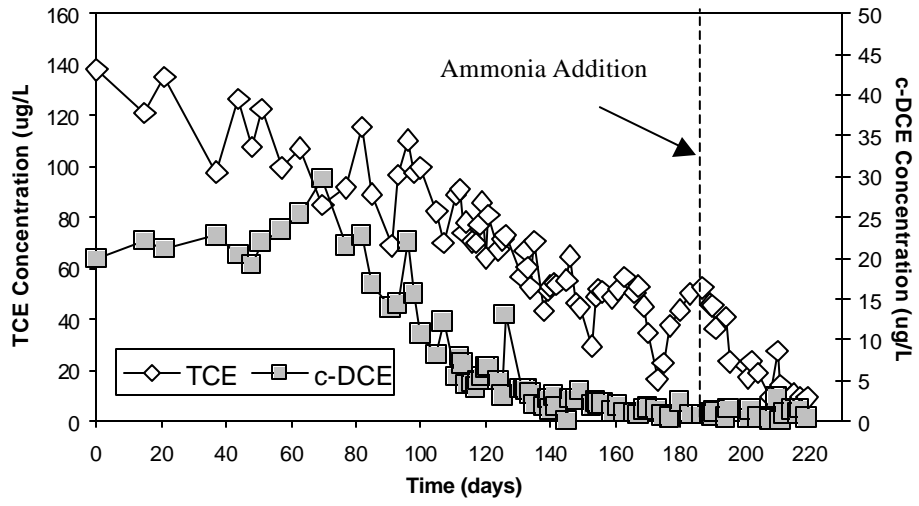


Figure 17. Groundwater Monitoring Point MW-C3-117 in the Active Test Plot

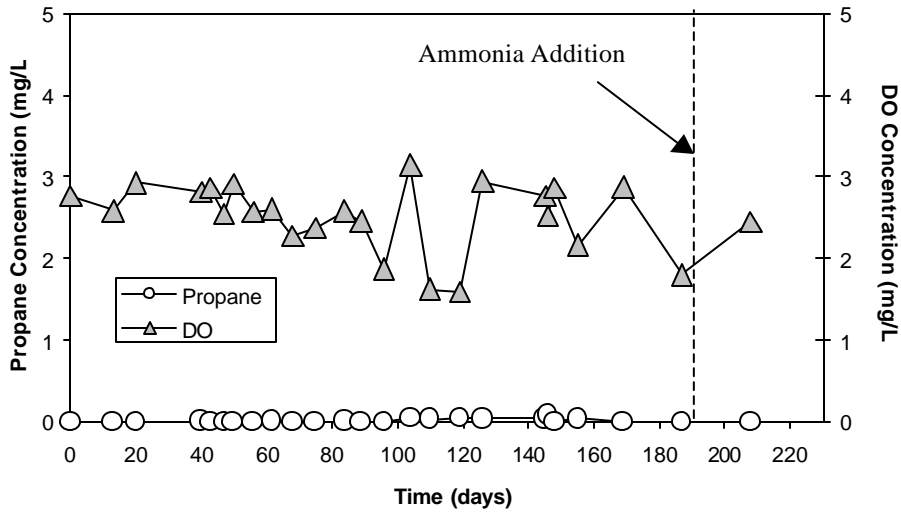
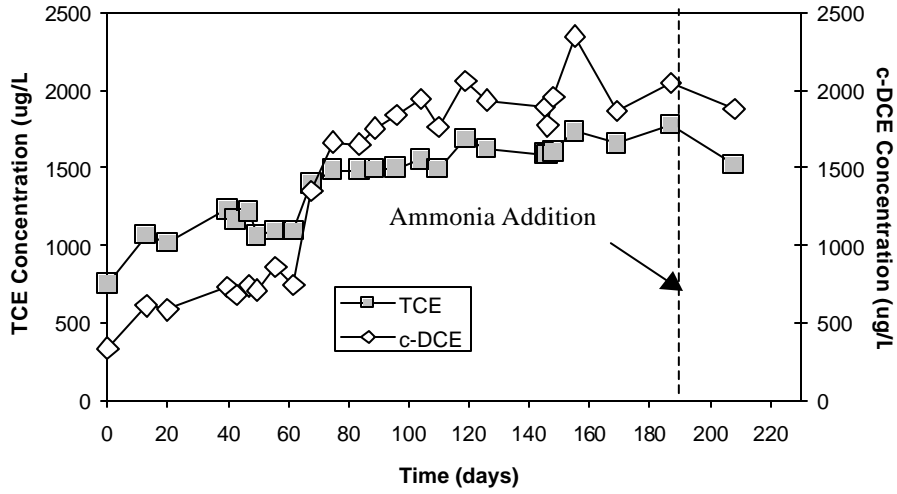


Figure 18. Groundwater Monitoring Point MW-C1-113 in the Active Test Plot

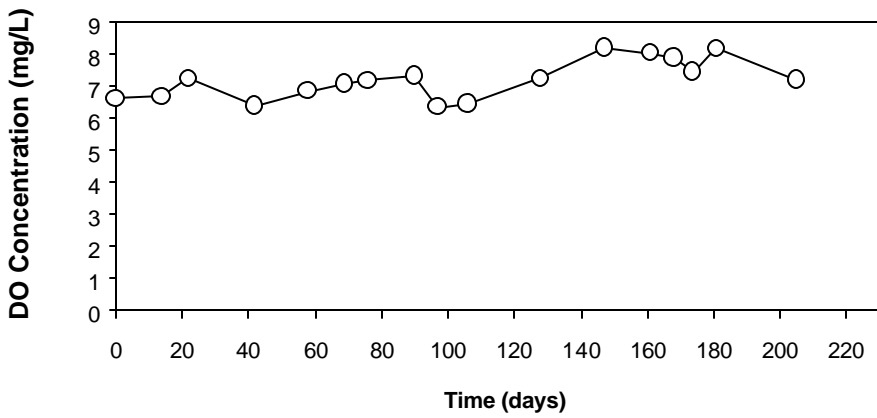
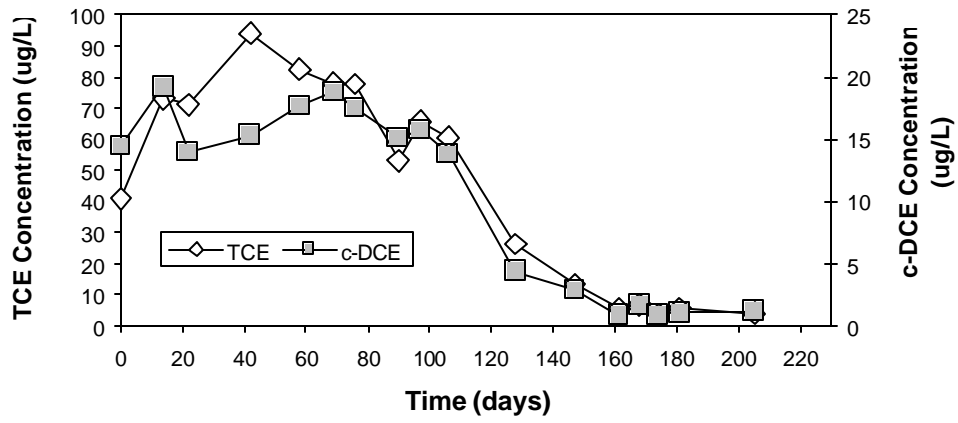


Figure 19. Groundwater Monitoring Point MW-A1-113 in the Control Test Plot

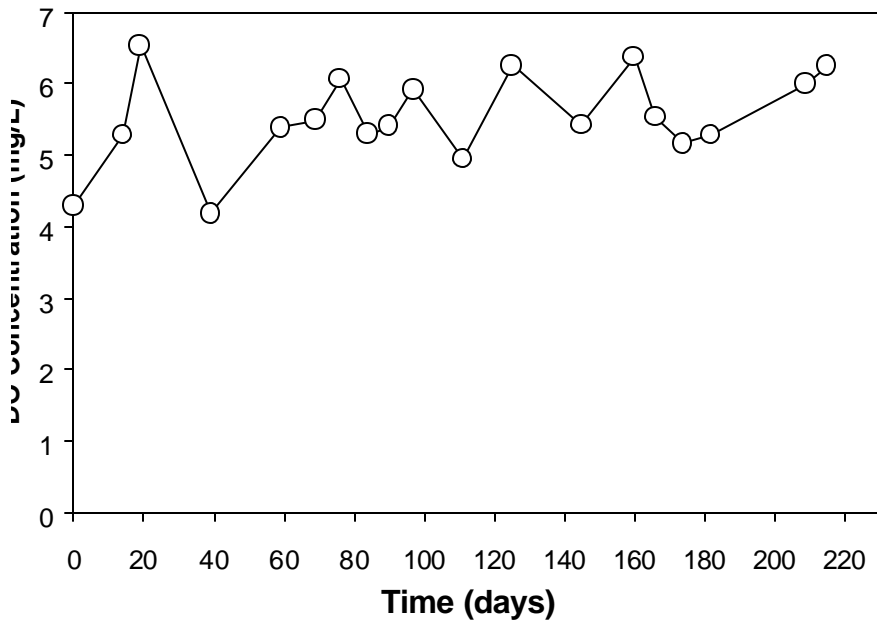
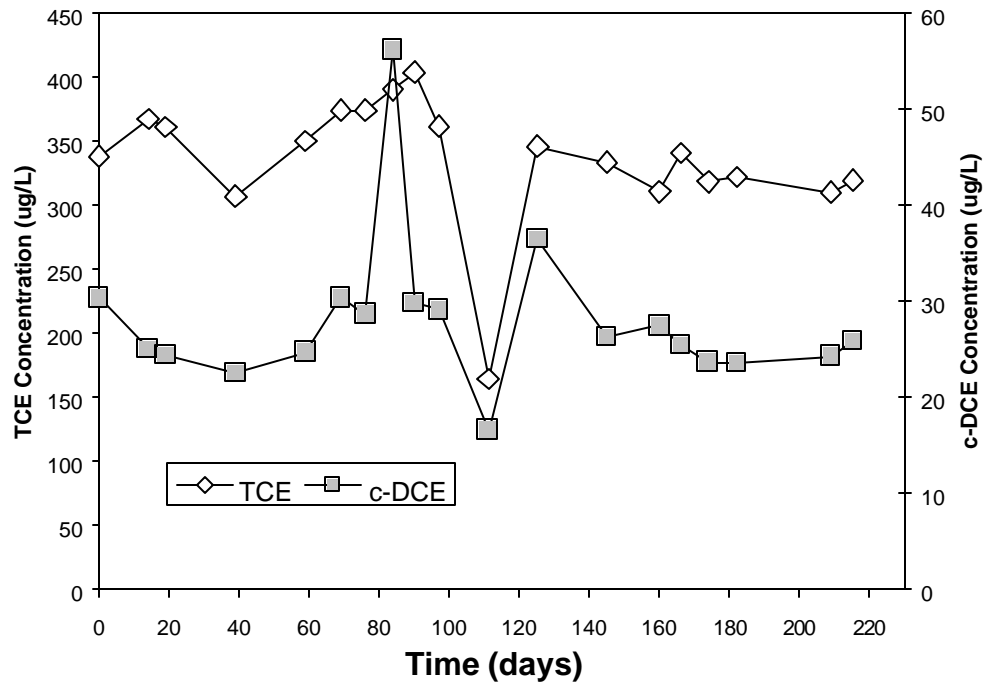


Figure 20. Groundwater Monitoring Point MW-A2-117 in the Control Test Plot

patterns, demonstrating a direct correlation between oxygen and propane utilization for each successive sparge event. Each sparge event resulted in elevated DO levels, followed by decreased DO levels when propane was degraded. These results demonstrated that propane was effectively degraded in the aquifer.

5.2.1.1.2 c-DCE and TCE Cometabolism. A wide range of contaminant concentrations was seen in initial groundwater samples (Table 5). Higher concentrations occurred in the active than the control test plot, and in both test plots, much higher TCE concentrations were seen than c-DCE concentrations. TCE and c-DCE in the groundwater in the active test plot ranging from 100 to 1,000 µg/L, compared to the control test plot where concentrations ranged from 60 to 400 µg/L. Only trace 1,1-DCE concentrations were detected, and only in the control test plot, while 1,1-DCA and CF were not detected. The presence of very low 1,1-DCE, 1,1-DCA, and CF concentrations was observed when the site was first being assessed for this study. Their disappearance before the study began may be due to initial air sparging activity conducted during the helium tracer test.

In the active test plot, the highest TCE and c-DCE removal rates occurred in the monitoring points that received the highest propane concentrations (Figures 15 and 16). Five out of the 12 groundwater monitoring points in the active test plot showed significant propane and oxygen utilization and corresponding TCE and c-DCE removals (MW-C2-117, MW-C3-113/117, MW-C4-113/117), while the other six monitoring points were ineffectively sparged due to soil heterogeneities and did not receive adequate propane to cometabolically degrade the TCE and

c-DCE (one additional monitoring point, MW-C6-113 could not be sampled). Concentrations of c-DCE consistently decreased more rapidly than TCE, which was consistent with the cometabolic transformation of these compounds observed in the microcosm tests.

In the control test plot, SF₆ tracer testing demonstrated that air reached monitoring point MW-A1-113, but not MW-A2-117 (Figure 13). This was further confirmed by results from contaminant monitoring, where much greater TCE and c-DCE removal were observed in monitoring point MW-A1-113 than MW-A2-117. Nonetheless, the TCE and c-DCE removal rates measured at MW-A1-113 (and all monitoring points in the control test plot) were much slower than in the active test plot, suggesting that cometabolism (combined with stripping) resulted in much more rapid removal of TCE and c-DCE than stripping alone. The fact that TCE and c-DCE were removed in the control test plot shows that physical removal by sparging was responsible for at least part of the contaminant removal in the active test plot, in addition to biodegradation.

Final CAH concentrations in the active and control test plots after approximately 200 days of operation are shown in Table 6. The table shows average values over the last 20 days of the Phase I operating period; the number of values averaged for each monitoring point is identified in the table. The last 20 days were used in lieu of simply recording the last data point, because this was thought to be more representative of the steady-state operation achieved in the system. Day to day fluctuations made using the last data point for each monitoring point impractical. Shaded portions of the table correspond to monitoring points where SF₆ concentrations were less than 10% saturation following the SF₆ tracer test. Such low SF₆ concentrations would suggest that these monitoring points were ineffectively sparged.

Table 5. Initial Groundwater CAH Concentrations¹ Measured During the First 36 Days of Operation (Before Propane Sparging)

Monitoring Point	Depth	Contaminant Concentration (mg/L)				
		TCE	c-DCE	1,1-DCE	1,1-DCA	CF
<i>Active Test Plot</i>						
C1	113	944 ± 170	511 ± 153	ND	ND	ND
	117	604 ± 33	286 ± 13	ND	ND	ND
C2	113	431 ± 46	193 ± 20	ND	ND	ND
	117	61 ± 11	14 ± 1.6	ND	ND	ND
C3	113	535 ± 127	238 ± 50	ND	ND	ND
	117	131 ± 9.1	21 ± 1.1	ND	ND	ND
C4	113	555 ± 14	342 ± 24	ND	ND	ND
	117	281 ± 13	107 ± 10	ND	ND	ND
C5	113	2500 ± 196	2095 ± 156	ND	ND	ND
	117	250 ± 15	75 ± 6.7	ND	ND	ND
C6	113	NA				
	117	355 ± 8.9	93 ± 4.2	ND	ND	ND
Average		604 ± 58	361 ± 40	ND	ND	ND
<i>Control Test Plot</i>						
A1	113	62 ± 18	16 ± 2.9	ND	ND	ND
	117	20 ± 8.6	8.0 ± 0.99	ND	ND	ND
A2	113	83 ± 23	11 ± 1.1	ND	ND	ND
	117	356 ± 15	27 ± 3.3	14 ± 12	ND	ND
A3	113	222 ± 36	47 ± 5.8	ND	ND	ND
	117	227 ± 24	18 ± 5.9	8.7 ± 7.7	ND	ND
A4	113	612 ± 134	72 ± 8.9	ND	ND	ND
	117	72 ± 3.2	2.6 ± 2.2	ND	ND	ND
A5	113	168 ± 72	35 ± 8.4	ND	ND	ND
	117	259 ± 7.9	17 ± 4.1	12 ± 5.7	ND	ND
A6	113	374 ± 30	132 ± 44	ND	ND	ND
	117	292 ± 25	14 ± 2.6	14 ± 2.8	ND	ND
Average		230 ± 33	33 ± 8	4 ± 2	ND	ND

¹Each monitoring point and depth had three samples taken during the 36 days the background was established; NA = Not analyzed; ND = Not detected

Table 6. Phase 1 CAH Concentrations During the Final 10 Days Of Phase 1 Operation

Monitoring point	Depth	No. of Samples	Contaminant Concentration (µg/L)					
			TCE	c-DCE	1,1-DCE	1,1-DCA	CF	
<i>Active Test Plot</i>								
C1	113	1	1514	1876	15	131	87	
	117	1	1305	1089	11	91	30	
C2	113	7	336 ± 13	57 ± 3.4	2.5 ± 2.3	5.6 ± 0.28	12 ± 6.3	
	117	7	5.9 ± 3.8	0.92 ± 1.3	2.7 ± 4.8	ND	2.8 ± 3.6	
C3	113	7	371 ± 53	56 ± 11	2.2 ± 4.4	6.1 ± 1.3	6.8 ± 1.2	
	117	7	12 ± 6.9	3.7 ± 7.6	1.8 ± 1.1	0.16 ± 0.42	6.2 ± 8.5	
C4	113	7	67 ± 35	6.7 ± 9.2	3.5 ± 2.9	0.91 ± 0.62	9.9 ± 13	
	117	7	38 ± 7.2	2.4 ± 0.76	2.8 ± 3.1	0.30 ± 0.14	5.6 ± 0.69	
C5	113	1	1635	1834	18	144	92	
	117	1	591	210	ND	14	34	
C6	113	NA						
	117	1	445	335	9.0	25	65	
Average ^(a)			99 ± 21	14 ± 6.0	2.6 ± 3.3	1.5 ± 0.50	6.3 ± 5.4	
<i>Control Test Plot</i>								
A1	113	1	4.0	1.2	ND	ND	ND	
	117	2	9.3 ± 0.52	1.7 ± 2.3	ND	ND	1.9 ± 3.2	
A2	113	1	29	4.0	3.6	0.86	ND	
	117	2	315 ± 6.6	25 ± 1.1	ND	16 ± 0.16	18 ± 26	
A3	113	1	61	29	1.8	1.6	15	
	117	2	186 ± 8.7	10 ± 1.2	11 ± 15	7.8 ± 0.95	5.1 ± 0.56	
A4	113	1	175	27	ND	8.4	17	
	117	2	185 ± 2.8	9.3 ± 0.17	9.1 ± 13	6.2 ± 0.15	13 ± 12	
A5	113	1	190	31	11	12	ND	
	117	2	119 ± 0.42	6.4 ± 0.02	6.4 ± 9.0	3.4 ± 0.29	11 ± 8.8	
A6	113	1	55	24	3.0	1.5	ND	
	117	2	126 ± 1.5	7.3 ± 1.0	5.0 ± 7.0	3.8 ± 0.06	12 ± 2.3	
Average ¹			92 ± 85	18 ± 15	3.3 ± 4.6	4.6 ± 5.3	6.4 ± 8.8	

(a) Average values were based on the active (i.e., unshaded) monitoring points only, based on the SF₆ test.

Except for MW-C3-113, final TCE concentrations in the active test plot ranged from 5.9 to 67 µg/L; the final MW-C3-113 groundwater averaged 371 µg/L. Similarly, c-DCE concentrations were low in the active test plot; final c-DCE concentrations ranged from 0.92 to 6.7 µg/L, except for MW-C3-113 where c-DCE concentrations averaged 56 µg/L. The reason for the high residual TCE/c-DCE concentrations in MW-C3-113 is unknown. The monitoring point appeared to receive propane to support propane degradation and subsequent CAH cometabolism. One possibility could be that this monitoring point had a greater influx of CAHs during testing, resulting in the replenishment of the degraded CAH fraction. Another possibility is that MW-C3-113 represents the low-end range of activity that could be expected for the CAS process.

Significant mass removal was also observed in the control test plot, indicating that contaminants were removed by air stripping only. Because the contaminant mass loading was much higher in the active test plot than the control test plot (the average initial TCE concentration in the active site was 604 mg/L compared to 230 mg/L in the control test plot), the CAS process in the active site resulted in a larger overall removal of mass than the air sparging alone. However, the fact that the final concentrations were similar may suggest that the CAHs reached low-concentration plateaus over time. Such plateaus would be influenced by the rate of contaminant removal, the sorption of contaminants on natural organic matter, and the incoming flux of fresh contaminants from upstream of the treatment area.

5.2.1.1.3 Nitrate Limitations. Nitrate was found to be limiting in the groundwater during the Phase 1 operating period, potentially limiting propane degradation and cometabolic TCE and c-DCE transformations. Microcosm testing indicated that low nitrogen levels could limit propane utilization and subsequent CAH degradation. Figure 21 shows nitrate, propane, and TCE concentrations over time in monitoring points MW-C4-113 and MW-C3-117. Nitrate was depleted steadily over time, from a starting concentration of approximately 5 mg/L. Nitrate concentrations were depleted to non-detectable levels by day 168 in MW-C4-113. Nitrate lasted longer in MW-C3-117, but concentrations were nearly completely depleted by the end of Phase 1.

The depletion of nitrate is attributed to the microbial utilization of propane, where nitrate was used as a microbial nitrogen source. Nitrate depletion resulted in significantly reduced propane utilization rates, which are seen between following the Day 170 sparge event in MW-C4-117. Before Day 150, propane concentrations fell to non-detectable levels within one week of each sparge event. Between days 150 and 170, propane continued, but concentrations remained above 0.5 mg/L. After Day 170, when the nitrate concentration was below its detection limit, propane degradation from 1.2 mg/L to 0.2 mg/L took approximately two weeks.

Experiments were conducted to supply nitrogen to the groundwater in the gas phase to determine whether nitrogen addition would stimulate propane and CAH degradation. The challenge facing the research team was to supply nitrogen in the gas phase, for two reasons: 1) a mechanism for soluble nitrate introduction to the groundwater was unavailable for this site; and 2) future application of this technology would benefit from gaseous nitrate addition. To supply nitrogen, ammonia gas was added to the sparge gases (air and propane) on Day 188. The ammonia addition tests were inconclusive, and in some cases were counterproductive. Upon adding ammonia, the propane uptake rate appeared to increase in MW-C4-117, but no long-term benefit

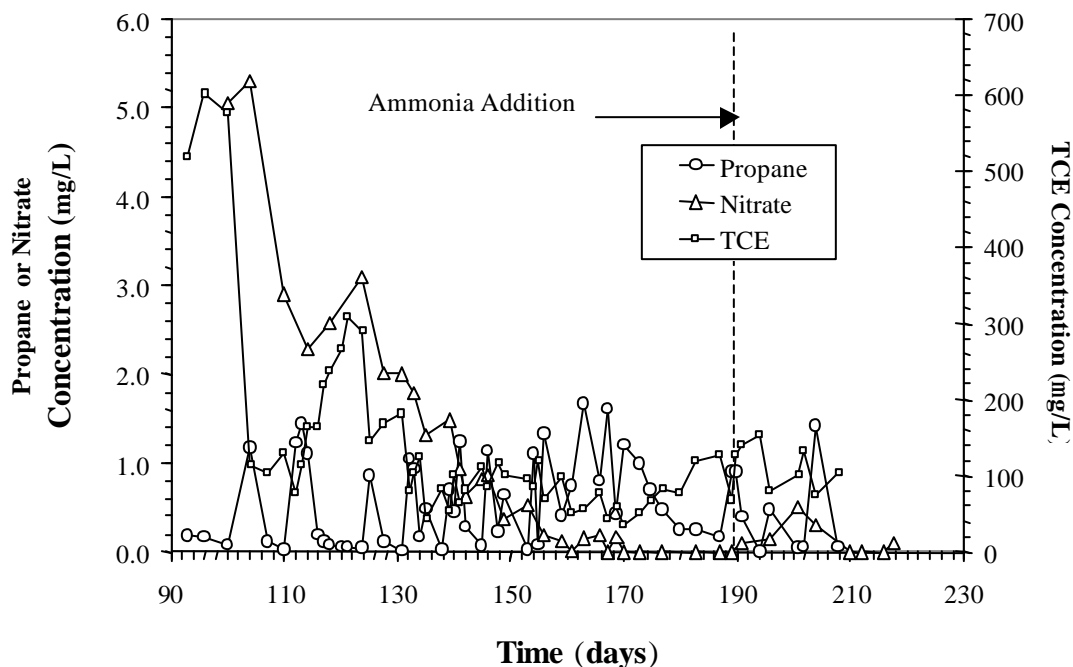


Figure 21. Nitrate, TCE, and Propane Consumption in Groundwater Monitoring Point MW-C4-113

was observed (Figure 21). Continuous ammonia addition was not possible, because ammonia addition led to a significant pH increase above pH 10 in some monitoring points, so ammonia addition was immediately discontinued. The ammonia addition had no observable benefit to propane degradation in the vadose zone (see Section 5.3).

Alternative nitrogen sources also were investigated, with no noticeable results. Dinitrogen tetroxide, a gaseous form of nitrite, was investigated, but its use was discontinued because of its severe corrosiveness and potential hazards to on-site staff. Nitrous oxide (N₂O) was investigated with no success. Laboratory microcosms confirmed that N₂O addition to microcosms with depleted nitrate levels provided no benefit to propane-degrading organisms.

Nitrogen fixation (the use of N₂ as a nitrogen source) was not observed at the site by the propane-degrading microorganisms. This does not rule out the possibility for nitrogen fixation to have occurred; it may have occurred without detection in the field study. However, evidence for nitrogen fixation could not be found during the field and microcosm studies.

5.2.1.2 Vadose Zone Results. Initial soil gas CAH concentrations are shown in Tables 7 and 8 for the control and active test plots, respectively, for the first 36 days of monitoring and before propane sparging commenced. Higher soil gas concentrations were seen in the active test plot compared to the control test plot. Soil gas points in the active test plot at the 105-ft depth were measured sporadically throughout the demonstration, except for soil gas point SG-C6-105, due to water saturation from water level fluctuation of these soil gas points.

Table 7. Initial Soil Gas CAH Concentrations Measured During the First 36 Days of Operation in the Control Test Plot (Before Propane Sparging)

Monitoring point ID	Contaminant Concentration (mg/L)				
	TCE	c-DCE	1,1-DCE	1,1-DCA	CF
<i>SG1 – 30 ft bgs</i>					
SG-A1-30	46 ± 5.0	54 ± 5.1	ND	ND	ND
SG-A2-30	32 ± 9.9	27 ± 4.2	ND	ND	ND
SG-A3-30	71 ± 16	36 ± 10	ND	ND	ND
SG-A4-30	36 ± 2.3	23 ± 2.7	ND	ND	ND
SG-A5-30	29 ± 1.6	13 ± 1.8	ND	ND	ND
SG-A6-30	23 ± 0.96	19 ± 1.3	ND	ND	ND
<i>SG2 – 85 ft bgs</i>					
SG-A1-85	326 ± 42	416 ± 2.7	ND	ND	ND
SG-A2-85	318 ± 21	359 ± 15	ND	ND	ND
SG-A3-85	302 ± 34	407 ± 44	ND	ND	ND
SG-A4-85	264 ± 19	485 ± 41	ND	ND	ND
SG-A5-85	275 ± 20	486 ± 34	ND	ND	ND
SG-A6-85	409 ± 53	476 ± 18	1.3 ± 2.2	6.6 ± 11	ND
<i>SG3 – 95 ft bgs</i>					
SG-A1-95	292 ± 49	249 ± 21	ND	ND	ND
SG-A2-95	367 ± 45	225 ± 25	ND	ND	ND
SG-A3-95	364 ± 4.0	236 ± 24	ND	ND	ND
SG-A4-95	361 ± 31	318 ± 28	ND	ND	ND
SG-A5-95	362 ± 37	352 ± 35	ND	ND	ND
SG-A6-95	374 ± 21	252 ± 47	ND	ND	ND
<i>SG4 – 105 ft bgs</i>					
SG-A1-105	280 ± 50	201 ± 63	ND	ND	ND
SG-A2-105	147 ± 8.5	53 ± 7.7	ND	ND	ND
SG-A3-105	125 ± 7.7	39 ± 5.6	ND	ND	ND
SG-A4-105	214 ± 30	68 ± 7.3	ND	ND	ND
SG-A5-105	223 ± 27	141 ± 15	ND	ND	ND
SG-A6-105	NA				

Note: Each soil-gas point had three samples taken during the 36 days the background was established; NA = Not analyzed; ND = Not detected

Table 8. Initial Soil Gas CAH Concentrations Measured During the First 36 Days of Operation in Active Test Plot (before Propane Sparging)

Monitoring point ID	Contaminant Concentration (mg/L)				
	TCE	c-DCE	1,1-DCE	1,1-DCA	CF
<i>SG1 – 30 ft bgs</i>					
SG-C1-30	32 ± 9.5	13 ± 4.0	ND	ND	ND
SG-C2-30	25 ± 0.73	23 ± 1.4	ND	ND	ND
SG-C3-30	46 ± 2.8	15 ± 0.74	ND	ND	ND
SG-C4-30	29 ± 5.6	11 ± 1.3	ND	ND	ND
SG-C5-30	47 ± 1.5	9.3 ± 0.92	ND	ND	ND
SG-C6-30	82 ± 109	7.0 ± 0.62	ND	ND	ND
<i>SG2 – 85 ft bgs</i>					
SG-C1-85	319 ± 49	312 ± 41	ND	ND	ND
SG-C2-85	420 ± 66	468 ± 125	ND	ND	ND
SG-C3-85	460 ± 25	267 ± 8.2	ND	ND	ND
SG-C4-85	436 ± 23	304 ± 17	ND	ND	ND
SG-C5-85	495 ± 31	294 ± 19	ND	ND	ND
SG-C6-85	380 ± 23	332 ± 51	ND	ND	ND
<i>SG3 – 95 ft bgs</i>					
SG-C1-95	482 ± 25	557 ± 32	ND	ND	ND
SG-C2-95	344 ± 48	315 ± 38	ND	ND	ND
SG-C3-95	410 ± 28	252 ± 18	ND	ND	ND
SG-C4-95	467 ± 43	302 ± 25	ND	ND	ND
SG-C5-95	654 ± 28	354 ± 17	ND	ND	ND
SG-C6-95	NA				
<i>SG4 – 105 ft bgs</i>					
SG-C1-105	NA				
SG-C2-105	NA				
SG-C3-105	NA				
SG-C4-105	NA				
SG-C5-105	NA				
SG-C6-105	617 ± 23	500 ± 4.3	ND	ND	ND

Each soil-gas point had three samples taken during the 36 days the background was established; NA = Not analyzed; ND = Not detected

It is not clear whether the presence of CAHs in the vadose zone was due to direct contamination of the vadose zone or partitioning of CAHs from the contaminated saturated zone. McAFB has a history of vadose zone contamination in OU A, suggesting that these contaminants were likely present before the onset of this study. The highest soil gas CAH concentrations were measured in the deepest monitoring points, closest to the groundwater table. If the CAH source is direct contamination of the vadose zone, these higher concentrations may be due to historical downward CAH migration. If the source is partitioning from contaminated groundwater, the lower shallow concentrations may be due to upward CAH diffusion after partitioning into the gas phase.

During Phase 1, soil gas propane, oxygen, TCE, and c-DCE concentrations were monitored to assess the efficacy of CAS in the vadose zone at the McAFB site. Results of two soil gas points in the active test plot, SG-C2-95 and SG-C6-105, are shown in Figures 22 and 23, respectively, and results of one soil gas point in the control test plot, SG-A3-95, are shown in Figure 24.

The active test plot soil gas points show increasing propane concentrations in the vadose zone, approaching the injection concentration (4% propane in air) between Days 80 and 160. After Day 160, propane concentrations appeared to stabilize and potentially decrease. For comparison, TCE and c-DCE concentrations were much more stable in soil gas points SG-A3-95. These results gave rise to the speculation that after a prolonged lag period (lasting from 80 to 160-days), propane degradation and corresponding TCE and c-DCE cometabolic degradation commenced in the vadose zone. Further evidence for propane degradation and cometabolic CAH degradation in the vadose zone was required, leading to Phase 2 studies, which focused on vadose zone activity at the site.

The appearance of propane degradation at the end of Phase 1 may also have been due in part to the addition of nitrogen (ammonia or dinitrogen tetroxide) to the soil gas on Day 188. However, a direct correlation between nitrate addition and vadose zone propane degradation could not be made using the field data collected during this time period.

5.2.2 Phase 2 Demonstration. Phase 1 provided strong indications that propane degradation in the saturated zone stimulated TCE and c-DCE cometabolism, and that the onset of propane degradation and CAH cometabolism in the vadose zone began toward the end of the experimental operating period. However, by Day 210, funds for the McAFB study were close to expiring and the CAS study was planned to continue at a second site. Two sites were tentatively identified at the time, Ft. Lewis (Washington) and Fairchild AFB (Washington). The interesting Phase 1 results led the research team and ESTCP to continue the CAS studies at McAFB in lieu of a second site, with the following goals in mind:

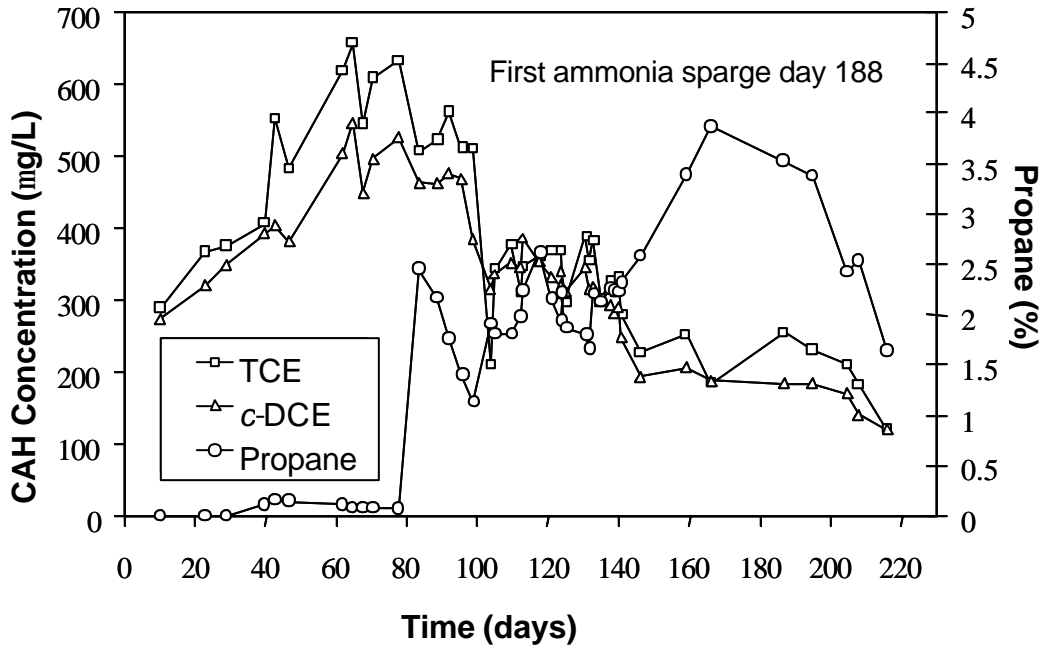


Figure 22. Vadose Zone Monitoring Point SG-C2-95

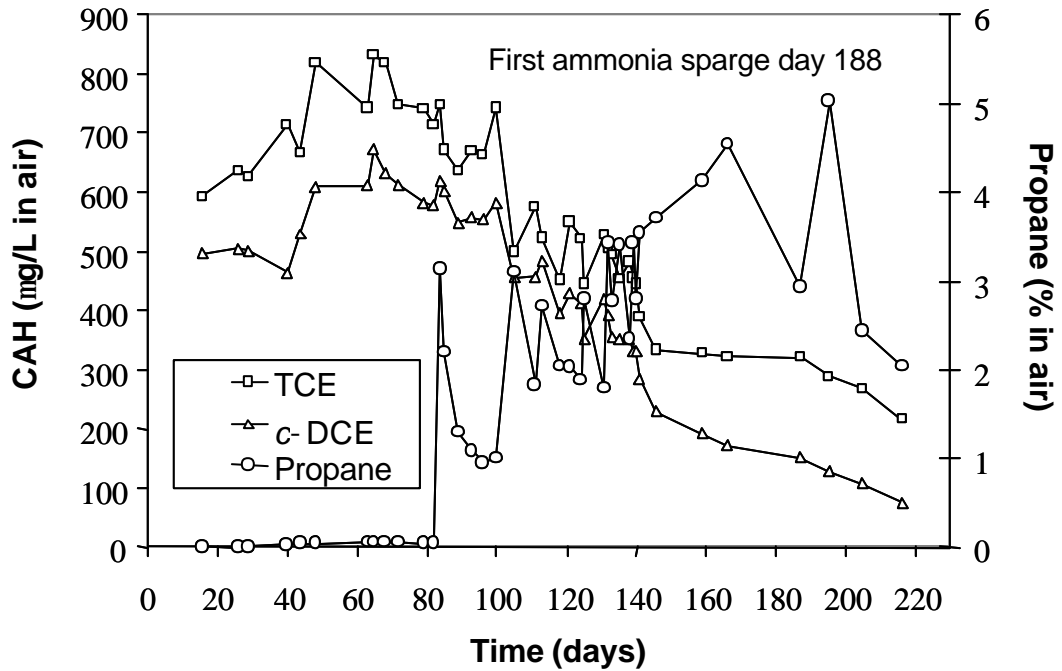


Figure 23. Vadose Zone Monitoring Point SG-C6-105

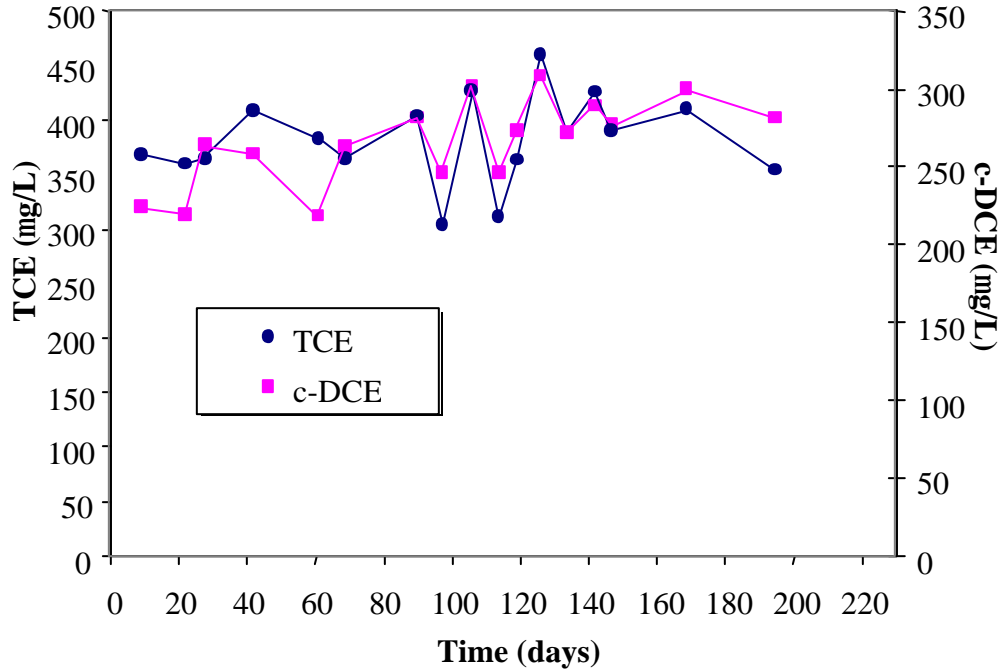


Figure 24. Control Vadose Zone Monitoring Point SG-A3-95

- Assess the potential for propane degradation and CAH cometabolism in the vadose zone
- Examine the rebound of TCE and c-DCE during a 4.5-month inactive period
- Determine whether CAS could promote lower CAH concentrations in the vadose zone to meet MCL concentrations in the saturated zone

Phase 2 was conducted for a total of 217 days between May and December 2000 (i.e., from Days 293 to 510).

5.2.2.1 Baseline Sampling and Rebound Effects. The system was inactive between December 17, 1999 and May 4, 2000. After this time, two complete rounds of baseline sampling took place, including groundwater and soil gas samples. This baseline set of samples was used to measure the rebound since the end of the Phase 1 experiment and to establish the initial propane and CAHs concentrations at the beginning of Phase 2. Results of the rebound period for groundwater are shown in Table 9, which shows groundwater propane and CAH concentrations at the beginning and end of the 4.5-month period.

Groundwater CAH concentrations increased consistently during the 4.5-month rebound period. The increased CAH could have been due to the influx of CAH-contaminated groundwater into the system or the desorption of CAH from soils in the active test plot. However, nitrate

concentrations also increased. Because increased nitrate concentrations could be due only to the influx of fresh groundwater to the site and not to the dissolution of the soil mineral phase within the treatment zone, the increased nitrate concentrations suggest that the change in CAH concentrations were due at least in part to the influx of groundwater from outside the treatment area.

Changes in vadose zone propane and CAH concentrations at the beginning and end of the 4.5-month rebound period are shown in Tables 10 and 11, for the control and active test plots, respectively. Vadose zone concentrations behaved differently than groundwater concentrations. In the upper-most soil gas points (i.e., 30 and 85 ft bgs), soil gas propane, TCE, and c-DCE concentrations remained relatively stable. However, closer to the groundwater table, the 95-ft monitoring points and SG-C6-105 (the only 105-ft soil gas monitoring point that could be measured, due to saturation from water level fluctuations of the remaining soil gas monitoring points) showed decreasing propane concentrations with relatively stable CAH concentrations. The exception to this was SG-C3-95, which showed both propane and corresponding CAH reductions.

5.2.2.2 Groundwater Results. Sparging in Phase 1 was conducted at 10 scfm with 2 to 4% propane in the sparge gas. Phase 2 attempted to optimize the sparging by reducing propane concentrations in the injected air. It was thought that reduced propane concentrations would (a) exert less of a demand on nitrate levels, (b) allow propane concentrations to be depleted to lower levels between sparge events to permit more efficient CAH cometabolism (propane and CAHs compete for monooxygenase activity and the presence of propane could have inhibited CAH cometabolism), and (c) to maintain higher residual dissolved oxygen levels between sparge events to promote more efficient CAH cometabolism.

The system was sparged with 5 scfm of air with 1% propane for 4 hours once a week from June 19, 2000 to July 25, 2000. Since propane in the groundwater seemed to be disappearing quickly during this period, the groundwater appeared to have excess capacity to degrade propane. Hence, the propane injection concentration was increased to 2%; from July 25 to September 5, 2000, the system was sparged with 5 scfm of air containing 2% propane for 4 hours once a week. At this point, the system seemed to be optimized and steady state propane and CAH degradation was achieved.

Figures 25 and 26 show typical examples of propane and CAH concentration profiles in the active test plot, for MW-C3-117 and MW-C4-117, respectively. Figure 27 shows that nitrogen concentrations were not depleted during Phase 2. These results, and the fact that propane degradation was rapid and uninhibited between March 23 and October 6, 2000, suggest that nitrogen was not limiting during Phase 2. The decreased nitrogen limitations are likely due to the decreased propane loading during Phase 2.

Table 9. Groundwater Propane and CAH Concentrations at the Beginning and End of the 4.5-Month Rebound Test Period

GW MW	Propane (mg/L)		TCE (mg/L)		c-DCE (mg/L)	
	Beginning	End	Beginning	End	Beginning	End
<i>Control Test Plot</i>						
A1-113	0.00	0.00	4.1	4.9	1.2	0.98
A1-117	0.00	0.00	9.6	254	0	12
A2-113	0.00	0.00	30	164	4.0	22
A2-117	0.00	0.00	320	332	26	19
A3-113	0.00	0.00	61	52	29	14
A3-117	0.00	0.00	190	208	11	14
A4-113	0.00	0.00	180	622	27	61
A4-117	0.00	0.00	180	129	9.2	13
A5-113	0.00	0.00	190	37	31	6.1
A5-117	0.00	0.00	119	212	6.4	8.8
A6-113	0.00	0.00	56	46	24	12
A6-117	0.00	0.00	127	252	8.1	21
<i>Active Test Plot</i>						
C1-113	0.00	0.00	1,510	2,190	1,880	2,000
C1-117	0.00	0.00	1,310	1,370	1,090	925
C2-113	0.21	0.00	335	632	51	70
C2-117	2.38	0.00	6.2	307	0.31	3.7
C3-113	0.01	0.00	447	733	71	116
C3-117	0.27	0.00	9.3	115	0.38	0.28
C4-113	0.40	0.00	53	150	2.6	1.9
C4-117	1.47	0.01	43	186	2.6	6.8
C5-113	0.00	0.00	1,640	2,060	1,830	1,540
C5-117	0.00	0.00	591	688	210	267
C6-117	0.02	0.00	445	624	335	703

NA = Not analyzed

ND = Not detected

Table 10. Soil Gas Propane and CAH Concentrations at the Beginning and End of the 4.5-Month Rebound Test Period in the Control Test Plot

GW MW	Propane (%)		TCE (mg/L)		c-DCE (mg/L)	
	Beginning	End	Beginning	End	Beginning	End
<i>30 ft bgs</i>						
SG-A1-30	0.00	0.00	43	28	61	30
SG-A2-30	0.00	0.00	35	27	24	16
SG-A3-30	0.00	0.00	37	28	24	17
SG-A4-30	0.00	0.00	39	36	34	24
SG-A5-30	0.00	0.00	26	18	16	8.8
SG-A6-30	0.00	0.07	16	14	27	3.7
<i>85 ft bgs</i>						
SG-A1-85	0.00	0.30	351	459	467	530
SG-A2-85	0.00	0.02	383	529	422	466
SG-A3-85	0.00	0.02	349	476	499	551
SG-A4-85	0.00	0.02	337	359	544	508
SG-A5-85	0.00	0.04	379	486	552	632
SG-A6-85	0.00	0.04	356	486	502	583
<i>95 ft bgs</i>						
SG-A1-95	0.00	0.32	222	255	223	174
SG-A2-95	0.00	0.22	281	272	241	188
SG-A3-95	0.00	0.07	357	413	281	292
SG-A4-95	0.00	0.07	445	689	213	178
SG-A5-95	0.00	0.27	313	369	359	368
SG-A6-95	0.00	0.42	266	348	225	215
<i>105 ft bgs</i>						
SG-A1-105	0.00	0.32	200	239	192	163
SG-A2-105	0.00	0.15	73	57	32	23
SG-A3-105	0.00	0.13	54	40	17	17
SG-A4-105	0.00	0.11	139	88	51	30
SG-A5-105	0.00	0.22	125	143	98	92
SG-A6-105	0.00	0.12	481	81	49	24

NA = Not analyzed.

ND = Not detected.

Table 11. Soil Gas Propane and CAH Concentrations at the Beginning and End of the 4.5-Month Rebound Test Period in the Active Test Plot

GW MW	Propane (%)		TCE (mg/L)		c-DCE (mg/L)	
	Beginning	End	Beginning	End	Beginning	End
<i>30 ft bgs</i>						
SG-C1-30	0.00	0.00	4.6	16	27	12
SG-C2-30	0.00	0.00	53	29	39	18
SG-C3-30	0.00	0.00	43	28	27	19
SG-C4-30	0.00	0.00	45	25	27	16
SG-C5-30	0.00	0.00	42	26	21	11
SG-C6-30	0.00	0.00	40	74	21	35
<i>85 ft bgs</i>						
SG-C1-85	2.4	1.42	768	593	758	477
SG-C2-85	0.77	1.01	668	610	530	417
SG-C3-85	0.74	1.02	685	759	376	355
SG-C4-85	1.05	1.23	617	562	421	320
SG-C5-85	1.77	1.57	639	554	382	272
SG-C6-85	1.18	1.37	590	372	450	368
<i>95 ft bgs</i>						
SG-C1-95	3.95	1.90	574	460	697	432
SG-C2-95	1.64	1.80	122	121	282	150
SG-C3-95	4.41	0.95	297	134	208	59
SG-C4-95	4.40	1.55	264	296	248	165
SG-C5-95	4.65	1.60	509	476	435	301
SG-C6-95	NA					
<i>SG4 - 105 ft bgs^(a)</i>						
SG-C1-105	NA					
SG-C2-105	NA					
SG-C3-105	NA					
SG-C4-105	NA					
SG-C5-105	NA					
SG-C6-105	2.04	1.59	216	428	76	156

(a) All 105-ft soil gas monitoring points, except SG-C6-105, were below the water table and could not be sampled for soil gas.

NA = Not analyzed

ND = Not detected

During this period of rapid propane degradation, TCE and c-DCE concentrations remained close to or below detection limits. On October 6, methane injection at 1% was initiated, and propane injection was discontinued for approximately 1.5 months. The purpose of using methane was to stimulate CAH degradation in the vadose zone. Groundwater methane concentrations reached 163 and 159 $\mu\text{g/L}$ in MW-C3-117 and MW-C4-117, respectively, indicating that methane was effectively introduced into the aquifer. After approximately a 1-month lag period, methane degradation was most evident in MW-C3-117, though concentrations also decreased in MW-C4-117. However, concurrent with the introduction of methane, CAH concentrations (particularly TCE) increased, indicating a loss of cometabolic activity. This may have been due to insufficient acclimation and growth of methanotrophs to stimulate cometabolic activity, or to an inhibition of methanotrophic cometabolism in the aquifer.

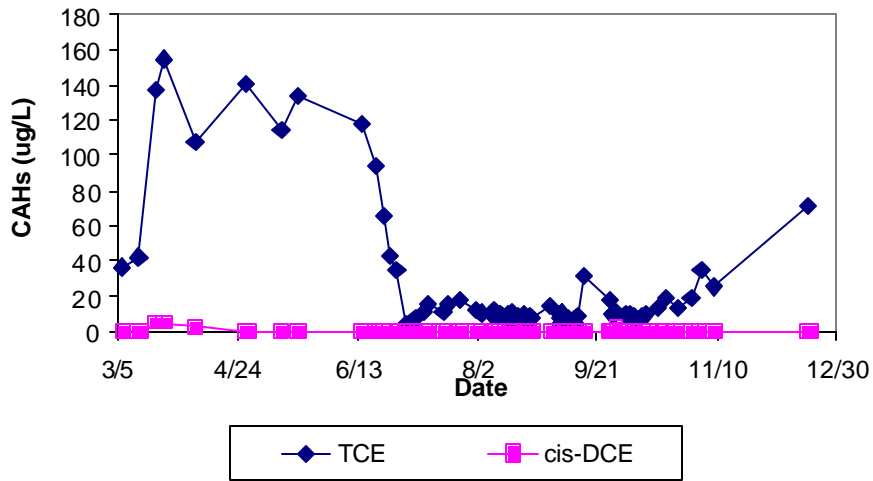
A summary of average CAH concentrations at the end of the propane- and methane-stimulation periods for Phase 2 is shown in Table 12. Only the shallow monitoring points in the control test plot are shown, because the deeper monitoring points did not show significant SF_6 levels during the tracer testing, indicating that they were ineffectively sparged. In the active test plot, trace or non-detectable c-DCE concentrations were measured, and TCE concentrations were very low, averaging 1.9, 8.5, and 20 $\mu\text{g/L}$ in the three most active monitoring points. Only non-detectable or trace 1,1-DCE, 1,1-DCA, and CF concentrations were measured. Except for 1,1-DCE, CAH concentrations increased during the period of methane injection into the aquifer.

5.2.2.3 Groundwater Kinetic Test Results. Kinetic tests were conducted to measure the rate of propane and CAH degradation in the saturated zone in the vicinity of the active sparge well. Kinetic tests were conducted by sparging in the same manner as previous tests (i.e., weekly sparging at approximately 1% to 2% propane in the sparge gas. Ethylene gas also was added to the sparge gas in one to two sparge events to determine the rate of ethylene degradation. In this case, ethylene was used as a surrogate for CAHs, because (a) CAHs could not be added to the sparge gas and (b) steady-state CAH concentrations were too low to measure degradation kinetics in groundwater.

The kinetic tests involved frequent sampling between sparge events to capture the propane and ethylene degradation rates before their rapid depletion. Figure 28 shows the results of the kinetic tests for propane and ethylene degradation in monitoring points C2, C3, and C4 at the 117 ft bgs depth interval. For kinetic tests conducted between Days 450 and 470, sparged propane concentrations were too low and sampling frequency was too low. Sparged concentrations were increased and sampling frequency was increased for the kinetic tests conducted on Day 480.

The rapid sampling approach successfully captured the kinetics of propane and ethylene degradation. Calculated degradation rates are shown in Table 13. This table shows maximum rates calculated between two or three consecutive points, and first order rates calculated for the first-order degradation regime, as seen when the propane and ethylene concentrations approached their respective detection limits. Zero-order degradation rates for ethylene were much higher than propane degradation rates, although first-order rates were lower. Whereas the use of ethylene was intended as a surrogate for CAH degradation, the possibility that ethylene was used as a growth substrate by ethylene-degrading bacteria cannot be ruled out.

Phase 2: C3-117



Phase 2: C3-117

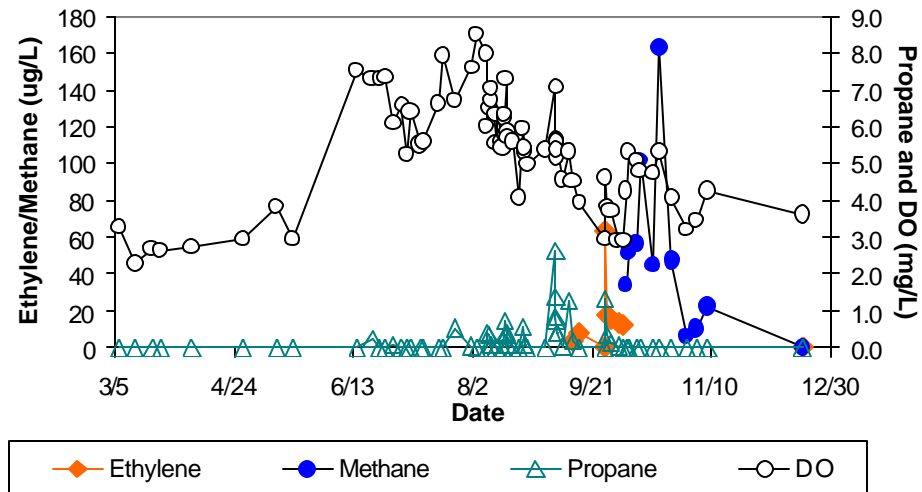
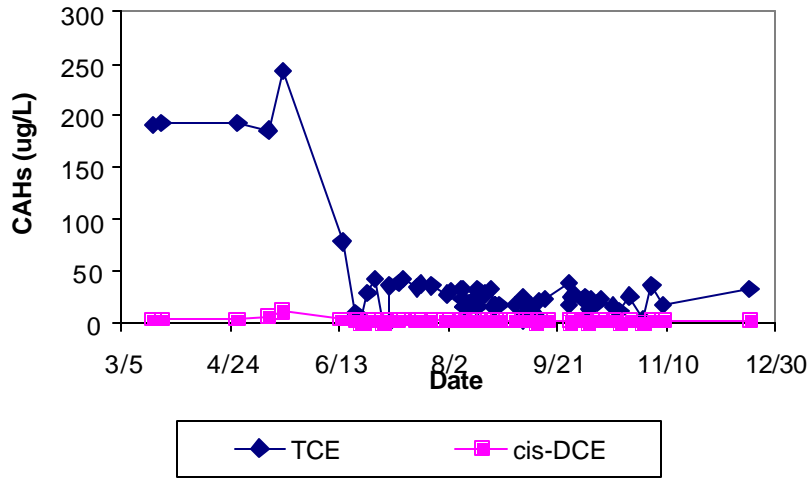


Figure 25. Concentrations of CAH Compounds and Primary Growth Substrates (Propane and Methane) in MW-C3-117 During Phase 2

Phase 2: C4-117



Phase 2: C4-117

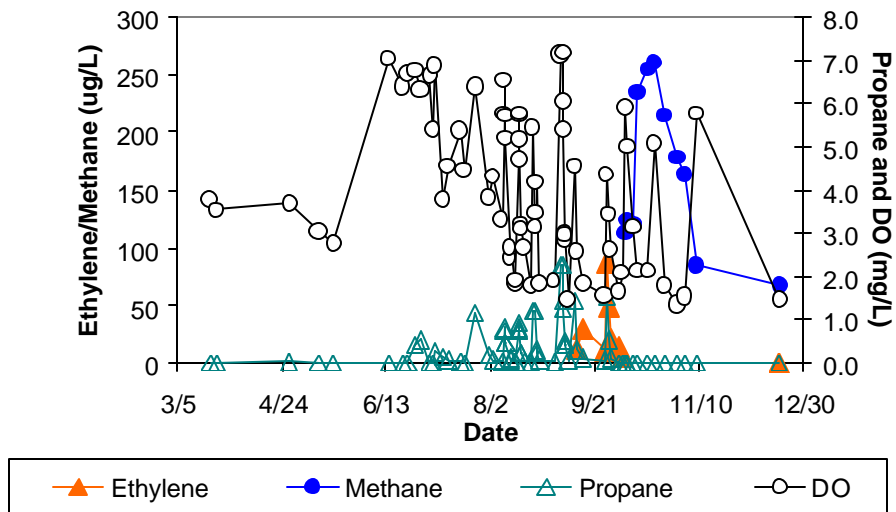


Figure 26. Concentrations of CAH Compounds and Primary Growth Substrates (Propane and Methane) in MW-C4-117 during Phase 2

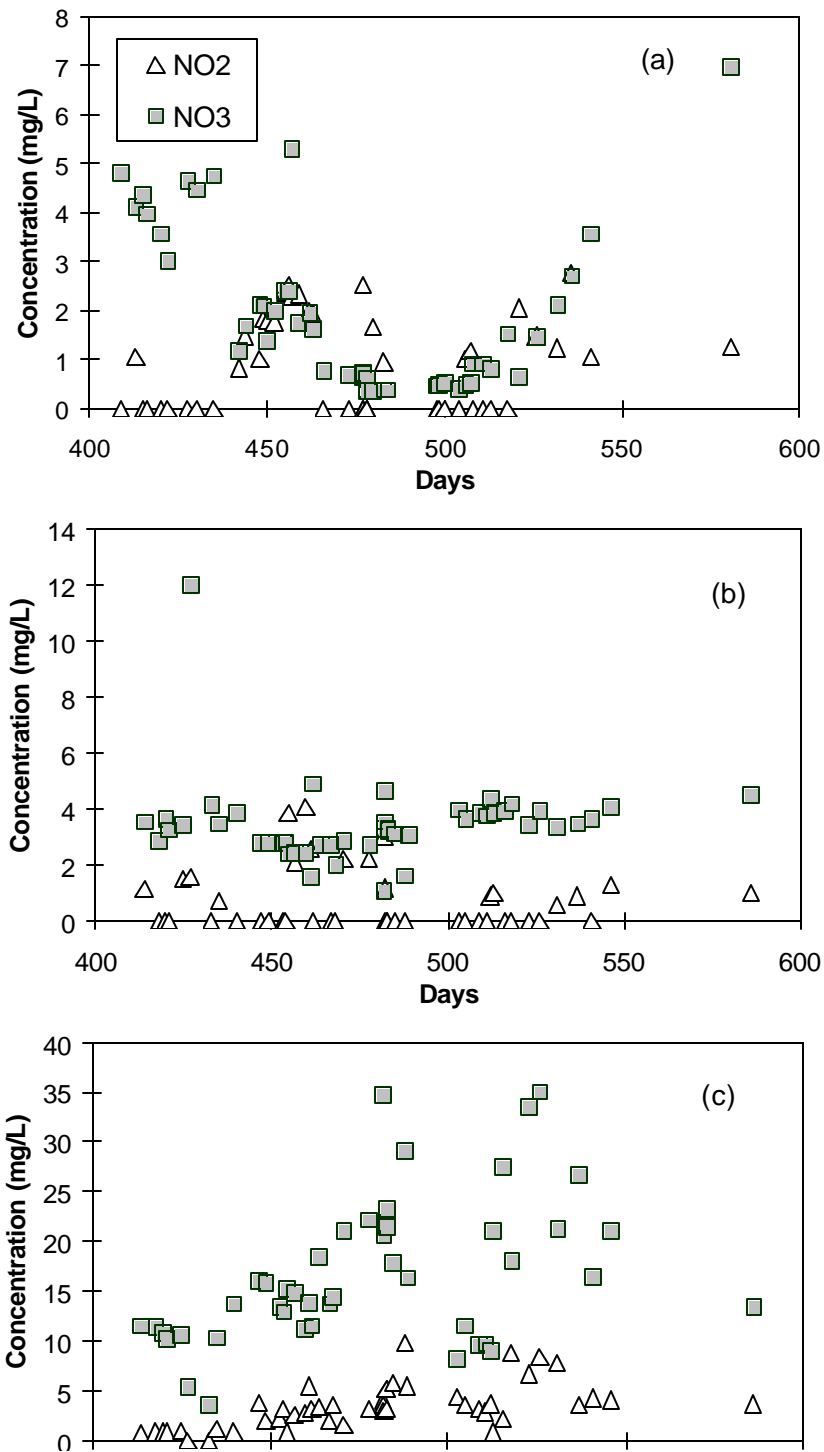


Figure 27. Nitrate/Nitrite Groundwater Concentrations During Phase 2 Operation in Monitoring Points MW-C2-117 (a); MW-C3-117 (b); and MW-C4-117 (c)

Table 12. Groundwater CAH Concentrations at the End of Propane Injection and End of Methane Injection for Monitoring Points that Show Activity

GW MW	No. of samples	Contaminant Concentration (mg/L)				
		TCE	c - DCE	1,1-DCE	1,1-DCA	CF
<i>Summary for active monitoring points in the control test plot</i>						
A1-113	5	4.6 ± 2.8	1.4 ± 1.1	ND	ND	ND
A2-113	5	93 ± 59	12 ± 7.5	0.79 ± 0.51	1.4 ± 2.1	ND
A3-113	2	206 ± 218	30 ± 22	1.1 ± 1.6	4.9 ± 6.9	ND
A4-113	5	474 ± 166	53 ± 13	4.1 ± 1.8	10 ± 2.3	ND
A5-113	4	22 ± 15	3.8 ± 2.6	ND	ND	ND
<i>Summary of last 14 d of 2% propane injection of active monitoring points in active test plot</i>						
C2-117	8	1.9 ± 1.7	ND	ND	ND	ND
C3-113	2	437 ± 110	51 ± 23	ND	2.8 ± 3.9	ND
C3-117	8	8.5 ± 2.5	0.04 ± 0.11	0.69 ± 0.97	ND	ND
C4-113	2	8.1 ± 9.7	1.8 ± 2.5	ND	ND	ND
C4-117	8	20 ± 6.0	1.5 ± 0.67	3.7 ± 4.8	ND	ND
<i>Summary of last 20 d of methane injection of active monitoring points in the active test plot</i>						
C2-117	5	6.2 ± 4.0	0.08 ± 0.13	0.09 ± 0.14	ND	ND
C3-117	5	22 ± 8.1	0.13 ± 0.15	ND	0.03 ± 0.06	ND
C4-117	5	19 ± 13	0.96 ± 0.88	0.21 ± 0.20	0.03 ± 0.06	ND

NA = Not analyzed

ND = Not detected



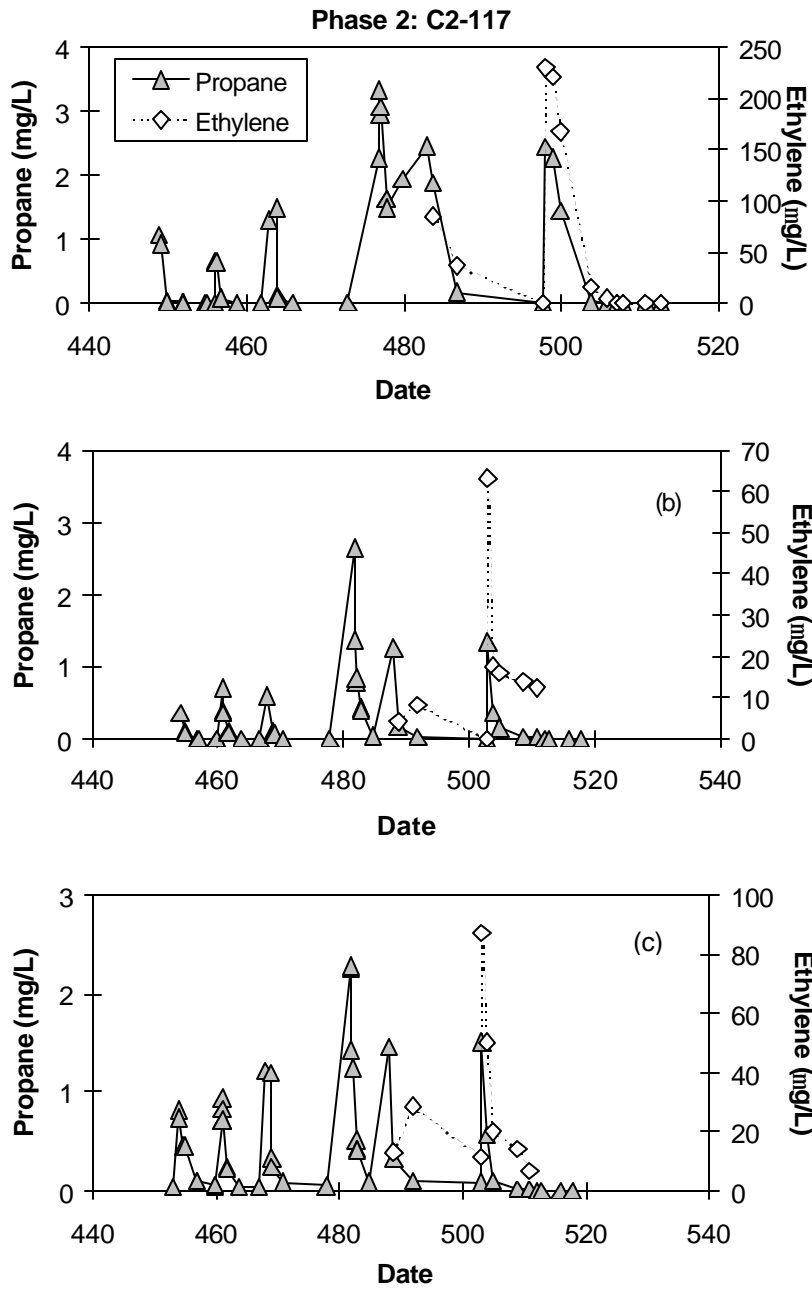


Figure 28. Kinetic Test Results to Determine Propane and Ethylene Degradation Rates in Groundwater Monitoring Points MW-C2-117 (a); MW-C3-117 (b); and MW-C4-117 (c)

Table 13. First-Order and Zero-Order Calculated Propane and Ethylene Degradation Rates in the Active Test Plot Saturated Zone

Monitoring Point	Propane Kinetics			Ethylene Kinetics	
	Zero-order (mg/L-d)		First-order (day ⁻¹)	Zero-order (mg/L-d)	First-order (day ⁻¹)
	Range	Avg ± Stdev			
MW-C2-117	0.68 – 1.84	1.14 ± 0.62	1.12	28.5	0.54
MW-C3-117	1.26 – 1.30	1.28 ± 0.02	0.52, 1.33	1.79	0.05
MW-C4-117	1.21 – 1.61	1.39 ± 0.20	0.79 ± 0.26	35.8	0.29

5.2.2.4 Vadose Zone Results. Vadose zone propane and CAH concentrations in two soil gas monitoring points (SG-C1-95 and SG-C3-95) are shown in Figures 29 and 30. SG-C1-95 showed very stable propane and CAH concentrations over the 200-day monitoring period. SG-C3-95 also showed very stable propane concentrations, while CAH concentrations were stable or increasing over time. The slow increase in CAH concentrations may be due to the migration of CAHs into the vicinity of SG-C3-95 from higher nearby concentrations in the vadose zone or from stripping from the saturated zone. Similar results were seen in the control test plot, where CAH concentrations were very stable and showed no sign of degradation.

Methane first appeared in the vadose zone in early December after the first injection on December 6. Methane was rapidly degraded at both monitoring points, followed immediately by the first signs of propane degradation. The immediate degradation of propane to non-detectable levels following methane injection into the aquifer came as a surprise, and suggested that either methane stimulated the direct degradation of propane or that propane was degraded cometabolically by the growth of methanotrophs in the vadose zone.

TCE concentrations in SG-C1-95 remained very stable, while c-DCE concentrations showed decreasing concentrations between Days 510 and 590, after methane was introduced into the aquifer. Much more significant decreases in both TCE and c-DCE concentrations were observed in SG-C3-95, in which concentrations were below detection limits for both compounds by the time of the last sampling event on Day 590. SG-C3-95 was the only soil gas monitoring point that showed complete CAH removal with the introduction of methane into the sparge gas.

The fact that propane and CAHs disappeared in SG-C3-95 strongly suggests that the CAHs were degraded cometabolically by methanotrophs (or propane-degrading bacteria if propane was not cometabolically degraded) in the vicinity of this soil gas monitoring point. While it is possible that clean soil gas migrated into the area, thereby displacing the CAHs in the vadose zone near SG-C3-95, the stable concentrations monitored in virtually all the deep soil gas monitoring points for over 500 days suggests that the CAHs did not disappear through displacement alone, and that biodegradation likely played a major role in their disappearance. Limited time did not permit confirmation of these results, nor did it permit the continued methane addition and monitoring to promote CAH cometabolism near the other soil gas monitoring points. Thus, it was not possible to confirm whether CAH cometabolism would have ensued after repeated

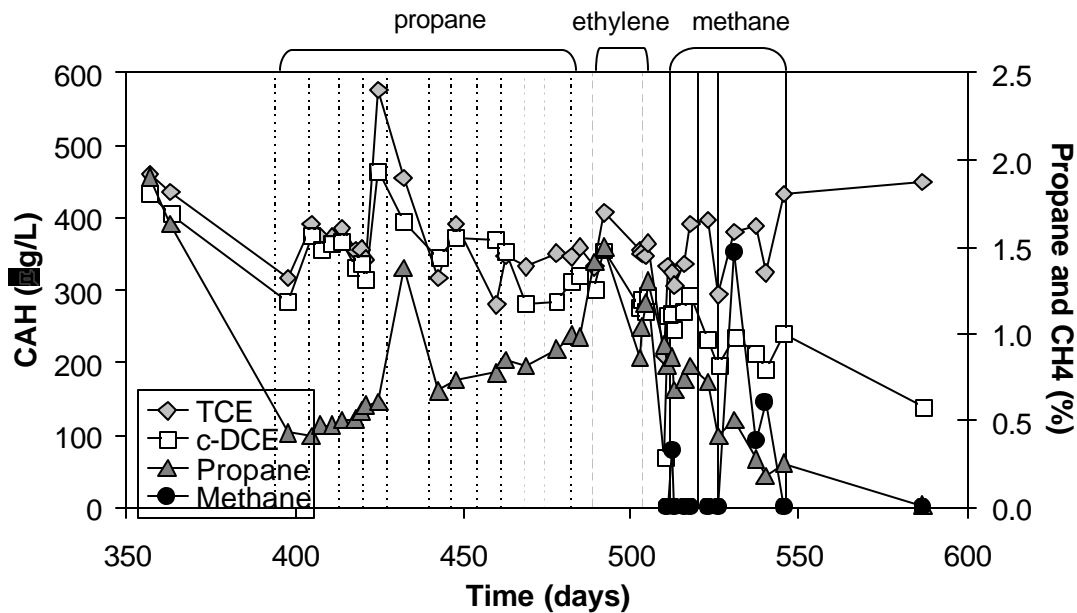


Figure 29. Active Test Plot Soil Gas CAH, Propane, and Methane Concentrations in SG-C1-95

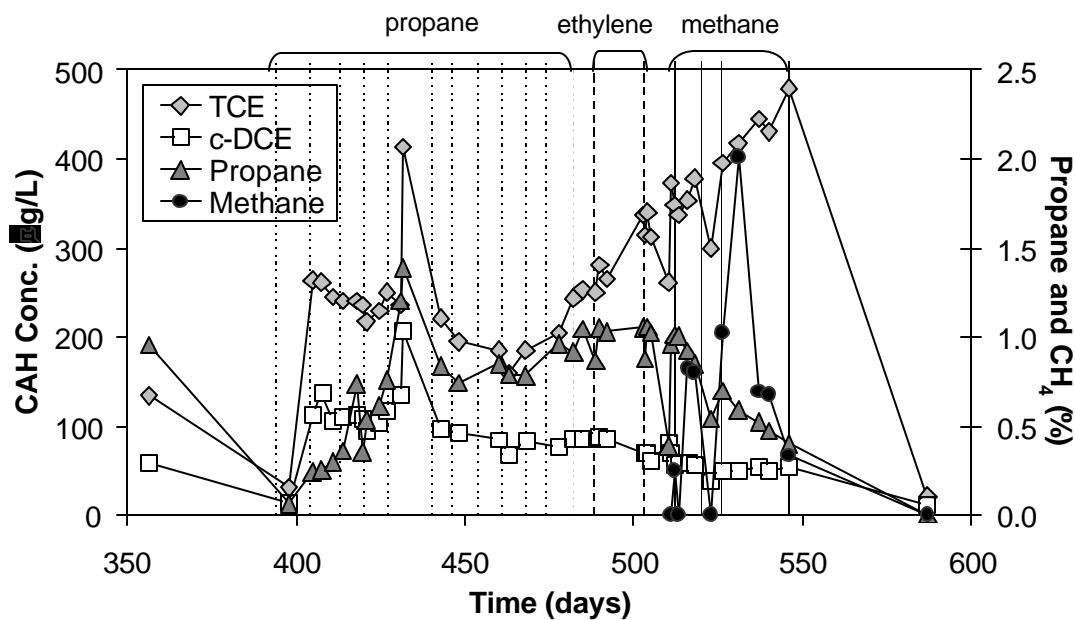


Figure 30. Active Test Plot Soil Gas CAH, Propane, and Methane Concentrations in SG-C3-95

methane injections and the stimulation and growth of methanotrophs throughout the vadose zone, or whether the degradation of CAHs near SG-C3-95 was an isolated event.

The fact that the propane degradation could not be stimulated after 200 days of operation, and that methane degradation did not readily stimulate cometabolic CAH degradation came as a disappointment to the research group conducting this study. Due to the potential for CAH volatilization into the vadose zone, and because many vadose zone environments may be contaminated with CAH compounds along with groundwater environments, it is preferable to achieve CAH cometabolism in the vadose zone. Without such degradation activity, additional treatment such as SVE with aboveground off-gas treatment may be necessary. Thus, the fact that propane was not degraded and CAH cometabolism did not occur in the McAFB vadose zone suggests that a careful cost evaluation must be completed to determine where CAS is a competitive technology with air sparging. Given that CAS resulted in more rapid CAH degradation and greater mass removal, CAS may still have a cost advantage, since the operation could likely be operated for shorter time periods (less O&M costs) and if SVE is necessary, GAC costs would likely be lower due to decreased contaminant loading.

Further research is needed to assess the potential for cometabolic CAH degradation in the vadose zone at other sites. Recently, the EPA successfully stimulated cometabolic TCE degradation by injecting propane directly into the vadose zone with a bioventing system (Sayles, 2001). Their successful results suggest that cometabolism in the vadose zone is possible.

5.3 Data Assessment

The data described in Section 5.2 provide a realistic assessment of the demonstration objectives at McAFB. Figures and results were shown for CAS performance in groundwater and the vadose zone and demonstrated that CAS is effective and very competitive with air stripping in the saturated zone. The data indicated that CAS was ineffective in the vadose zone within the time frame of this study, necessitating a careful cost benefit analysis for implementation at this site. The inability to stimulate cometabolism in the vadose zone at McAFB is not indicative of results at other sites; therefore, this would have to be examined during pilot testing.

The difficulty in stimulating propane degradation and subsequent CAS cometabolism in the vadose zone was not anticipated by the researchers in this study. For this reason, early microcosm studies focused on stimulating propane degradation and cometabolism in soil and groundwater samples from the saturated zone but neglected to study their properties in unsaturated vadose zone samples. In hind-site, and in anticipation of implementing this technology at other sites, confirmation of cometabolic activity in both the saturated and vadose zones using microcosms is imperative, before implementing the technology in the field.

The assumption that propane degradation would occur in the vadose zone if it occurred in the saturated zone was not entirely misguided. Researchers at the U.S. EPA National Risk Management Research Laboratory (NRMRL), Cincinnati, OH, have effectively demonstrated the cometabolic bioventing process using propane as the cometabolic growth substrate, for vadose zone soils at Dover AFB (Sayles, 2001). At Dover AFB, propane uptake was rapid, and TCE

concentrations were relatively low, typically only about 1 ppmv with a few samples up to 20 ppmv.

When conducting a similar study at Hill AFB, the same researchers were unable to stimulate propane degradation and cometabolic CAH degradation in the vadose zone, despite successful microcosm studies that demonstrated propane degradation using the Hill AFB soils (Sayles, 2001). One significant difference between Dover AFB and Hill AFB conditions was the CAH concentration at each base. Concentrations at Hill AFB were around 1000 ppmv. Using Henry's law, 1000 ppmv would equate to approximately 300 mg/L (solubility is approximately 1,100 mg/L). Dr. Sayles and his coworkers speculate that their inability to stimulate propane degradation at Hill AFB is attributed to the high TCE concentrations in the vadose zone, resulting in high aqueous phase concentrations in the vadose zone and potentially toxic conditions for propane-degrading bacteria.

TCE concentrations in the vadose zone at McAFB were approximately 400 to 800 $\mu\text{g/L}$, and c-DCE concentrations were approximately 300 to 600 $\mu\text{g/L}$. Using dimensionless Henry's law constants of 0.3 and 0.1 for TCE and c-DCE, respectively (Verschueren, 1996), the vadose zone gas-phase concentrations equate to approximately 1.3 to 2.7 $\mu\text{g/L}$ TCE and 3 to 6 $\mu\text{g/L}$ c-DCE in the aqueous phase of the vadose zone (i.e., vadose zone moisture). While these concentrations are much lower than those observed at Hill AFB, they are higher than the concentrations at Dover AFB where vadose zone oxidation of propane and CAH cometabolism was successful.

Based on the analysis above, there are two possible explanations of why propane degradation was not observed in the vadose zone at McAFB. The first explanation is that the bacteria were not present in the vadose zone at the site or that conditions were not suitable for their growth. The second explanation is that the individual CAH concentrations or the combination of CAHs at McAFB were toxic to the bacteria.

5.4 Technology Comparison

The CAS technology may be compared to conventional pump and treat (P&T), which is known to require decades to remediate aquifers contaminated with CAHs, or it may be compared with conventional air sparging combined with SVE and off-gas treatment. Cost savings using CAS would be realized because CAS would remove the requirement for aboveground water or off-gas treatment, thereby potentially reducing long-term operation and maintenance costs. All three technologies (P&T, air sparging, and CAS) are expected to be able to achieve MCLs in groundwater. CAS and air sparging would be very competitive in their ability to achieve groundwater MCLs, because both would rely on stripping contaminants from groundwater, in part or in whole. CAS would have an advantage over conventional air sparging because it could rely on both the stripping mechanism in addition to in situ CAH biodegradation.

A comparison of CAS and SVE for vadose zone remediation could not be made at the McAFB site, because propane could not be degraded in the vadose zone. However, assuming both technologies are comparably effective, a cost comparison between these technologies is made in Section 6.

6. Cost Assessment

Implementation costs for the CAS effort at McAFB are shown in Table 14. Costs include fixed and variable costs, and estimated funding by McAFB. Various major costs included on-site labor for the continuous O&M and sampling of the system, and labor associated with the significant analytical load of the demonstration. Much lower costs are expected under full-scale implementation, as shown in Table 15. Table 15 shows the estimated full-scale demonstration costs for a full-scale demonstration, for site with a 130-ft by 30-ft by 20-ft deep aquifer and a 100' deep vadose zone. Tables 16 and 17 show costs for a similar 130-ft by 30-ft by 20-ft deep aquifer using conventional air sparging with GAC to capture the sparged off gas and using P&T, respectively. Backup information and tables are provided in Appendix G, and additional information on cost and performance can be found in the accompanying *Cost and Performance Report* for this study.

Once cometabolism is established in the saturated and vadose zones, the CAS monitoring costs should not differ significantly compared to Air Sparging monitoring costs. Several more labor hours per week were included for safety reasons, assuming the on-site operator would have to check the safety of the system and ensure that the system was not leaking. Both Air Sparging and CAS have groundwater and soil gas monitoring requirements, and above-ground system monitoring requirements. Air Sparging has the added requirement to monitor and sample SVE off-gas concentrations and the SVE off-gas treatment system. Lab testing cost details are provided in Appendix G. The detail includes the assumed sample frequency per week, the number of weeks, the cost per sample, and the total analytical cost.

Operation of the CAS and air sparging processes is virtually the same, besides the enhanced safety requirements for CAS and the use of SVE and off-gas treatment for air sparging. If an SVE system and SVE off-gas treatment is required for the CAS process, there would be little or no cost benefit with CAS over conventional air sparging. Thus, despite the fact that cometabolic CAH degradation was not observed in the McAFB vadose zone, for costing purposes it was assumed that vadose zone cometabolic CAH degradation is achievable; CAS would be implemented at full scale only under the condition that CAHs are degraded in the saturated and vadose zones. For this reason, an SVE system was not included in the CAS cost estimate.

Estimated CAS (\$161/cy) and conventional AS (\$163/cy) costs were very competitive at the selected scale for comparison, while P&T costs (\$313/cy) were much higher, as expected. Although the costs of CAS and conventional AS were similar for the scale selected for this cost comparison, the relative costs of CAS would likely decrease per unit treated volume, while the cost of conventional AS would be relatively linear. This is because CAS has several up-front costs whose relative costs would decrease in proportion to the total project cost with increased scale. Such upfront costs include the microcosm studies (estimated at approximately \$50,000), pilot testing (estimated at approximately \$36,000), and groundwater and vadose zone monitoring, both of which could decrease significantly once the efficacy of the process at the site is confirmed.

Table 14. McClellan AFB, CA Demonstration Costs

Cost Category	Sub Category	Costs (\$)
FIXED COSTS		
1. CAPITAL COSTS	Mobilization/demobilization	\$16,000
	Planning/Preparation	\$24,000
	Site investigation and testing	
	- Nutrient Addition Testing	\$16,500
	- Microcosm Study – field work	\$16,000
	- Other	\$8,000
	Equipment Cost	
	- Total hydrocarbon analyzer	\$16,000
	- Oil-less air compressor	\$12,500
	Start-up and Testing	\$10,000
	Other	
- Non process equipment	\$20,600	
- Installation	\$30,000	
- Engineering	\$20,000	
- Management Support	\$15,000	
Sub-Total		\$204,600
VARIABLE COSTS		
2. OPERATION AND MAINTENANCE	Labor	
	- Field personnel – on-site	\$90,000
	- Battelle personnel – on-site	\$25,000
	- Travel	\$24,000
	- OSU on-site lodging	\$16,000
	Materials and Consumables	\$16,000
	Utilities and Fuel	\$300
	Equipment Rentals	
	- 2 Conex boxes	\$3,500
	- Analytical tank rentals	\$4,000
	- Other rentals	\$3,400
	Performance Testing/Analysis	
	- Outside lab analysis	\$4,300
	- Battelle lab & data analyses	\$15,000
- Field GC work	\$19,000	
- Other	\$2,300	
Other direct costs	\$400	
Oregon State University	\$264,000	
*MCCLELLAN AFB FUNDING		\$200,000
Sub-Total		\$687,200
TOTAL COSTS		
TOTAL TECHNOLOGY COST: \$891,800		
Quantity Treated: 523 yd ³		
Unit Cost (\$): \$1,705/yd ³		

Table 15. Estimated Full-Scale Implementation Costs for Conducting Cometabolic Air Sparging at McClellan AFB, CA^{(a)(b)}

Cost Category	Sub Category	Costs (\$)
FIXED COSTS		
CAPITAL COSTS	Mobilization/demobilization	\$50,000
	Planning and Preparation	\$40,000
	Site Investigation	
	- Microcosm	\$50,000
	- Pilot Testing	\$36,500
	Equipment Cost	
	- Oil-less air compressor	\$20,000
	- Total hydrocarbon analyzer	\$26,000
Start-up and Testing	\$17,000	
Other		
- Propane Tank	\$5,000	
- Installation	\$49,500	
- Engineering	\$20,000	
- Management Support	\$15,000	
		Sub-Total \$319,000
VARIABLE COSTS		
OPERATION AND MAINTENANCE	Labor	\$17,200
	Materials and Consumables	\$18,000
	Utilities and Fuel	\$6,000
	Equipment Rentals	
	- 1 Conex boxes	\$2,200
	- Water Quality Meter	\$2,000
	Performance Testing/Analysis	
- Lab analysis	\$92,200	
- Testing after completion for one year on quarterly basis	\$9,400	
		Sub-Total \$147,000
TOTAL COSTS		
		TOTAL TECHNOLOGY COST \$465,600
		Quantity Treated: 2,888 yd ³
		Unit Cost (\$): \$161/yd ³

(a) Estimates based on pilot testing of 1 sparge well and three 2" PVC monitoring wells 120 ft deep with 1 ft. screened depth.

(b) Based on an area 130 by 30 by 20 with 5 sparge wells and 10 monitoring wells operated for a period of 2 years.

Table 16. Estimated Full-Scale Implementation Costs for Conducting Air Sparging at McClellan AFB, CA^(a)

Cost Category	Sub Category	Costs (\$)
FIXED COSTS		
CAPITAL COSTS	Mobilization/demobilization	\$50,000
	Planning/Preparation	\$40,000
	Investigation and Testing	\$37,700
	Equipment Cost	
	- GAC Canister	\$6,000
	- Oil-less Compressor	\$20,000
	Blower (20 hp)	\$2,600
	Start-up and Testing	\$41,300
	Other	
- Installation	\$56,600	
- Engineering	\$20,000	
- Management Support	\$15,000	
		Sub-Total \$289,100
VARIABLE COSTS		
OPERATION AND MAINTENANCE	Labor	\$12,700
	Materials and Consumables	\$90,000
	Utilities and Fuel	\$6,000
	Equipment Rentals	
	- Conex Box	\$2,200
	- Water Quality Meter	\$2,000
	Performance Testing/Analysis	
	- During sparging – water for VOCs	\$56,200
	- Air sampling	\$2,900
- After completion VOCs	\$9,400	
		Sub-Total \$181,000
TOTAL COSTS		
		TOTAL TECHNOLOGY COST \$470,100
		Quantity Treated: 2,888 yd ³
		Unit Cost (\$): \$163/yd ³

(a) Based on an area 130 by 30 by 20 with 5 sparge wells and 10 monitoring wells operated for a period of 2 years.

Table 17. Estimated Full-Scale Implementation Costs for Pump and Treat at McClellan AFB, CA^(a)

Cost Category	Sub Category	Costs (\$)
FIXED COSTS		
CAPITAL COSTS	Mobilization/demobilization	\$50,000
	Planning/Preparation	\$40,000
	Site Work	\$20,000
	Equipment Cost	
	- Pump	\$10,000
	- GAC Canister	\$60,000
	- Holding Tank	\$15,000
	Start-up and Testing	\$16,300
Other		
- Installation	\$45,400	
- Engineering	\$20,000	
- Management Support	\$15,000	
		Sub-Total \$291,700
VARIABLE COSTS		
OPERATION AND MAINTENANCE	Labor	\$19,500
	Materials and Consumables	
	- GAC replacement	\$540,000
	- Other	\$15,000
	Utilities and Fuel	\$12,000
	Performance Testing/Analysis	
- VOCs during pump and treat	\$30,500	
- After pump and treat completed	\$7,000	
		Sub-Total \$613,100
TOTAL COSTS		
		TOTAL TECHNOLOGY COST \$904,800
		Quantity Treated: 2,888 yd ³
		Unit Cost (\$): \$313/yd ³

(a) Based on an area 130 by 30 by 20 with 10 monitoring wells and one extraction well operated for a period of 10 years.

7. Implementation Issues

7.1 Cost Observations

Key factors that affected project costs were depth to groundwater, the size of the plume, and operating and monitoring requirements. These are factors that would affect virtually any technology, specifically any sparging-related technology.

Depth to groundwater required drilling to over 110 ft bgs. For full-scale treatment, even deeper drilling would be required to extend the technology beneath the area of groundwater contamination. Depth to groundwater cannot easily be avoided and there are no factors that could be enhanced to eliminate this treatment obstacle. For this study, drilling cost approximately \$100,000 to drill sparge and monitoring points for the control and active test plots combined.

At McAFB, the size of the plume would significantly impact a sparging-related technology. With a radius of influence of approximately 15 ft per well, sparging requires frequent well placement to gain coverage within the plume. At the OU A plume, the 15-ft spacing would result in several hundred sparge wells.

System operation and maintenance significantly impacted costs for this demonstration. However, enhanced maintenance and monitoring of groundwater and soil gas points were required due to the experimental nature of this demonstration. For a full-scale sparging or CAS site, efforts would be made to minimize the number of monitoring points, monitoring frequency, and to automate a sparge system to minimize the operation and maintenance (O&M) time required in the field. The addition of propane adds a level of complexity, due to safety concerns, that makes reduction of O&M for CAS more difficult than conventional AS.

At most sites, a pilot demonstration of this technology would be necessary, before it is implemented at full scale. We learned that prolonged exposure to propane for over 500 days did not stimulate propane degraders in the vadose zone. Thus, it is likely that such pilot studies could be operated for a much shorter time period than used for this demonstration. This would significantly reduce demonstration costs. Furthermore, pilot studies should be conducted only if propane degradation and CAH cometabolism can be demonstrated for the saturated and vadose zones in laboratory microcosm studies before the field demonstrations.

For sites where sparging is already being applied, the addition of a propane injection system would be a much smaller incremental cost than for sites where no sparging is intended and all equipment would have to be purchased or leased for the CAS demonstration alone.

7.2 Performance Observations

CAS performance in the saturated zone met expectations and showed effective control of groundwater CAH concentrations. CAS was competitive with sparging only, and maintained concentrations near or below groundwater MCLs. Rapid propane degradation and subsequent

CAH cometabolism were seen after a 40-day lag period, which matched laboratory microcosm results. These results indicate that the laboratory microcosms were good indicators of propane degradation, CAH cometabolism, and lag periods in the field.

Performance in the vadose zone did not meet expectations. After over 500 days of exposure to propane in soil gas (approximately 1 to 4%), there was no evidence of propane degradation in the vadose zone and no evidence of CAH cometabolism. Attempts were made to stimulate methanotrophic CAH cometabolism by injecting methane into the vadose zone. These attempts were successful after a lag period.

The inability of the CAS process to stimulate cometabolic degradation of CAHs in the vadose zone will decrease the cost competitiveness of the technology. Hypothetically, the CAS process could still result in lower O&M costs due to more rapid CAH degradation and potentially reduced SVE off-gas treatment requirements, but the cost estimate in Section 6 suggests that adding an SVE system to the CAS process would significantly reduce its cost competitiveness. Other sites may achieve cometabolic degradation in the vadose zone, and it is unknown why this vadose zone cometabolism using propane did not occur at McAFB. It is probable and even likely that propane (or another growth substrate) would degrade in the vadose zones of other sites, making this technology much more applicable to other sites. The methanotrophic cometabolism results at the end of the study suggest a potential for using methane as the growth substrate for cometabolism of CAH compounds at McAFB. Furthermore, had propane degradation been stimulated at McAFB, there is every reason to believe that CAH cometabolism would have occurred, based on the success of propane as a growth substrate in the vadose zone.

7.3 Scale-up

Scale up of CAS would be very similar to any sparging technology. Cost reductions would be realized by sharing equipment among sparge wells (i.e., compressors and propane injection), minimizing monitoring points and monitoring requirements, and minimizing the number of sparge points. Sparge points could be minimized by creating sparge curtains or barriers or by focusing only on hot spots, rather than trying to treat an entire aqueous plume. However, these savings would have to be balanced against other factors such as prolonged treatment and O&M requirements.

Any full-scale implementation of CAS would require first the demonstration of CAS in saturated and unsaturated soils using laboratory microcosms. This would be followed by the demonstration of CAS in the field using a simple, scaled down version of this demonstration. Cost reductions for the field demonstration would be seen by (1) eliminating the control test plot; (2) reducing the number of groundwater monitoring wells and vertical monitoring points; (3) reducing monitoring frequency; and (4) reducing the duration of the pilot test.

The size of a site will impact virtually any treatment technology. In the case with CAS, as with conventional air sparging, sparge wells have a limited radius of influence (generally approximately 15 ft is used as a rule of thumb, unless otherwise measured in the field). Increased sparge rates or sparge pressures cannot expand this limited radius of influence. Thus, in general, the number of sparge wells is directly proportional to the size of the site. CAS costs

can be minimized by strategically placing sparge wells to optimize their efficacy for either hot-spot removal or plume control.

7.4 Lessons Learned

CAS was effective for treatment of groundwater but ineffective in the vadose zone, resulting in incomplete contaminant removal from the site. Based on work by others, such as at Dover AFB (Sayles, 2001), it is not unreasonable to conclude that CAS could effectively treat vadose zone contaminants at different sites. However, CAS should be demonstrated using microcosms of saturated and vadose zone soils before entering into a field effort.

In particular, users should be aware of the following:

- It is critical that propane degradation and CAH cometabolism be demonstrated in laboratory microcosms before initiating field work.
- Laboratory studies should be conducted using CAH concentrations similar to those observed in the field.
- Nutrient requirements should be assessed in the laboratory. Sites where nitrogen or other nutrient limitations persist may limit the efficacy of this process.

The primary lesson learned was the importance of establishing vadose zone and saturated zone biological activity before initiating field work; this would be established in the laboratory, using laboratory microcosms.

Based on the costs established for this report and the corresponding *Cost and Performance Report*, CAS is only marginally competitive with conventional air sparging. However, normalized CAS costs could reduce with an increasing volume of contaminated material. This is because the up-front cost of microcosm testing would be seen only once, while the on-going O&M would not increase significantly due to the fact that off-gas treatment is not required; thus the major impact of a larger site to O&M would be possible increased monitoring requirements.

Site experience is very likely to reduce costs, particularly O&M costs. Experience and increased confidence in the success and long-term stability of this technology will permit reduced sampling and analysis and reduced O&M efforts. However, the is also the case for conventional air sparging and pump and treat technologies.

Methane injection, or the use of alternative growth substrates for CAH cometabolism, should be considered for future work. There may be no single compound that is best suited for any given site. Rather, the use of a suite of compounds may be necessary and could optimize the potential for CAH remediation. Methanotrophs also are unique because they can fix nitrogen more readily than propane degrading bacteria. This gives them a unique advantage in the vadose zone where nitrogen gas is readily available but where other nitrogen sources may be limited due to the low water content in the soils. Thus, a cometabolic strategy may be one that includes a combination

of propane sparging and methane sparging, either simultaneously or in sequence. Experience at McAFB suggests that low gaseous concentrations are effective (e.g., less than 2 to 4%).

7.5 End-User Issues

The air sparging technology has been widely applied for many years at DoD installations and has already gained fairly widespread acceptance. The modification of the air sparging process to include a cometabolic growth substrate such as propane or butane remains promising, but may require more investigation. Additional work is required to evaluate conditions under which cometabolism can be stimulated in the vadose zone. Such studies can be conducted at a significantly reduced cost, compared to this study, by reducing the number of wells and monitoring points, eliminating the need for a control site, and simplifying the overall treatment process.

7.6 Approach to Regulatory Compliance and Acceptance

Air sparging is now well accepted by regulators and is routinely employed at a number of sites throughout the country. Permitting issues are often involved in the discussion of vapor capture and treatment. While air sparging systems can operate efficiently without vapor capture, SVE systems are often routinely installed in conjunction with air sparging systems. SVE systems are necessary if subsurface structures or buildings exist within the zone of influence of the air sparging system, or when chlorinated solvents that cannot easily be degraded in the vadose zone are sparged.

At sites where chlorinated solvents are present, the addition of cometabolic growth substrates could hypothetically stimulate biological processes in the saturated zone, thereby eliminating the need to capture and treat volatilized contaminants using an SVE process. The success of this process for both the saturated and vadose zones has yet to be fully demonstrated. The goal of this research effort was to demonstrate propane degradation and CAH cometabolism in both the saturated and vadose zones. Success was seen only in the saturated zone during the time allotted for this study. Potential success in the vadose zone occurred at the end of the study, when CAH compounds disappeared in the presence of methane degradation in the vadose zone; however these results could not be verified. Additional work is needed to demonstrate the efficacy of this technology for both saturated and vadose zones before regulatory acceptance can be expected. Concentrations in the saturated zone dropped below or approached MCLs for TCE and c-DCE, suggesting that this technology should prove acceptable to regulators once the additional work for vadose zone treatment is conducted.

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APPENDIX A
POINTS OF CONTACT

Appendix A: Points of Contact

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APPENDIX B
SCHEDULE OF OPERATING CONDITIONS AND FIELD OBSERVATIONS

APPENDIX C
GROUNDWATER MONITORING POINT DATA
C.1. Groundwater Monitoring point Data for the Active Test Plot
C.2. Groundwater Monitoring point Data for the Control Test Plot

APPENDIX D

SOIL-GAS MONITORING POINT DATA

- D.1. Soil-Gas Monitoring Point Data for the Active Test Plot**
- D.2. Soil-Gas Monitoring Point Data for the Control Test Plot**

APPENDIX E
HISTORICAL FIGURES FOR THE GROUNDWATER MONITORING POINTS
E.1. Groundwater Monitoring Point Historical Figures for the Active Test Plot
E.2. Groundwater Monitoring Point Historical Figures for the Control Test Plot

APPENDIX F
HISTORICAL FIGURES FOR THE SOIL-GAS MONITORING POINTS
F.1. Soil-Gas Monitoring Point Historical Figures for the Active Test Plot
F.2. Soil-Gas Monitoring Point Historical Figures for the Control Test Plot

APPENDIX G
COST AND PERFORMANCE BACKUP