

Cost and Performance Report

for

Enhanced In-Situ Biotransformation Pilot Study

at

**Naval Weapons Industrial
Reserve Plant
Dallas, Texas**

August 2002

EXECUTIVE SUMMARY

This report presents the cost and performance data for an Enhanced In-Situ Biotransformation Pilot Study, located at the Naval Weapons Industrial Reserve Plant Dallas, Texas. It is a condensed version of the final technical report entitled "*Enhanced In-Situ Biotransformation Pilot Study Report*" which was prepared by ARCADIS Geraghty & Miller, Inc., for the Naval Facilities Engineering Command.

Chlorinated solvent contamination of soils and groundwater is a widespread problem at many military and civilian facilities. This class of compounds includes widely used industrial chlorinated aliphatic hydrocarbons (CAHs) such as carbon tetrachloride, methylene chloride, trichloroethane (TCA), trichloroethene (TCE) and tetrachloroethene (PCE).

The conventional remedial approach for groundwater contaminated with CAHs was "pump and treat," where the recovered groundwater was treated through air stripping, granular activated carbon adsorption, or ultraviolet oxidation prior to discharge (Nyer, 1998). Pump and treat systems are considered effective for hydraulic control, but do little to actually decrease the CAH concentrations within the dissolved plume.

ARCADIS was contracted by the NAVFAC in 1998 to conduct a pilot study to evaluate enhanced in-situ biotransformation as a possible remedy for the impacted groundwater. This remedial approach involves the addition of a molasses solution into the impacted groundwater-bearing zones. The molasses solution serves as a supplemental energy source for indigenous microbes and enhances the existing microbial processes occurring within the subsurface. As the energy source is consumed, the existing subsurface environment changes from aerobic to anaerobic, a condition that is more conducive to biodegradation of CAHs.

The pilot study was conducted in an area near Solid Waste Management Unit (SWMU) #15, an unlined acid neutralization pond. The study consisted of two injection wells (one in the upper water-bearing zone and one in the lower zone), one upgradient monitoring well, and six downgradient monitoring wells (three in the upper zone and three in the lower zone). System performance was monitored monthly by collecting groundwater samples and analyzing for field parameters and laboratory analyses for volatile organic compounds (VOC's) and geochemical indicators.

The results indicated favorable positive trends from the treatment program. The limitation that may adversely affect treatment by this method is the ability to adequately distribute the nutrient solution within the impacted area due to poor transport properties of the water-bearing zones. This is particularly true of the lower zone. This means that although the pilot study was effective, actual treatment of the larger zone would require increased treatment time due to less than ideal hydrologic conditions.

TABLE OF CONTENTS

1.0 SITE INFORMATION.....	1
1.1 Site History/Source Of Contamination	1
1.2 Remedial Options.....	4
1.3 Site Contacts	4
2.0 MATRIX DESCRIPTION	4
2.1 Geology.....	4
2.2 Hydrology	5
2.3 Aquifer Characteristics	6
2.4 Contaminant Characterization	7
3.0 TECHNOLOGY SYSTEM DESCRIPTION	7
3.1 Background And Applications.....	7
3.2 Advantages And Limitations	10
3.3 System Description And Operation	13
3.3.1 Timeline	13
3.3.2 System Description	14
3.3.3 System Operation.....	15
3.4 Operating Parameters Affecting Technology Cost Or Performance	17
3.4.1 Biological Factors	18
3.4.2 Hydrogeological Factors.....	19
3.4.3 Chemical Factors	20
4.0 TECHNOLOGY SYSTEM PERFORMANCE	21
4.1 Cleanup Goals/Standards	21
4.2 Performance Data.....	21
4.2.1 Analytical Data for the Lower Water-Bearing Zone	22
4.2.2 Analytical Data for the Upper Water-Bearing Zone.....	23
4.2.3 Field Parameters.....	25
4.3 Performance Data Assessment.....	30
4.4 Performance Data Quality.....	32
4.4.1 Accuracy	33
4.4.2 Precision.....	33
4.4.3 Sensitivity	34
4.4.4 Completeness.....	34
5.0 COST OF THE TECHNOLOGY SYSTEM.....	34
5.1 Procurement Process.....	34
5.2 Cost Data.....	35
6.0 REGULATORY/INSTITUTIONAL ISSUES.....	36
7.0 TECHNOLOGY APPLICABILITY AND ALTERNATIVES	37
8.0 OBSERVATIONS AND LESSONS LEARNED	39
9.0 REFERENCES.....	41

TABLES

Table 1. Key information about the study	1
Table 2. Timeline	13
Table 3. Molasses Injection Record.....	16
Table 4.1 Summary of Data, Monitor Well DWP-4-16.....	25
Table 4.2 Summary of Data, Monitor Well DWP-4-IW1	26
Table 4.3 Summary of Data, Monitor Well DWP-4-IDW1.....	26
Table 4.4 Summary of Data, Monitor Well DWP-4-DW1	27
Table 4.5 Summary of Data, Monitor Well DWP-4-DW3	27
Table 4.6 Summary of Data, Monitor Well DWP-4-17.....	28
Table 4.7 Summary of Data, Monitor Well DWP-4-18.....	28
Table 4.8 Summary of Data, Monitor Well DWP-4-DW4.....	29
Table 5. Summary of Performance Information for Pilot System	31
Table 6. Cost Summary for Pilot System.....	35
Table 7. Estimated Unit Costs for Groundwater Remediation System Components	37

FIGURES

Figure 1. Site location map	2
Figure 2. Layout of the pilot study area	3
Figure 3. Process flow diagram for the system	14

1.0 SITE INFORMATION

This report presents the results of a pilot scale study conducted at the Naval Weapons Industrial Reserve Plant (NWIRP) in Dallas, Texas. The pilot study was performed to evaluate the effectiveness and feasibility of enhanced in-situ biotransformation for remediating impacted ground water at the site. The study was conducted by ARCADIS Geraghty & Miller, Inc. (ARCADIS), on behalf of the Southern Division of the Naval Facilities Engineering Command (NAVFAC). The study was conducted according to the Work Plan prepared by ARCADIS Geraghty & Miller, Inc. titled, *Enhanced In-Situ Biotransformation Remedial Technology Pilot Study* (the work plan) dated February 19, 1999 (ARCADIS Geraghty & Miller, 1999b) which included a Sampling and Analysis Plan (SAP) and Quality Assurance Project Plan (QAPP). A separate Health & Safety Plan (HSP) (ARCADIS Geraghty & Miller, 1999a) was also prepared and followed throughout the entire study. This report was prepared according to the guidelines established in the document titled *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* (USEPA, 1998). Table 1 listed below shows key information about the study.

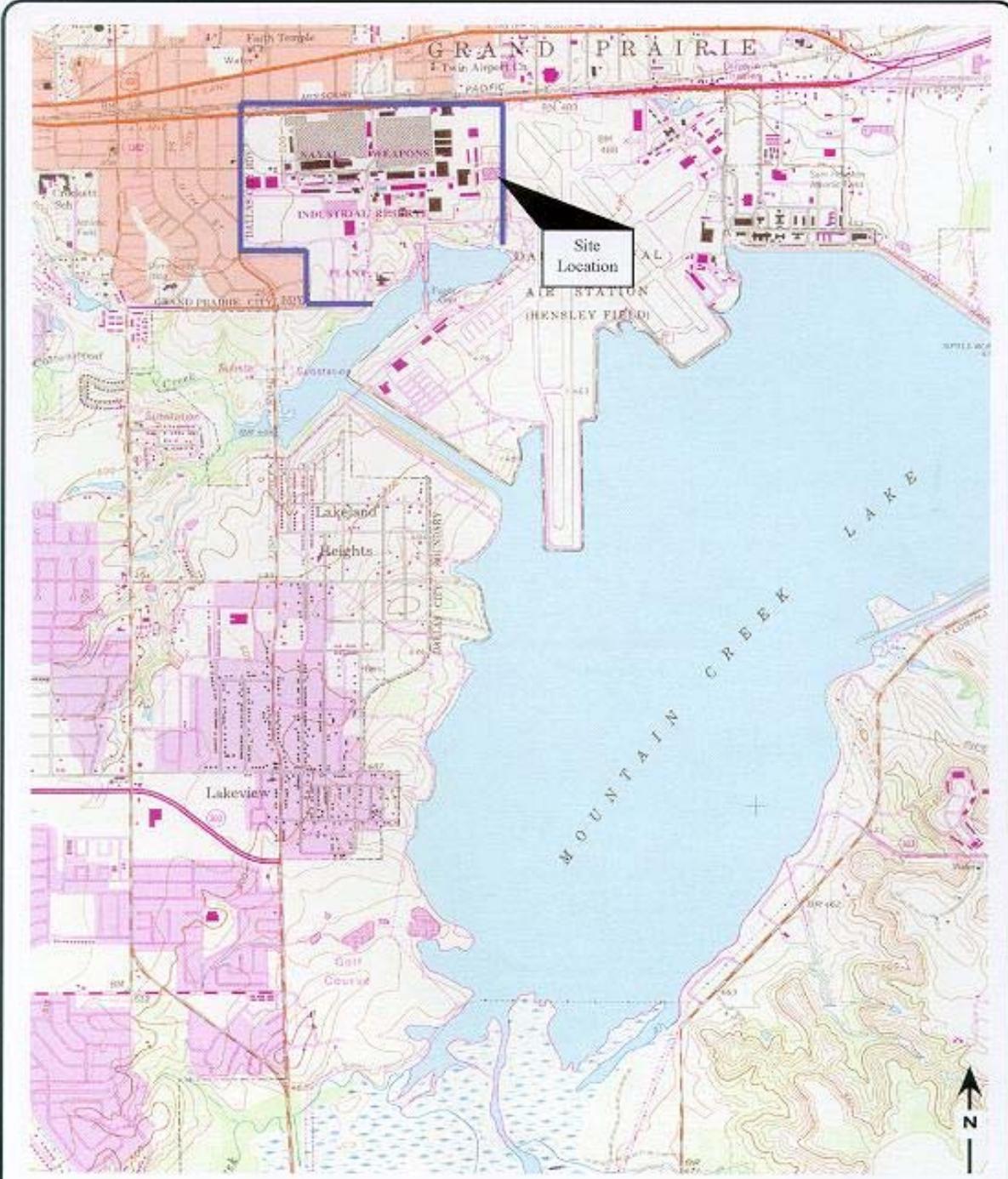
TABLE 1. KEY INFORMATION ABOUT THE STUDY

Site Name, Location	Naval Weapons Industrial Reserve Plant, Dallas Texas
USEPA ID No.	TX6170022770
Mechanisms	Groundwater through Enhanced In-Situ Biotransformation
Technology	Enhanced Bioremediation through Injection of Molasses Solution
Configuration	Direct Injection of Carbon Source
Technology Scale	Pilot Study
Media/Matrix Treated	Groundwater
Contaminates Targeted	Trichloroethene (TCE) and daughter products
Period of Pilot System Operation	October 1999 to September 2000

1.1 SITE HISTORY/SOURCE OF CONTAMINATION

The NWIRP in Dallas, Texas manufactures and assembles military and commercial aircraft components and weapons systems. The facility has been in operation since 1940. The site is currently leased by Vought Aircraft Company. A site location map is presented as Figure 1. Figure 2 shows a layout of the pilot study area.

The pilot study discussed in this report was conducted in an area near Solid Waste Management Unit (SWMU) #15, which was an unlined acid neutralization pit. The pit received liquid wastes from 1970 until 1983. The waste managed in the pit included degreasers that contained trichloroethene (TCE). Groundwater in the pilot study area contains dissolved TCE and various daughter products including cis-1,2-dichloroethene, 1,1-dichloroethene and vinyl chloride.



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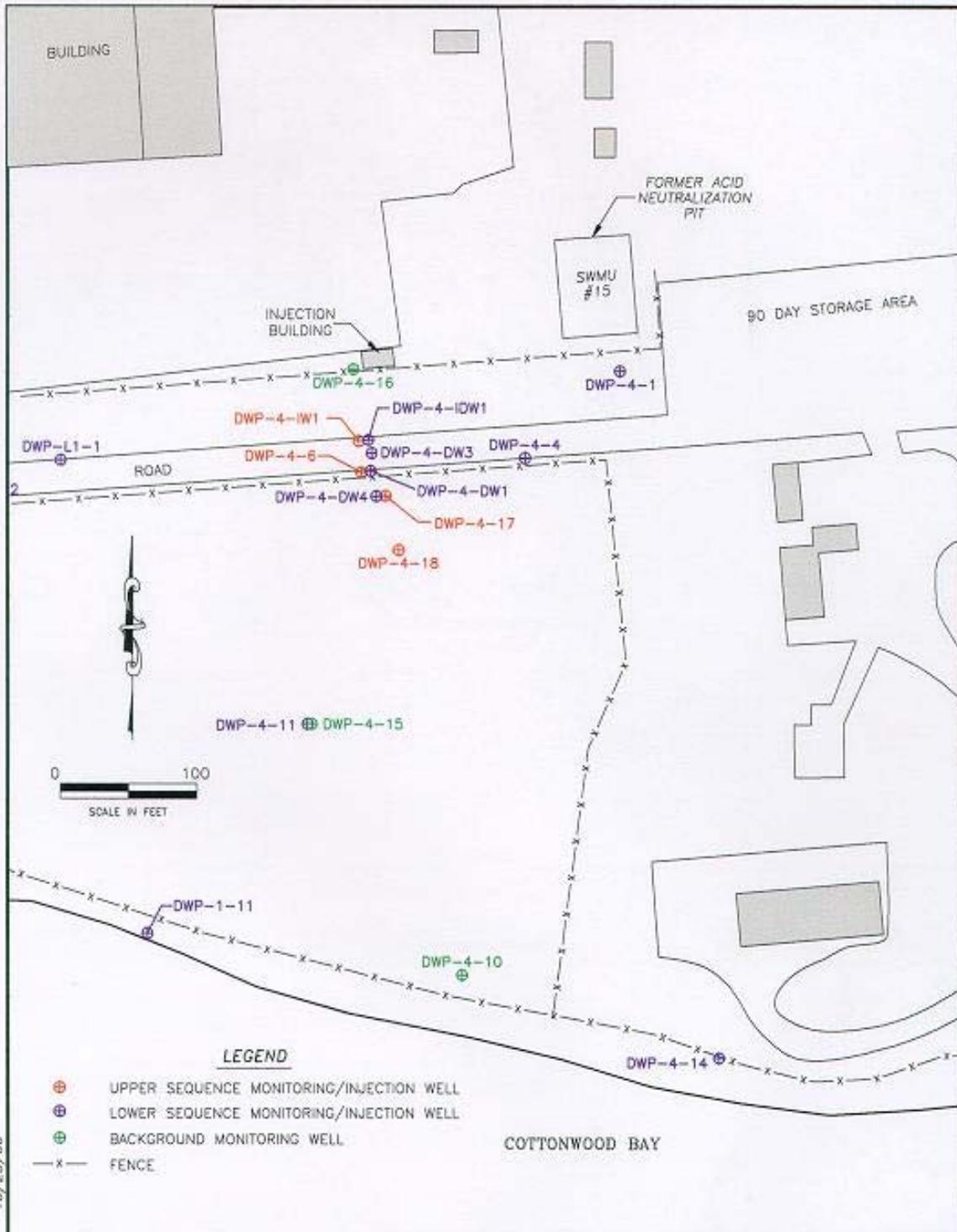
SITE LOCATION AND LOCAL TOPOGRAPHY MAP
 U.S.G.S. 7.5-minute Duncanville, Texas, Revised 1981

Enhanced In-Situ Biotransformation Remedial
 Technology Demonstration
 Naval Weapons Industrial Reserve Plant
 Dallas, Texas

FIGURE

1

0  2000 FEET



DALLAS-SITE.DWG 10/25/00

ARCADIS GERAGHTY & MILLER



5608 PARKCREST DRIVE, SUITE 300
 AUSTIN, TEXAS 78731
 Tel: 512/451-1188 Fax: 512/451-2930

SITE PLAN
 NAVAL WEAPONS
 INDUSTRIAL RESERVE PLANT
 DALLAS, TEXAS

FIGURE
2

AT000961.2005

1.2 REMEDIAL OPTIONS

Chlorinated solvent contamination of soils and groundwater is a widespread problem at many military and civilian facilities. This class of compounds includes widely used industrial chlorinated aliphatic hydrocarbons (CAHs) such as carbon tetrachloride, methylene chloride, trichloroethane (TCA), trichloroethene (TCE) and tetrachloroethene (PCE). In addition to their roles in many industrial processes, CAHs have historically been used for cleaning and degreasing aircraft engines, automobile parts, machinery, electronic components, and clothing.

As late as 1998, the conventional remedial approach for groundwater contaminated with CAHs was “pump and treat”, where the recovered groundwater was treated through air stripping, granular activated carbon adsorption, or ultraviolet oxidation prior to discharge (Nyer, 1998). Pump and treat systems are considered effective for hydraulic control, but do little to actually decrease the CAH concentrations within the dissolved plume. In addition, pump and treat systems typically require many years of operation and operation and maintenance of these systems can be cost prohibitive. These limitations stem from the fact that many contaminants partition preferentially to aquifer solids rather than the groundwater itself, so that vast quantities of groundwater must be removed in order to remove increasingly smaller portions of contaminant mass over the operating time of the system.

ARCADIS was contracted by the NAVFAC in 1998 to conduct a pilot study to evaluate enhanced in-situ biotransformation as a possible remedy for the impacted groundwater. This remedial approach involves the addition of a molasses solution into the impacted groundwater-bearing zones. The molasses solution serves as a supplemental energy source for indigenous microbes and enhances the existing microbial processes occurring within the subsurface. As the energy source is consumed, the existing subsurface environment changes from aerobic to anaerobic, a condition that is more conducive to biodegradation of CAHs.

1.3 SITE CONTACTS

	Name	Company / Agency	Address	Phone
Site Lead	Greg Penland	NAVFAC	2155 Eagle Drive, North Charleston, SC 29406	843-820-5509
Consultant	Rodriguez and David Vance	ARCADIS Geraghty & Miller, Inc.	5608 Parkcrest Drive, Ste. 300, Austin, Texas 78731	512-451-1188
Additional Contacts	Martha Araujo	NFESC	1100 23rd Ave., Port Hueneme, CA 93043	805-982-5270
	Michael Maughon	EFD Southern	2155 Eagle Drive, North Charleston, SC 29406	843-820-7422

2.0 MATRIX DESCRIPTION

2.1 GEOLOGY

According to the Geologic Atlas of Texas, Dallas Sheet, the NWIRP site overlies fluvial terrace deposits consisting of gravel, sand, silt, and clay. Directly beneath these terrace deposits lies the

Cretaceous aged Eagle Ford shale. The shale ranges in thickness from about 200 to 300 feet in the vicinity of the site.

Prior to developing the work plan, available geologic logs of all existing monitoring wells and cone penetration test (CPT) probes completed within a 500-foot radius of Monitoring Well DWP-4-6 were reviewed. These geologic logs and CPT probe logs were prepared by ENSAFE and are reproduced in Appendices A and B of the entitled "*Enhanced In-Situ Biotransformation Pilot Study Report*". Also in Appendix C this final technical report are the geologic logs for the monitoring and injection wells completed in the study area by ARCADIS. The following stratigraphic units for the shallow subsurface study area are presented as follows in descending order: 1) fill material; 2) Pleistocene fluvial deposits; and 3) Upper Cretaceous bedrock (the Eagle Ford Formation). The total thickness of the unconsolidated materials (fill material and Pleistocene deposits) in the study area ranges from about 35 to 45 feet, and the materials thin toward Cotton Wood Bay, located immediately to the south of the NWIRP site.

2.2 HYDROLOGY

In the study area, groundwater occurs at depths ranging from about seven feet below ground surface near Well DWP-4-18 to about 20 feet below ground surface at Well DWP-4-16. Based on previous site investigation data provided by ENSAFE, two distinct water-bearing zones were identified within the unconsolidated materials. These water-bearing zones are referred to as the upper and lower water-bearing zones. The upper water-bearing zone is identified in the ENSAFE monitoring well logs as occurring at a depth of 12 feet below ground surface. The lower waterbearing zone occurs at an estimated depth of 35 feet below ground surface. Part of this study, as described below, was to determine whether these two zones are distinct in the pilot study area, or if the two zones are hydrologically connected. The bedrock appears to act as an aquitard preventing vertical groundwater migration below the lower water-bearing zone.

During the field investigation conducted by ARCADIS, it was determined that there is only one saturated zone upgradient of the study area near Well DWP-4-16, while two saturated zones were encountered in the rest of the study area as determined by field observations during well installations. Based on the stratigraphy observed at Well DWP-4-16 and on pumping test data (discussed later in this report), the upper and lower water-bearing zones appear to be in hydraulic communication. The hydrogeology within the study area is laterally and vertically anisotropic and heterogeneous. The heterogeneity is due to the dynamic fluvial deposition and historical "cut and fill" practices which disturbed the natural stratigraphic sequence in the pilot study area.

A groundwater flow data for the upper water-bearing zone was developed using data provided by ENSAFE. Seepage velocities for longitudinal transects along the groundwater flow path were also provided by ENSAFE. These historical data show that the shallow groundwater flows in a southerly direction across the site. Data gathered by ARCADIS during this investigation, however, show that the hydraulic gradient in the immediate vicinity of the injection wells is much flatter than the surrounding gradients. During some periods, the hydraulic gradient in the immediate vicinity of the injection wells shows a northerly groundwater flow direction. Potentiometric surface maps were developed from data collected throughout the pilot study.

Hydraulic gradient reversals in the study area were not anticipated, and have significantly affected the performance of the pilot study demonstration.

2.3 AQUIFER CHARACTERISTICS

A 24-hour pumping test followed by an eight hour recovery test, was conducted by ARCADIS using injection well DWP-4-IW1 installed in the lower water-bearing zone to determine the hydraulic characteristics of that zone, and to evaluate the potential hydraulic interconnection between the upper and lower water-bearing zones. The data generated from the pumping test and recovery test were used to establish the locations for downgradient monitor wells (DWP-4-DW3, DWP-4-17, DWP-4-18, and DWP-4-DW4). Slug tests were performed in these four new wells to collect additional hydraulic information. Pumping test data for monitoring well DWP-4-11 (provided by ENSAFE) were also used to determine appropriate well spacing. The well locations are shown on Figure 2.

Based on the data collected from the aquifer tests, a range of values for hydraulic conductivity were estimated:

- Upper water-bearing zone 35.7 to 13.5 feet per day
- Lower water-bearing zone 29.0 to 2.2 feet per day
- Upper and lower water-bearing zone (not separated) 6.2 to 1.4 feet per day

The following conclusions were made from the aquifer test data:

- Both the upper and lower water-bearing zones were sufficiently transmissive to support the pilot test.
- There is connectivity between the upper and lower water-bearing zones in the area tested.

The information provided to ARCADIS prior to the implementation of the hydraulic testing program was extensive in the sense of providing site-wide data on a complex site. The spacing of the wells used in the hydraulic testing, however, was too small to yield a valid assessment of local gradient. In addition, the pilot test area data was very limited. In the center of what was estimated to be the pilot study area the gradient was 0.008. For the purposes of the analysis a hydraulic gradient of 0.01 ft/ft and a porosity of 30 percent were assumed. The following groundwater velocities were calculated:

- Upper water-bearing zone 1.2 to 0.45 feet per day.
- Lower water-bearing zone 0.97 to 0.07 feet per day.

The reversals in groundwater direction were not observed until the pilot test commenced with its more rigorous and frequent data collection effort.

2.4 CONTAMINANT CHARACTERIZATION

Volatile Organic Compounds (VOCs) are the only contaminants detected in the groundwater in the pilot study area. Most of the VOCs in the study area are CAHs. The CAHs have been reported in groundwater samples collected from both the upper and lower water-bearing zones. TCE is the most common CAH, reported at a concentration of 10,000 parts per billion (ppb or $\mu\text{g/L}$) in a sample collected from Well DWP-4-6 by ENSAFE in 1997. The majority of the remaining CAHs are TCE daughter products [1,1-dichloroethene (1,1-DCE); 1,2-dichloroethene (1,2-DCE) isomers, and vinyl chloride (VC)]. Prior to beginning the pilot test study, analytical data collected in 1997 by ENSAFE were reviewed by ARCADIS for monitoring wells (collected in 1997) and CPT probes (collected in 1994), within a 500-foot radius of Well DWP-4-6. Isoconcentration maps developed by ENSAFE for TCE, cis-1,2-DCE, 1,1-DCE and vinyl chloride in the upper water-bearing zone were also reviewed. The pilot study injection and monitoring wells were installed near the center of the TCE plume (Figure 2).

3.0 TECHNOLOGY SYSTEM DESCRIPTION

3.1 BACKGROUND AND APPLICATIONS

The groundwater treatment technology used in this pilot study is intended to generate an in-situ reactive zone (IRZ). IRZs are based on the concept of enhancing natural processes in a groundwater system to drive the biogeochemical conditions to a state that is more conducive to degradation of CAHs. This technology is considered an enhanced anaerobic bioremediation technology or as a co-metabolic process as described in the United States Environmental Protection Agency (USEPA) Guidance Document No. 542-B93-005 titled “*Remediation Technologies Screening Matrix and Reference Guide*” and dated 1993.

Often, natural processes are limited in rate or stalled at a site due to one or more of the following conditions:

- Aerobic or oxidizing conditions.
- Weak reducing conditions.
- Deficiency of organic carbon.
- Deficiency of electron acceptors.
- Deficiency of nutrients.
- Stressed bacterial population.

Typically, the most common rate-limiting factor that results in slow degradation of CAHs is a lack of readily available organic carbon at a site. The lack of carbon can result in an oxidation-reduction potential (ORP) condition that is too high for reductive dechlorination to occur. Optimal degradation rates can be achieved when carbon concentrations (as measured by total

organic carbon/total dissolved organic carbon (TOC/DOC) are at least 100 times the organic CAH concentrations. Degradation is often slowed due to the depletion of natural organic carbon in the groundwater and the less than optimal reducing conditions present in the aquifer (greater than -200 millivolts [mV]).

IRZ technology relies on enhancing the biologically-mediated reactions by supplying additional organic carbon as an energy substrate to the groundwater system and driving oxidation-reduction potential (ORP) to a lower, more strongly reduced state. This is accomplished by supplying the groundwater system with a sucrose and carbohydrate source in the form of a mixture of molasses and water. Molasses is a cost-effective, and innocuous amendment for groundwater that is accepted by both state and federal regulatory agencies.

The process by which the IRZ technology thrives is through the indigenous heterotrophic microorganisms that readily degrade the molasses carbohydrates consisting mostly of sucrose. This metabolic degradation process uses available dissolved oxygen in groundwater, thus driving the system to a condition where oxygen is absent or referred to as an anaerobic system, and to a more reduced state. Anaerobic bacteria biodegrade highly chlorinated compounds, but both anaerobic and aerobic bacteria can biodegrade less chlorinated compounds as well. Some of the bacterial community present in the aquifer prior to molasses injection becomes superseded by the bacterial species that adapt to the changed anaerobic aquifer condition and some of the initial types of the bacterial community remain and metabolize the injected molasses to the extent that oxygen recharge permits. In a low oxygen environment, other bacterial communities capable of fermenting molasses sugars develop causing a production of acetate and hydrogen. The reductive dechlorination of PCE under those conditions can be facilitated by sulfate reducers, methanogenic bacteria, or acetogenic species (Loffler, et al, 1999). Dehalogenating organisms compete with other methanogenic, sulfate reducing, iron reducing, manganese reducing or nitrate reducing organisms for the hydrogen (Yang and McCarty, 1998), impacting actual in situ stimulated dehalogenation rates. Under these conditions the methanogens use CO_2 as an electron acceptor and are the most noted metabolic group of anaerobic bacteria responsible for reductive dechlorination, which transforms CAHs into less chlorinated intermediates and finally to CO_2 and water. The breakdown of this process is described below:

Oxygen Reduction Denitrification (Nitrate reduction) \rightarrow Iron and Manganese Reduction
 \rightarrow Sulfate Reduction \rightarrow Methanogenesis (Carbon Dioxide Reduction).

Generally, stronger reducing conditions and the depletion of more thermodynamically favorable electron acceptors, is needed to foster the latter processes in this sequence, such as sulfate reduction and methanogenesis.

In the past several years, it has been determined that some microbes can use the CAH itself as an electron acceptor and source of metabolic energy. In other words, the microbes can use energy released from the breakdown of the CAH to “breathe,” just as energy is used from the alternate electron acceptors when oxygen is not present. These bacteria are termed dehalorespirators and they can degrade some CAHs, such as PCE and TCE directly to ethene, without forming the typical intermediates, such as DCE and vinyl chloride. Conditions favorable to dehalorespiration are similar to that of reductive dechlorination (anaerobic and strongly reducing), so it is difficult

to quantify the relative contribution of each of these processes without expensive and tedious site specific microcosm studies that can take months to years to complete. It is currently unclear if the organisms required for this process have evolved and are present at a minority or a majority of CAH impacted sites. Although cultures of dehalorespiring organisms have been successfully introduced in the field in at least one instance, introduction of microorganisms at field sites is often subject to regulatory barriers. Introduced organisms have also often failed to out-compete indigenous communities and become established. Therefore this pilot study focused on the use of electron donor source (molasses) amendment and indigenous bacteria rather than the use of introduced organisms.

Because a molasses-based reagent isn't directly used to degrade CAHs in the sense of a simple chemical reaction, there are many site-specific factors that greatly affect the efficiency and use of the molasses to stimulate microbial degradation of CAHs. These factors, which make efficiency very difficult to estimate from our commercial full-scale data include the following:

- Amount of CAH mass present at the site is seldom well known, sufficient borings are rarely installed to fully delineate the amount of sorbed material in an aquifer.
- Molasses, or other reagents, is typically used at concentrations significantly exceeding the most efficient possible use because the cost to fully delineate the plume and labor for injection is often more significant.
- Reagent dosage often varies significantly from site to site depending on the concentrations of other electron acceptors such as ferric iron and sulfate.
- Efficiency most likely varies over time at a given site, with the use of molasses probably being more efficient at relatively high concentrations than at relatively low concentrations.
- Reagent dose will vary significantly from site to site, depending on the initial redox condition of the site, with higher redox potentials requiring more reagent.
- The nature of the microbial population (and the kinetics of a growing and adapting microbial population) differs from site to site.

An advantage of establishing an IRZ through the injection of an organic carbon substrate is the ability to treat mass that is adsorbed to the subsurface soil matrix. More traditional groundwater treatment technologies rely on physical flushing of this mass from the aquifer, which requires multiple pore volumes of the aquifer to be removed over decades, often with only a small percentage of the total mass removed.

The ability of IRZ technology to treat adsorbed mass is due to several factors:

- In a carbon-rich aqueous environment, hydrophobic contaminants will tend to partition from the soil matrix into the aqueous environment.

- A flourishing microbial community produces natural surfactants (consisting of carbohydrates and lipids), which aid in desorbing mass from the soil matrix.

Once the desired aquifer microbiology has been attained, carefully timed subsequent additions of molasses are used to support the altered aquifer microbiology until remediation is complete. This maintenance dosing should occur at planned, regular intervals to avoid fluctuations in the size of various metabolic components of the bacterial community. Unnecessarily irregular molasses dosing during the maintenance portion of a remediation program can complicate the complex biochemical chain through which energy substrates cycle in the IRZ. In addition, inconsistent dosing can complicate efforts to interpret aquifer microbiology using biogeochemical-monitoring data. The IRZ performance is measured by monitoring target contaminants and relative concentrations of degradation products as well as other indicator parameters in groundwater such as dissolved oxygen, ORP and changes in concentrations of electron acceptors within the treatment area.

3.2 ADVANTAGES AND LIMITATIONS

The IRZ technology has numerous advantages compared to other remediation methods. The technology is based on modification of the geochemical conditions in a contaminated aquifer to enhance or control the rate of biochemical reactions in the treated zone. The goal is to gain increased control of the aquifer environment, and to increase the speed of contaminant mass removal or alteration.

The primary advantages for IRZ include the following:

- *In-situ* processes eliminates the need for transferring contaminant mass to other media (such as groundwater pumping and subsequent treatment with air stripping)
- IRZ processes have a potential application to a wide spectrum of contaminants such as:
 - chlorinated aliphatic hydrocarbons;
 - chlorinated cyclic hydrocarbons;
 - chlorinated pesticides;
 - metal precipitation; and other halogenated organic contaminants.
- No waste is generated as a result of the treatment process itself.
- Uses innocuous, off-the-shelf electron donor sources.
- Biologically mediated reactions are driven by indigenous micro flora.
- Flexible application allows a spectrum of contaminant mass treatment options from passive/containment barrier applications to aggressive source area applications.
- Promotes reduction of residual contaminant mass through desorption and disruption of the contaminant phase equilibrium.

- Enhances natural attenuation processes.
- Applicable to various geological settings and aquifer conditions.
- Electron donor source is highly soluble and can move through both diffusive and advective processes into difficult lithologies such as fractured bedrock.
- Can be designed with flexible operation approaches from automated systems to manual bulk application.
- Increased rates of mass removal coupled with simple operation requirements reduce long-term operations and maintenance costs.
- Can be used in tandem with current remediation systems to optimize performance.
- Can be designed with minimal site and facility operation disturbance.

All *in-situ* remediation technologies have an inherent limitation associated with subsurface conditions. The geology in which the technology is being applied will exert considerable control over remediation efficacy. Mass transfer and distribution rates in porous media are the primary factors influencing the efficiency of the IRZ technology. Limitations to the application of the IRZ technology included the following:

- Excessive depth of contamination may result in prohibitively expensive injection Costs
- Low permeability soils require a larger number of injection wells
- High permeability soils require an excessive amount of reactant to establish a reducing environment due to dilution and oxygen recharge.
- Heterogeneous lithology, which incorporates preferential flow paths, can limit the distribution of the injected molasses.
- Limited porosity of contaminated media such as fractured bedrock minimizes the propagation in the treated area.
- Very large dissolved plumes require an excessive number of injection wells.
- Biological fouling of injection wells or aquifer can result from reagent injection.
- High frequency applications may be required in response to the labile nature of molasses, increasing operations and maintenance costs.

- Competition from other naturally occurring terminal electron acceptors, such as sulfate, reduces remediation efficiency.
- Potential production of excessive quantities of reduced gasses, such as methane.
- Longer lag times prior to effective treatment are noted in low concentration plumes.
- Production of noxious organic compounds containing reduced sulfur or nitrogen.
- Progressively inefficient dechlorination of intermediate products.
- Incomplete reaction and production of intermediate products such as vinyl chloride.
- Brackish aquifers can pose problematic microbial ecology.
- Limited effects on free-phase or large adsorbed/residual contaminant mass.
- Rebound of dissolved-phase contaminant mass resulting from equilibrium with residual-phase contaminant mass.
- Desorption effects associated with the production of natural surfactants can necessitate a sizable downgradient area free of receptors.
- Inhibitory/toxic effect of high CAH concentrations that are associated with source zones.
- Fermentation effects of excessive molasses loading can create conditions conducive to formation of aldehydes, ketones, and mercaptans.

These potential limitations are general guidelines to be considered when evaluating potential sites for IRZ treatment. Site-specific constraints should be considered for all remediation technology options. The most effective approach includes development of a remediation strategy to match technology options with site conditions.

The limitations associated with site conditions such as lithology, hydrogeology, geochemistry, and access will also affect other *in-situ* technologies. Competing remediation technologies using biological systems will have similar limitations, and chemical or physical-based technologies are often influenced to a greater extent by the same constraints.

3.3 SYSTEM DESCRIPTION AND OPERATION

3.3.1 Timeline

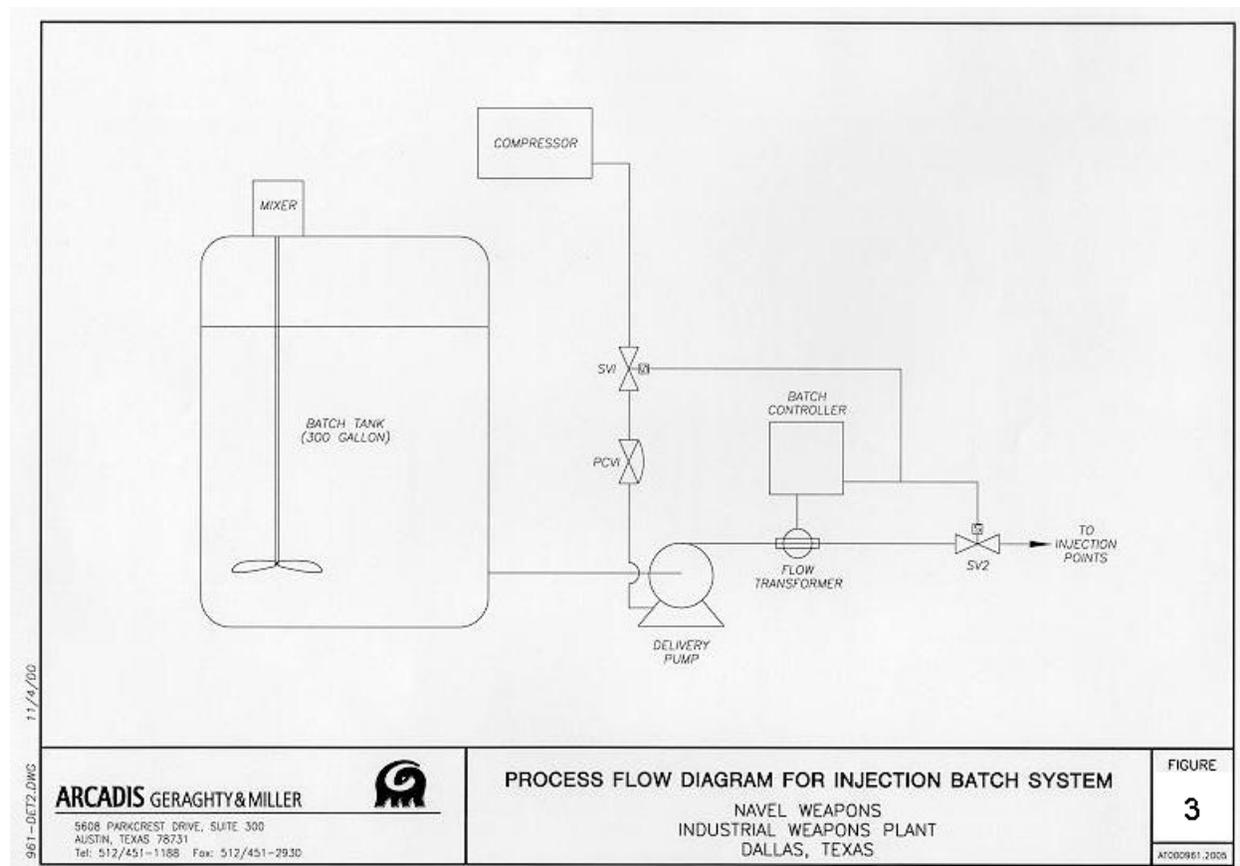
Table 2. shows the actual timeline used for the pilot study. The pilot study was originally scheduled to conclude about six months earlier than shown on this table. However, the complex hydrogeology at the site resulted in slower than anticipated distribution of the aquifer amendments. With the approval of the NAVFAC, the schedule was extended to allow extra time for the amendments to be dispersed within the water-bearing zones.

TABLE 2. TIMELINE

Date	Activity
Oct-98	Kick off meeting.
Nov-15-98	Conceptual design for expansion of the remediation system was prepared and submitted.
Feb-23-99	Work Plan, Sampling & Analysis Plan, & Quality Assurance Project Plan were submitted to TNRCC.
March-4-99	Injection permits were issued.
May-31-99	Health & Safety Plan was submitted.
June-1-99	Two injection wells and two monitoring wells were installed.
June-14-99	Pump Test, Recovery Test, and Slug Tests.
July-1-99	Four additional monitoring wells were installed.
July-20-99	Groundwater samples were collected for field parameters and for a full suite of lab analyses.
Aug through Sept 1999	The molasses injection system, including the system building, electrical supply, solution tanks, injection pumps, and piping and control system, was installed.
Sept through Nov-99	September through November 1999 - Nutrient solution was injected. The shallow injection well received 564 gallons of injection solution at an average concentration of 14.7% molasses, while the deep injection well received 139 gallons at an average concentration of 11.8% molasses.
Sept-22-99	Field parameters were measured.
Sept-28-99	Field parameters were measured.
Oct-5-99	Field parameters were measured.
Oct-12-99	Field parameters were measured.
Oct-19-99	Field parameters were measured.
Oct-26-99	Field parameters were measured.
Nov-9-99	Field parameters were measured.
Dec-7-99	Field parameters were measured and TOC samples were collected from the injection wells.
Jan-25-00	Field parameters were measured.
Feb-22-00	Field parameters were measured and TOC samples were collected from the injection wells.
March-1-00	A separate injection event was conducted. The shallow injection well received 1800 gallons of injection solution at a concentration of 2% molasses, while the deep injection well received 325 gallons at a concentration of 2% molasses.
March-21-00	Field parameters were measured.
April-18-00	Field parameters were measured and TOC samples were collected from the injection wells.
May-17-00	Groundwater samples were collected for field parameters and for a full suite of lab analyses.
June-19-00	Field parameters were measured.
July-21-00	Field parameters were measured.
Aug-16-00	A separate injection event was conducted. The shallow injection well received 1800 gallons of injection solution at a concentration of 2% molasses, while the deep injection well received 325 gallons at a concentration of 2% molasses.
Aug-17-00	Field parameters were measured.
Sept-18-00	Groundwater samples were collected for field parameters and for a full suite of lab analyses.

3.3.2 System Description

The pilot system used at this site consisted of two injection wells [one screened in the upper water-bearing zone (DWP-4-IW1) and one screened in the lower waterbearing zone (DWP-4-IDW1)], one upgradient monitoring well (DWP-4-16), three downgradient monitoring wells screened in the upper water-bearing zone (DWP-4-6, DWP-4-17, and DWP-4-18) and three downgradient monitoring wells screened in the lower water-bearing zone (DWP-4-DW1, DWP-4-DW3, and DWP-4-DW4). As previously discussed, there were no distinct upper and lower water-bearing zones encountered upgradient of the pilot study area. Therefore, only one upgradient monitoring well was installed (DWP-4-16). Groundwater sampling equipment used for collection of samples from these wells included a peristaltic pump and polyethylene tubing, the YSI 600DM multiprobe and a water-level meter. The injection equipment included two 300-gallon polyethylene mixing tanks equipped with propeller type mixers, a pneumatic pump and controller, an automatic timer and tubing running from the tanks to the injection wells. With the exception of the tubing, the equipment was stored in a small warehouse. A process flow diagram for the system is provided as Figure 3.



The IRZ technology did not require substantial customization of injection components. Local resources for drilling and construction contractors were sufficient for the delivery system, as were local suppliers for the molasses.

3.3.3 System Operation

The implementation of an IRZ is a dynamic process that requires a detailed understanding of the site geochemistry and hydrogeologic conditions both before and as a result of the pilot program itself. The IRZ can be successful when there is considerable process monitoring during the initial deployment of the pilot study, which allows for adjustment of reagent deliverability (strength and frequency). TOC loading and induced gradients must be reviewed early in the pilot process to allow delivery rates to be increased (for greater spreading and greater TOC levels within the treatment area) or reduced (if pH levels drop too quickly). Similarly, the effects of reagent injections must be reviewed in context of how the addition of aqueous solutions effect hydraulic gradients (i.e. mounding) and flow directions.

The overall treatment system was reliable and easy to operate from one injection event to the next. The types of equipment being employed (transfer pumps, tanks, mixers, and controls) are commonly used for similar applications and in our experience can be expected to perform as designed and intended for the duration of the demonstration. No routine preventative maintenance was required for any equipment, with exception of the data logger for the YSI 600DM multiprobe. This instrument was repaired and did not affect the overall collection of data. This work was performed at planned intervals, according to manufacturer's recommendations and did not affect system reliability.

During the demonstration, an injection log was kept to record the solution strength, molasses and water volumes used, and the volume of dilute solution injected into each injection well. The log was used to record any other relevant observations. A copy of this log is shown as Table 3. The concentration and volume of molasses injection solutions were determined by the volume of water-bearing zone being treated, with the goal of attaining a minimum carbon concentration of approximately 200 mg/L. The increases in the volume of injected solutions in the latter stages of the test were to evaluate the hydrodynamic effects of creating small groundwater mounds around the injection wells. The only foreseeable non-routine maintenance for the project was injection well and/or injection diffuser tube rehabilitation. Fortunately, there was no biological fouling development in the injection wells or related piping. There were, however, problems encountered with mold forming on the surface of the molasses solution inside the mixing tanks.

Originally, the injection system was designed and installed to conduct unmanned, automated injections at several times during each week at very low volumes. After several weeks of operation, mold colonies developed and flourished on the surface of the molasses solution. Attempts were made to prohibit this occurrence such as adding food preservative to the molasses solution in an attempt to reduce the mold growth and an air conditioner was installed to control the climate within the warehouse. The mold growth was reduced, but not eliminated. The solution to this event was to switch from automated injection events to manual events, follow by thorough cleaning of the molasses mixing tanks.

TABLE 3. MOLASSES INJECTION RECORD

Deep Well		
Date	Percent Molasses Solution	Quantity (gal)
9/10/99	20%	20
9/14/99	20%	17
9/23/99	10%	6.6
9/25/99	10%	2
9/28/99	10%	2
9/30/99	10%	2
10/2/99	10%	2
10/5/99	10%	2
10/7/99	10%	2
10/9/99	10%	2
10/12/99	10%	2
10/12/99	10%	35
10/14/99	10%	4
10/16/99	10%	4
10/19/99	10%	4
10/21/99	10%	4
10/23/99	10%	4
10/26/99	10%	4
10/26/99	10%	0
10/28/99	10%	4
10/30/99	10%	4
11/2/99	10%	4
11/4/99	10%	4
11/6/99	10%	4
3/22/00	2%	325
8/16/00	2%	325

Total Solution Gallons Injected 788.6

Bold - Manual Injection

Unbold - Automated Injection

Shallow Well		
Date	Percent Molasses Solution	Quantity (gal)
9/10/99	20%	50
9/14/99	20%	52
9/23/99	10%	13.6
9/25/99	10%	13
9/28/99	10%	13
9/30/99	10%	13
10/2/99	10%	13
10/5/99	10%	13
10/7/99	10%	13
10/9/99	10%	13
10/12/99	10%	13
10/12/99	10%	40
10/14/99	10%	26
10/16/99	10%	26
10/19/99	10%	26
10/21/99	10%	26
10/23/99	10%	26
10/26/99	10%	26
10/26/99	10%	18
10/28/99	10%	26
10/30/99	10%	26
11/2/99	10%	26
11/4/99	10%	26
11/6/99	10%	26
3/22/00	2%	1800
8/17/00	2%	1800

Total Solution Gallons Injected 4163.6

As outlined previously, the reagent solution added to the subsurface consisted of a dilute solution of potable water and food-grade molasses. Based on ARCADIS field-testing and full-scale experience in implementing this technology at similar sites, the proposed dilute molasses feed solution initially consisted of a 5:1 mixture (by volume) of potable water and raw blackstrap molasses (i.e., one gallon of blackstrap molasses for every five gallons of potable water). Typical blackstrap molasses contains sucrose, reducing sugars, organic non-sugars, and water, all of which are fully soluble in water. The total consumable carbohydrate concentration in the molasses is expected to be approximately 60 percent by weight.

After the initial manual injections of the 5:1 mixture, the concentration was modified to a 10:1 mixture (i.e., one gallon of molasses for every ten gallons of potable water). The final two manual injections consisted of a 50:1 mixture of water to molasses. These changes were made partially in response to the successful creation of low redox conditions in the injection wells. In

addition, it became apparent that the groundwater gradients in the test area were very low and in some cases gradients were reversing. Mix concentrations were decreased so that the level of carbon loading could remain the same while increased fluid volumes might induce local groundwater mounding around the injection wells and increase the gradient between the injection wells and the nearby monitoring wells.

The composition, volume, and frequency of injection of the molasses solution varied throughout the demonstration period based on the field measurements made in the observation wells and the analytical results gathered during the initial rounds of groundwater sampling. Variations were governed by field parameter measurements and a review of the entire data set in light of professional judgment and experience at other sites.

The system performance was monitored monthly by collecting groundwater samples that were analyzed in the field for pH, conductivity, temperature, ORP, DO, ferrous iron, sulfate, and hydrogen sulfide. In addition, groundwater samples were collected periodically for laboratory analysis of VOCs and an extensive suite of geochemical parameters.

Baseline samples were collected in July 1999 prior to installing the treatment system, in May 2000 and again in September 2000. VOCs samples were also collected in October 1999. Consistent equipment was used for each sampling event so that variability related to field measurements was eliminated. Similarly, consistent low flow rates were assigned for each sampling event. Dedicated tubing remained in each well, and was permanently marked so that samples were consistently collected from the same depth in each well.

All field monitoring was conducted at regularly spaced intervals and before initiating an injection event, when possible. This eliminated temporal variations in water elevations and chemistry that could be present immediately following an injection event. Efforts were made to conduct field monitoring events during fair weather conditions to reduce the risk of moisture-induced electronic circuitry anomalies. All field instruments were calibrated at the beginning of each field day.

Based on the rate of groundwater flow and on the observation well locations in the study area, ARCADIS Geraghty & Miller anticipated that evidence of reducing conditions would be observed in the closest monitoring wells within several months of the initial injections. However, little evidence of reducing conditions was observed in the monitoring wells during the first half of the pilot study. As a result, the duration of the pilot study was extended to accommodate the actual site conditions (i.e., groundwater flow reversal, anisotropic heterogeneous vertical and horizontal lithology, etc.). All changes to the pilot study schedule were approved by the NAVFAC.

3.4 OPERATING PARAMETERS AFFECTING TECHNOLOGY COST OR PERFORMANCE

The predominant factors affecting the performance of the IRZ technology for CAHs are biological, hydrogeological, and chemical in nature. These factors are discussed in detail in the following paragraphs.

3.4.1 Biological Factors

IRZ technology as implemented for CAH remediation relies on multifaceted indigenous bacterial communities in order to function. Successful remediation of CAHs relies on aerobic bacteria to degrade the sugars injected into the reactive zone while consuming oxygen at a rate sufficient to outstrip recharge. This generation of an anaerobic condition is the first stage in the creation of the reactive zone. The second stage in the creation of certain reactive zones is the fermentation of molasses sugars. Fermentation is an integral part of global carbon cycling in which complex carbon molecules are incompletely oxidized to form organic acids, alcohols, and hydrogen (Chapelle, 1993). These fermentation waste products serve as substrates for bacteria like methanogens and sulfate reducing bacteria (SRB) that are involved in the terminal cycling of carbon from simple molecules that are dissolved in groundwater back into the atmosphere in the form of carbon dioxide. The third and final stage in the development of some IRZs is the proliferation of bacteria capable of using molasses fermentation waste products as substrates. Both methanogens and SRBs play important roles in the IRZ technology, depending on the nature of the contaminant being treated.

Perhaps the most complex IRZs are those intended to remediate CAHs. The first stage of reactive zone creation, driving the zone anaerobic, is shared by all IRZ projects. Following the establishment of an anaerobic zone, the primary mode of sugar degradation shifts from aerobic bacterial metabolism to sugar fermentation. Fermentation of molasses sugars produces low molecular weight organic acids and hydrogen as waste products of bacterial fermentation. During transition into the third stage of IRZ formation, the availability of these waste products affects the development of the bacterial community that actually reductively dehalogenates the CAHs. Methanogenic bacteria are anaerobic, require low molecular weight organic acids/hydrogen as substrates, and can reductively dechlorinate CAHs. Their distribution and relative presence at a CAH-impacted site is another factor that affects the length of the remedial interval and the ultimate success of each CAH IRZ remediation project.

The consumption of reagents, redox buffering capacity, and time required to establish a reductively dehalogenating IRZ can also be impacted by the iron and manganese biogeochemistry of a site. If ferric iron is readily available it will be consumed and converted to ferrous iron by the iron reducing bacterial consortia. Some reductive dehalogenation or anaerobic oxidation of DCE or vinyl chloride (Bradley and Chapelle, 1997) may take place under these conditions, but the processes are not likely to be optimum with regards to the dehalogenation of TCE. The evidence of ferric iron reduction is the production of ferrous iron. Only a slight increase in ferrous iron concentrations was seen in DWP-4-6 (the 22 foot shallow monitor well). It is possible that ferric iron reduction with the production of ferrous iron did take place, but the ferrous iron reacted with hydrogen sulfide and was taken out of the soluble system. However, there were no significant levels of hydrogen sulfide detected in any of the monitor wells or injection wells during the pilot test. In addition, the use of ferric iron takes place using bio-available iron. The ability to use mineralized iron varies from species to species, but in general the amount of bio-utilized iron is orders of magnitude less than the iron actually present (Hacherl, et al, 2001). The average abundance of iron in surface sediments and rocks is near 5%. In the experience of ARCADIS it is relatively rare to see ferrous iron concentrations greater than 10 mg/L in an IRZ.

Hydrogen concentrations were monitored during the test. Due to the generation of large volumes of gas (carbon dioxide and methane) in the injection wells it was not possible to sample the injection wells for hydrogen using approved bubble strip methodology. In the monitor wells there was no distinct trend in hydrogen concentrations that cannot be separated from potential sampling bias (i.e. during the last sampling event the hydrogen concentrations were significantly lower in all of the wells sampled). There did appear to be a trend difference between the deep and shallow water-bearing units, with the deeper unit having hydrogen concentrations approximately an order of magnitude lower than the shallow unit. With regards to the CVOCs; in the shallow unit TCE was reduced from around 4,000 µg/L to 323 µg/L, while the 1st daughter product (DCE) increased from 790 µg/L to 1910 µg/L. The vinyl chloride went from ND to 1070 µg/L. In the deeper unit little attenuation of the TCE was seen (from the 3,000 to 4,000 µg/L range to 2,300 µg/L). But the production DCE daughter product was almost as intense as that seen in the shallow unit (from ND to 2,370 µg/L), vinyl chloride production was much less at 77.1 µg/L. The data available is not sufficient to correlate the hydrogen concentration to the observed dechlorination trends seen in both units at the end of the test.

Distribution and concentrations of bacteria affect IRZ performance. Methods to characterize site-specific bacterial communities in a conclusive and inexpensive manner are generally not available. Variations in bacterial community diversity and size remain a significant performance issue for IRZ implementation. To date, the absence of an appropriate microbial community has rarely prevented successful treatment at the 40 sites at which ARCADIS has implemented this technology, thus this issue can generally be left to the site-specific pilot study for final verification, since it most often impacts the time line, not the ultimate success of the IRZ approach. The results of the pilot study indicate that there is an indigenous microbial community that is diverse enough to support an IRZ for reductive dehalogenation.

3.4.2 Hydrogeological Factors

Successful implementation of the IRZ technology for CAHs depends on controlled subsurface distribution of molasses solution. At one extreme, geological/hydrogeological site characteristics can make IRZ impractical when groundwater velocity is too slow. The groundwater velocities were slow and exhibited reversals in the treatment area during the course of the pilot test.

A typical IRZ system relies on native groundwater flow to imprint the IRZ into the treated water-bearing zone downgradient of the injection wells. The economic power of this approach is that it obviates the costs associated with a conventional pump and treat system. However, extremely slow groundwater velocities impact the IRZ technology in two ways. First, it impacts the time that it takes for an IRZ to develop from an injection point. Trying to achieve more rapid time frames can involve the installation of monitor well arrays with much closer spacing. Secondly, the reagents injected are biologically active. They typically are consumed at a rate that essentially follows first order decay kinetics. With an increase time caused by slower groundwater flow rates, the soluble carbon substrate reagents are consumed in relatively short distances as well. The latter effect can be overcome by the use of carbon substrates that have longer decay half lives.

Factors contributing to this hydrogeologic behavior included unusual drought conditions in the area, and extreme vertical and horizontal heterogeneity within the water-bearing zones. Recharge was also impacted by the area having an extremely high concrete cover, inhibiting local recharge. The pilot area is also located in a zone in which there are transitions of the three water-bearing zones. In the background well only one transmissive zone is seen. In the pilot area two, rather than 3 zones are observed. During operation of the pilot study the groundwater gradients were lower than that estimated after the completion of the pumping test. Absolute groundwater velocities were further slowed by observed reversals of groundwater flow directions in the treatment area. These slow absolute groundwater velocities (i.e. < 50 to 100 feet/year) associated with very “tight” geology would necessitate a larger number of injection wells when applied on large plumes. Depending on depth to the water table, plume size, and what means of well installation are practical, installation of a suitable number of injection wells can become economically infeasible at sites where injection wells must be spaced very closely. At the end of the pilot study larger volumes of water were injected to stimulate mounding and higher groundwater flow rates locally. The subsequent changes observed in the nearest monitor wells after the mounding event, indicate that mounding was successful in enhancing groundwater velocities locally.

3.4.3 Chemical Factors

The chemistry of groundwater is highly variable and known to be partially determined by specific bacterial communities. Thus scientists have often used groundwater chemistry to provide indications of the dominant bacterial metabolic processes and bacterial ecology in aquifer systems. Groundwater chemistry can be indicative of bacterial metabolic functions as well as acting as an agent of selection that shapes bacterial community diversity and size.

In its role as an indicator of bacterial metabolism, interpretation of groundwater chemistry is an integral part of the application of the IRZ technology for CAHs. Results of sequential chemical analyses performed on groundwater samples reveal changes in the structure of bacterial communities within the reactive zone resulting in potential changes in the quantity and timing of subsequent molasses injections. Equally important, existing groundwater chemistry, both prior to and following the introduction of CAH, plays an important role in determining the diversity and size of the bacterial community present prior to molasses injection. The size and diversity of the indigenous bacterial community is possibly the single most important variable in determining the performance of the IRZ technology.

Since this is a biologically oriented technology, chemical properties that affect the technology’s biological drivers are important considerations. Groundwater pH is as an agent of biological selection both prior to and after the spread of the contaminating chemical(s). In general, pH values ranging from 4 s.u. to 8 s.u. are acceptable for the application of biological remedies. All pH values for this demonstration fell within this range with exception to Well DWP-4-DW3. This monitor well produced pH values as high as 12 s.u. when sampling was initiated. After purging for an extended period, the pH in this well dropped to an acceptable level between 7 s.u. and 8 s.u.. The high pH in Well DWP-4-DW3 was probably the result of grout contamination and not indicative of groundwater conditions in the area. Due to the nature of the end products of bacterial molasses fermentation, the IRZ demonstration experienced a decrease in pH during

system operation. This pH decreased to a range of 4 s.u. to 5 s.u. within the injection wells. After injection, both injection wells demonstrated a slow rise in pH.

Sulfate, whether injected or already present in the water-bearing zones, often needs to be reduced to achieve methanogenic conditions. However, the organic carbon provided in the molasses was sufficiently high to overwhelm the sulfate load. Generation of hydrogen sulfide is a problem in certain applications, including those where there is a direct route between the reactive zones and receptors. Generation of other reduced sulfur compounds, such as thiols (also known as mercaptans), is most likely to occur where the hydrogeology is unfavorable for dispersion due to low permeability or shallow gradient leading to fermentative conditions. Molasses that is somewhat lower in sulfate (although the amount in all grades is relatively low) can be used in those circumstances at a cost somewhat higher than that of our typically used blackstrap molasses. The molasses used for this demonstration was edible blackstrap containing about 3,200 parts per million sulfate at a cost of about \$2 per gallon. During the course of the pilot study there were no significant changes in sulfate concentrations. Background sulfate was around 200 mg/L the injection and monitor wells remained in the 200 to 100 mg/L sulfate range over the course of the pilot test. The trend with time was for a slight decrease in sulfate concentrations in the shallow water-bearing unit. Little to no sulfide was detected during the pilot study.

4.0 TECHNOLOGY SYSTEM PERFORMANCE

4.1 CLEANUP GOALS/STANDARDS

In the state of Texas, health-based standards published under the Texas Natural Resource Conservation Commission's Texas Risk Reduction Program are generally used as ideal cleanup goal for impacted media including groundwater. However, at many sites involving large plumes of dissolved chlorinated solvents, the Texas Natural Resource Conservation Commission (TNRCC) acknowledges that health-based standards cannot be achieved within a reasonable timeframe. As a result, the TNRCC will allow higher concentrations of the contaminants to remain in the subsurface as long as engineering and/or institutional controls are used to eliminate human or ecological exposure to the impacted media, and the plume is not allowed to migrate or grow beyond the boundaries of a predetermined plume management zone. Under these conditions, monitored natural attenuation (MNA) can be used to manage the plume, even though contaminant concentrations in the groundwater may exceed the health-based standards. In many instances, plume stability cannot be achieved without some form of active remediation.

No cleanup goals were established for this pilot study. However, the ultimate goal of any full-scale system implemented at this site would be to reduce contaminant concentrations to the extent practical in order to stabilize plume growth so that MNA could eventually be used to manage the plume.

4.2 PERFORMANCE DATA

Throughout the duration of the pilot study, field and analytical parameters were collected to monitor the progress of the pilot study. The samples were collected following the schedule set in the Sampling and Analysis Plan. The samples were collected in laboratory supplied sample

containers, properly preserved and submitted to the laboratories under appropriate chain-of-custody procedures. Permanent gas samples were submitted to Microseeps laboratory for analysis, while all other samples were submitted to Gulf Coast Analytical laboratory. A detailed discussion of observations made for each well is provided below.

4.2.1 Analytical Data for the Lower Water-Bearing Zone

As previously discussed, based on the boring logs ARCADIS determined that there is only one saturated zone upgradient of the injection wells. Therefore, Well DWP-4-16 represents background conditions for both the upper and lower water-bearing zones. TCE concentrations in Well DWP-4-16 fluctuated slightly during the pilot study. Baseline sampling results from this well indicated a TCE concentration of 3850 µg/L, while the final sample event indicated a concentration of 3070 µg/L. Similar fluctuations were observed in the cis-1,2-DCE concentrations. The baseline-sampling event indicated a cis-1,2-DCE concentration of 1920 µg/L, while the final sampling event indicated a concentration of 1440 µg/L. The geochemical parameters measured in samples from Well DWP-4-16 remained generally consistent throughout the study. This is particularly true for parameters that do not significantly engage in biological processes, chloride and TDS, and to a lesser degree (with regards to biological activity) the alkalinity. Based on the data collected from Well DWP-4-16, it represents an appropriate background well for comparison with the monitoring wells within the study area.

Well DWP-4-IDW1 is the injection well for the lower water-bearing zone. Prior to injection of molasses, analytical results indicated a TCE concentration in Well DWP- 4- IDW1 of 26.5 (µg/L). The cis-1,2-DCE concentrations in this well prior to molasses injection were less than 5 µg/L. Analytical results show minor fluctuations in the concentrations of these two compounds over time. The final analytical results from the September 2000 sampling event indicated concentrations of TCE and cis- 1,2-DCE of less than 100 µg/L, with an elevated detection limit. Methyl ethyl ketone (MEK) and acetone were detected at concentrations of 1810 µg/L and 479 (J) µg/L, respectively, during the final sampling event [“J” values are analytical values estimated by the laboratory, and are reported below the detection limit]. Because of elevated detection limits of VOCs during the final sampling event, it is difficult to evaluate trends in the VOC concentrations in this injection well. However, the presence of MEK and acetone during the final sampling event suggest that some of the molasses solution affected the lower water-bearing zone in this area. The production of ketones is a process seen in almost all molasses stimulated IRZ systems that ARCADIS has implemented (over 100). These ketone products are subsequently rapidly consumed by the bacterial consortia. In addition, significant increases in some of the biogeochemical parameters were observed. Total iron concentrations increased from 0.128 milligrams per liter (mg/L) during the baseline-sampling event to 119 mg/L during the final sampling event. In this case the iron is most likely from the injected molasses. It is almost exclusively in the ferrous form, therefore not available for further biogenic processing. In the presence of the molasses solution the soluble carbon concentration is orders of magnitude higher than that of the iron, further dampening any influence that the iron redox chemistry may have had on overall redox processes. Chemical Oxygen Demand (COD), Dissolved Organic Carbon (DOC), ferrous iron, and total alkalinity, dissolved solids, organic carbon (TOC) showed similar increases. These increases provide evidence that the treatment system caused positive effects on the geochemical environment in the subsurface near the injection point. Some parameters were

particularly high in this well during the May 2000 sampling event. This is likely due to stagnant groundwater flow conditions. The deep water-bearing zone underwent a reversal in flow direction between March 2000 and June 2000. The methane concentration is reported at 95.3 mg/L, which is significantly above the solubility of methane in water of approximately 24 mg/L. However, due to the stagnant conditions the sampled groundwater was supersaturated (off-gas bubbles are frequently observed when mature injection wells are sampled) and the sample was collected using the bubble strip method allowing for a higher than solubility value.

Well DWP-4-DW3 is screened in the lower water-bearing zone and located 11 feet downgradient from the injection point. At the start of the pilot test in July, 1999 the TCE concentration was 2,770 µg/L. In October 1999 the TCE concentration had decreased to 1,670 µg/L, in May, 2000 increased to 4,650 µg/L, and decreased again to 2,300 µg/L in June, 2000 µg/L at the end of the pilot test. This pattern is very common in IRZ's and other biological remediation systems as well. It is due to the production of biosurfactants as the indigenous bacterial populations increase. Biosurfactants are used by bacteria to facilitate the solubility of carbon sources for transport through their cell walls. In remediation systems these extracellular biosurfactants serve to release hydrocarbons that have adsorbed to the mineral matrix, thus creating a brief pulse of increased soluble hydrocarbon concentration. During the same period, cis-1,2-DCE concentrations in this well prior increased from less than 250 µg/L to 2370 µg/L. Methane and ethylene also show increases between the initial and final sampling events for this monitor well. Results from this well indicate significant positive effects from the treatment program. Although, it appears that this data is reflective of the transport of IRZ treated groundwater to the monitor well, not the actual stimulation of an IRZ in the well.

Well DWP-4-DW1 is screened in the lower water-bearing zone and located 22 feet downgradient from the injection point. Results from this well did not show the same favorable trends that were observed in Well DWP-3-DW3. Prior to injection of molasses, analytical results from Well DWP-4-DW1 indicated a TCE concentrations of 3170 µg/L. Results from the final sampling event indicated TCE a concentrations of 4450 µg/L. Cis-1,2-DCE concentrations in this well were 1020 µg/L during the baseline sampling event and 354 µg/L during the final sampling event. There were no significant trends observed in the geochemical results from this well.

Well DWP-4-DW4 is screened in the lower water-bearing zone and located 45 feet downgradient from the injection point. Again, results from this well did not show the same favorable trends that were observed in Well DWP-3-DW3. TCE concentrations in samples from this well were 1020 µg/L during the baseline-sampling event and 2150 µg/L during the final sampling event. 1,2-Dichloroethane (DCA) concentrations were 73.7 µg/L during the baseline sampling event and 72 µg/L (J) during the final sampling event. Cis-1,2-DCE concentrations were 56.5 µg/L during the baseline-sampling event and 192 µg/L during the final sampling event. There were no significant trends observed in the geochemical results from this well.

4.2.2 Analytical Data for the Upper Water-Bearing Zone

Well DWP-4-IW1 is the injection well for the upper water-bearing zone. Between the baseline-sampling event in July 1999 and the final sampling event in September 2000, TCE concentrations in the samples collected from the injection well decreased dramatically from 5300

to 6.49 (J) $\mu\text{g/L}$. During the same time period, concentrations of cis-1,2-DCE in samples from the injection well decreased from 2070 to 5.88 (J) $\mu\text{g/L}$. The final analytical results also indicated MEK at a concentration of 967 $\mu\text{g/L}$ and acetone at a concentration of 319 $\mu\text{g/L}$. Total iron concentrations increased from 0.444 to 218 mg/L between the baseline-sampling event and the final sampling event. Dissolved iron, COD, DOC, ferrous iron, TOC, total alkalinity and dissolved solids indicated similar increases. These results provide evidence that the treatment system caused significant positive effects on the geochemical environment in the subsurface near the injection point.

Well DWP-4-6 is screened in the upper water-bearing zone and located 22 feet downgradient from the injection point. This monitoring well was installed by ENSAFE. Between the baseline-sampling event and the final sampling event, TCE concentrations in samples from this well decreased significantly from 4110 to 323 $\mu\text{g/L}$. Cis-1,2-DCE concentrations increased from 790 to 1910 $\mu\text{g/L}$ during the same time period. Vinyl chloride, while not detected during the baseline-sampling event, was present during the final sampling event at a concentration of 1070 $\mu\text{g/L}$. Methane and ethylene concentrations increased between the baseline and final sampling events, as did several of the geochemical parameters. Total iron increased from 0.069 to 2.17 mg/L . Dissolved iron, ferrous iron, COD, DOC, TOC, and total alkalinity showed similar increases. The decrease in TCE concentrations coupled with the increase in daughter products indicates significant degradation has occurred in the subsurface near this well. In addition, the increases in the geochemical parameters confirm that the subsurface conditions have been altered to favor degradation of the contaminants.

Well DWP-4-17 is screened in the upper water-bearing zone and located 45 feet downgradient from the injection point. Between the baseline sampling event and the final sampling event, TCE concentrations in samples from this well decreased from 3310 to 345 $\mu\text{g/L}$. Cis-1,2-DCE concentrations increased from 1990 to 3000 $\mu\text{g/L}$ during the same time period. Vinyl chloride, while not detected during the baseline sampling event, was present during the final sampling event at a concentration of 663 $\mu\text{g/L}$. Similar to Well DWP-4-6, the decrease in TCE concentrations coupled with the increase in daughter products indicates significant degradation has occurred in the subsurface near this well. Total iron, ferrous iron and total organic carbon concentrations in this well showed moderate increases during the pilot study.

Well DWP-4-18 is screened in the upper water-bearing zone and located 90 feet downgradient from the injection point. TCE concentrations in samples from this well changed very little between the baseline-sampling event (378 $\mu\text{g/L}$) and the final sampling event (376 $\mu\text{g/L}$). Concentrations of cis-1,2-DCE increased from 1740 to 2910 $\mu\text{g/L}$ during the same timeframe. Vinyl chloride also increased from nondetectable levels to 259 $\mu\text{g/L}$. Because there was no apparent change in the TCE concentrations, it is not clear whether the injection program resulted in degradation of the constituents in this area. A slight increase in methane and ethylene were observed in this well during the pilot study, which could be an indication that enhanced degradation is occurring near this well. However, there were no positive trends observed in the geochemical parameters.

4.2.3 Field Parameters

As previously stated, the reactive zone performance is measured by monitoring for the target contaminants and relative concentrations of degradation products; as well as, other indicator parameters in groundwater such as dissolved oxygen, ORP and changes in concentrations of electron acceptors within the treatment area. Field parameters including pH, DO, ORP, ferrous iron, sulfate, hydrogen, and conductance were measured monthly throughout the pilot study to monitor changes in the biogeochemical conditions. Summaries of the field parameter data are presented in Table 4.1

TABLE 4.1 SUMMARY OF DATA, MONITOR WELL DWP-4-16

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (MV)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/21/99	24.33	1.066	5.0	6.89	101.0	0.0	>200	0.0
8/3/99	24.75	1.073	5.6	6.88	156.5	0.0	>200	0.0
9/22/99	24.17	1.043	4.6	6.87	89.9	0.0	>200	0.0
9/28/99	25.33	1.069	5.3	6.89	31.2	0.0	180	0.0
10/5/99	23.85	0.996	4.8	6.93	127.7	0.0	190	0.0
10/12/99	24.77	1.107	5.3	6.91	49.6	0.0	150	0.0
10/19/26	23.11	0.846	5.6	6.95	71.2	0.0	200	0.0
10/26/99	24.89	0.963	5.8	6.89	130.6	0.0	150	0.0
11/9/99	24.28	0.937	5.9	6.86	92.2	0.0	200	0.0
12/7/99	22.47	0.760	7.1	6.95	61.7	0.0	180	0.0
1/25/00	21.64	0.814	9.2	6.93	88.0	0.0	180	0.0
2/22/00	23.2	0.880	5.2	7.02	57.3	0.0	>200	0.0
3/21/00	21.92	0.907	4.1	6.88	57.1	0.0	200	0.0
4/18/00	23.22	0.937	3.3	6.94	25.2	0.0	180	0.0
5/17/00	23.15	1.052	5.2	6.81	66.0	0.0	150	0.0
6/19/00	23.99	1.089	3.9	6.90	56.2	0.0	>200	0.0
7/21/00	24.26	1.173	3.2	6.47	-131.3	1.0	125	0.0
8/17/00	24.12	1.039	2.8	6.40	-153.9	3.0	180	0.0
9/18/00	25.13	1.003	2.7	6.75	-257.4	1.6	150	0.0

TABLE 4.2 SUMMARY OF DATA, MONITOR WELL DWP-4-IW1

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (mv)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/21/99	23.82	1.071	3.9	7.07	-53.2	0.8	>200	0.0
9/22/99	27.26	16.320	6.9	4.50	-430.8	NA	NA	NA
9/28/99	26.00	11.630	9.8	4.31	-425.7	NA	NA	NA
10/5/99	25.74	10.410	6.3	4.18	-430.7	NA	NA	NA
10/12/99	25.56	12.420	10.1	4.45	-441.8	NA	NA	NA
10/19/99	23.72	8.256	11.3	4.16	-323.8	NA	NA	NA
10/26/99	24.69	10.260	13.0	4.00	-247.6	NA	NA	NA
11/9/99	24.73	10.360	8.7	4.23	-297.0	NA	NA	NA
12R/99	22.70	11.760	14.8	4.95	-452.2	NA	NA	NA
1/25/00	22.30	15.020	13.0	5.30	-175.2	NA	NA	NA
2/22/00	22.84	15.690	8.9	5.47	-149.6	NA	NA	NA
3/21/00	21.22	15.970	4.6	5.43	-138.2	NA	NA	NA
4/18/00	23.06	8.658	5.4	5.10	-102.8	NA	NA	NA
5/16/00	23.79	10.270	11.5	5.89	-205.2	NA	NA	NA
6/19/00	23.65	7.846	10.7	6.64	-280.1	NA	NA	NA
7/20/00	24.90	6.754	14.3	6.31	-332.9	NA	NA	NA
9/19/00	26.40	4.736	3.2	6.27	-305.1	NA	NA	NA

TABLE 4.3 SUMMARY OF DATA, MONITOR WELL DWP-4-IDW1

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (mv)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/21/99	25.94	0.305	2.0	9.38	28.5	0.4	55	0.0
9/22/99	27.66	14.770	7.4	4.39	-414.8	NA	NA	NA
9/28/99	25.39	12.080	11.2	4.40	-420.8	NA	NA	NA
10/5/99	25.95	11.030	9.2	4.42	-397.1	NA	NA	NA
10/12/99	25.31	12.780	10.9	4.51	-441.8	NA	NA	NA
10/19/99	22.25	8.492	11.0	4.56	-420.4	NA	NA	NA
10/26/99	26.13	10.830	13.2	4.43	-175.4	NA	NA	NA
11/9/99	24.89	10.680	11.6	4.42	-81.0	NA	NA	NA
12/7/99	21.50	9.758	13.1	4.75	-171.5	NA	NA	NA
1/25/00	21.23	12.310	12.4	5.18	-136.3	NA	NA	NA
2/22/00	21.45	13.510	8.9	5.33	-90.4	NA	NA	NA
3/21/00	20.91	13.390	5.8	5.28	-102.0	NA	NA	NA
4/18/00	23.18	9.303	5.0	5.43	-144.4	NA	NA	NA
5/16/00	25.45	10.570	28.5	5.95	-208.1	NA	NA	NA
6/19/00	23.89	7.579	10.7	6.75	-219.9	NA	NA	NA
7/20/00	25.56	5.520	12.7	6.32	-220.9	NA	NA	NA
9/19/00	25.60	4.614	2.6	6.94	-383.1	NA	NA	NA

TABLE 4.4 SUMMARY OF DATA, MONITOR WELL DWP-4-DW1

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (mv)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/22/99	24.01	1.080	5.1	7.02	-28.9	0.6	>200	0.0
9/22/99	24.17	1.043	4.6	6.87	89.9	0.0	>200	0.0
9/28/99	25.07	1.088	5.5	6.99	-17.5	0.4	>200	0.0
10/5/99	23.79	1.022	4.7	7.03	-38.7	0.6	>200	0.0
10/12/99	24.35	1.131	4.7	7.01	-28.9	0.8	>200	0.0
10/19/99	22.40	0.882	6.0	7.04	-6.3	0.6	>200	0.0
10/26/99	24.34	0.983	5.5	6.99	-26.0	0.8	>200	0.0
11/9/99	23.67	0.957	4.4	6.96	-41.6	0.8	>200	0.0
12/7/99	21.90	0.777	8.2	7.03	-52.7	0.6	200	0.0
1/25/00	20.16	0.829	6.3	6.99	-27.6	0.4	200	0.0
2/22/00	22.73	0.891	2.2	7.03	-31.6	0.6	200	0.0
3/21/00	22.00	0.919	3.9	6.91	-40.4	0.6	>200	0.0
4/18/00	23.16	0.950	3.7	6.95	-40.8	0.4	>200	0.0
5/17/00	23.71	1.064	5.2	6.92	-31.5	0.6	200	0.0
6/19/00	24.73	1.054	4.8	6.96	-34.3	0.6	>200	0.0
7/21/00	24.40	1.083	2.0	6.61	-94.6	0.6	>200	0.0
8/17/00	24.01	0.961	2.5	6.57	-80.4	0.0	200	0.0
9/19/00	24.66	0.925	4.4	7.11	-162.8	0.2	200	0.0

TABLE 4.5 SUMMARY OF DATA, MONITOR WELL DWP-4-DW3

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (mv)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/21/99	26.03	1.163	3.4	7.76	-160.2	0.4	>200	0.0
9/22/99	25.10	1.377	2.0	10.02	-138.7	0.0	>200	0.0
9/28/99	25.25	1.395	3.1	10.04	-152.0	0.0	>200	0.0
10/5/99	24.39	1.302	2.3	9.99	-61.9	0.0	>200	0.0
10/12/99	24.80	1.490	3.1	10.15	-161.0	0.0	200	0.0
10/19/99	22.71	1.626	5A	11.29	-149.9	0.0	>200	0.0
10/26/99	25.10	1.852	5.8	10.97	-129.8	0.0	>200	0.0
11/9/99	24.63	2.276	5.3	11.48	-156.0	0.0	>200	0.0
12/7/99	21.74	2.526	9.9	11.81	-168.9	0.0	>200	0.0
1/25/00	21.44	0.923	2.9	8.64	1.6	0.0	>200	0.0
2/22/00	22.52	0.971	3.4	8.41	-50.4	0.0	>200	0.0
3/21/00	21.88	1.001	3.1	7.70	-80.9	0.2	>200	0.0
4/18/00	23.19	1.047	4.6	7.85	-113.0	0.0	>200	0.0
5/16/00	24.62	1.153	5.7	7.48	-96.1	0.4	>200	0.0
6/19/00	24.43	1.229	4.9	7.54	-87.1	0.8	>200	0.0
7/21/00	25.16	1.240	4.4	7.27	-131.8	0.8	>200	0.0
8/17/00	23.77	1.092	3.3	7.17	-25.6	0.8	>200	0.0
9/18/00	25.83	1.016	2.6	7.03	-142.0	0.8	>200	0.0

TABLE 4.6 SUMMARY OF DATA, MONITOR WELL DWP-4-17

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (MV)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/22/99	23.72	1.062	22.9	6.91	-64.5	0.8	>200	0.0
9/23/99	23.84	1.066	5.6	6.94	-44.5	1.2	200	0.0
9/28/99	25.76	1.072	5.2	6.85	-41.2	1.2	200	0.0
10/5/99	24.80	1.005	5.5	6.93	-63.6	1.2	>200	0.0
10/12/99	25.18	1.101	5.1	6.88	-50.7	1.4	150	0.0
10/19/99	23.80	0.860	5.4	6.93	-47.4	1.4	>200	0.0
10/26/99	25.38	0.959	6.0	6.89	-55.2	1.4	>200	0.0
11/9/99	24.51	0.930	5.5	6.86	-54.4	1.4	200	0.0
12/7/99	22.95	0.755	5.8	6.90	-32.0	1.1	>200	0.0
1/25/00	21.23	0.815	4.6	6.90	-14.0	0.6	180	0.0
2/22/00	22.39	0.863	6.4	6.90	-27.1	0.4	>200	0.0
3/21/00	22.11	0.895	3.7	6.82	-47.0	0.6	180	0.0
4/18/00	22.68	0.934	3.2	6.85	-31.5	0.6	>200	0.0
5/17/00	22.88	1.040	5.4	6.84	-51.9	0.8	>200	0.0
6/19/00	23.41	1.048	5.1	6.79	-58.9	1.2	>200	0.0
7/21/00	23.95	1.105	3.1	6.50	-127.8	1.0	>200	0.0
8/17/00	24.24	1.004	2.6	6.37	-114.1	1.8	>200	0.0
9/19/00	24.73	1.051	2.6	6.92	-205.0	1.8	>200	0.0

TABLE 4.7 SUMMARY OF DATA, MONITOR WELL DWP-4-18

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (mv)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/22/99	23.10	1.104	18.8	6.84	43.9	0.0	>200	0.0
9/23/99	24.10	1.095	5.3	6.83	-64.5	0.2	200	0.0
9/28/99	24.73	1.113	6.8	6.74	18.9	0.2	200	0.0
10/5/99	24.8	1.036	6.3	6.81	-14.9	0.4	>200	0.0
10/12/99	25.23	1.146	6.6	6.77	-10.4	0.0	>200	0.0
10/19/99	23.62	0.896	5.8	6.83	-18.0	0.2	200.0	0.0
10/26/99	24.96	0.998	6.3	6.79	-16.1	0.2	200.0	0.0
11/9/99	24.28	0.969	5.3	6.75	-2.0	0.2	>200	0.0
12/7/99	22.13	0.770	6.6	6.84	32.9	0.2	200	0.0
1/25/00	20.81	0.834	7.3	6.82	86.2	0.0	200	0.0
2/22/00	20.92	0.881	10.9	6.85	78.1	0.0	>200	0.0
3/21/00	20.48	0.915	5.9	6.74	53.6	0.0	>200	0.0
4/18/00	21.53	0.950	4.5	6.79	56.8	0.0	>200	0.0
5/17/00	22.02	1.072	5.7	6.70	1.5	0.0	>200	0.0
6/19/00	22.52	1.054	3.7	6.70	-9.2	0.0	>200	0.0
7/21/00	23.62	1.093	6.3	6.37	-54.5	0.0	>200	0.0
8/17/00	24.04	0.965	3.4	6.29	-30.5	0.0	>200	0.0
9/19/00	23.69	0.924	28.3	6.94	-100.6	0.2	200	0.0

TABLE 4.8 SUMMARY OF DATA, MONITOR WELL DWP-4-DW4

Date	Temperature (Celsius)	Specific Conductivity (millisiemens/cm)	Dissolved Oxygen (percent)	pH	Oxidation-Reduction Potential (MV)	Ferrous Iron (mg/L)	Sulfate (mg/L)	Hydrogen Sulfide (mg/L)
7/23/99	24.86	1.122	4.8	7.04	-79.5	0.6	>200	0.0
9/23/99	23.50	1.092	5.8	7.06	-96.5	0.4	>200	0.0
9/28/99	25.21	1.115	5.2	6.94	-20.2	0.6	>200	0.0
10/5/99	24.41	1.030	5.1	7.02	-49.5	0.6	>200	0.0
10/12/99	24.28	1.166	5.0	6.99	-38.4	0.4	>200	0.0
10/19/99	22.63	0.918	6.1	7.04	-21.3	0.4	>200	0.0
10/26/99	24.26	1.000	5.3	7.01	-33.0	0.6	>200	0.0
11/9/99	23.88	0.976	8.8	6.98	-35.6	0.6	>200	0.0
12/7/99	22.22	0.786	5.1	7.04	-41.5	0.6	>200	0.0
1/25/00	21.06	0.845	5.6	7.00	-38.9	0.4	>200	0.0
2/22/00	22.46	0.901	-1.0	7.02	-46.7	0.4	>200	0.0
3/21/00	21.87	0.932	4.0	6.92	-43.0	0.4	200	0.0
4/18/00	23.25	0.960	4.0	6.95	-44.7	0.4	>200	0.0
5/17/00	23.66	1.089	5.4	6.90	-36.5	0.4	>200	0.0
6/19/00	24.41	1.064	4.3	6.92	-23.6	0.2	>200	0.0
7/21/00	24.18	1.103	5.5	6.61	-78.6	0.2	>200	0.0
8/17/00	24.03	0.977	2.5	6.50	-58.8	0.0	>200	0.0
9/11/00	23.57	0.957	3.7	7.16	-171.5	0.2	>200	0.0

Monitor Well DWP-4-16, the upgradient well, showed only minor fluctuations for all of the field parameters. These minor variations indicate no influence from the injection program.

Field parameters collected from the two injection wells (DWP-4-IW1 and DWP-4-IDW1) indicate obvious effects in the groundwater in the immediate vicinity of the injection wells. Ferrous iron, sulfate, and hydrogen sulfide are only reported for the baseline-sampling event, which occurred on July 21, 1999. Due to the dark color of the molasses, the colorimetric field kits used to measure these parameters could not be used after the initial injection. As shown in the table, pH and ORP decreased significantly in both injection wells immediately after injections began. Specific conductivity also increased sharply after the injections began. Although DO concentrations fluctuated throughout the study, increases were observed after each injection.

The monitoring wells screened in the lower water-bearing zone (Wells DWP-4-DW3, DWP-4-DW-1, and DWP-4-DW-4) showed only minor fluctuations for all field parameters. Although no significant trends in the field parameters were observed in any of these monitoring wells, ORP measurements collected during the final two months of the pilot study showed promising results in DWP-4-DW-1 and DWP-4-DW-4. As previously discussed, the pH measured in Well-DWP-4-16 was affected by possible grout contamination and is not considered representative of subsurface conditions in the area.

Field parameters measured in the monitoring wells screened in the upper waterbearing zone (Wells DWP-4-6, DWP-4-17 and DWP-4-18) also fluctuated throughout the study. However, decreasing trends in ORP measurements were more distinctive in these wells during the final two to three months of the study. Ferrous iron measurements in Wells DWP-4-6 and DWP-4-17 also showed favorable trends during the last three months of the study.

It should be noted that some very high dissolved oxygen concentrations (greater than 20%) were observed periodically in a number of the wells. Dissolved oxygen can be very difficult to measure accurately in the field. These extreme measurements are considered anomalous and were not considered in our evaluation of the field data.

4.3 PERFORMANCE DATA ASSESSMENT

Field parameters and laboratory data clearly indicate that the injection solution had a positive effect on the biogeochemical conditions in the immediate vicinity of the injection wells. As discussed in the previous sections, samples from the injection wells generally indicated decreases in TCE concentrations, increases in concentrations of daughter products and bi-products, decreases in ORP, and increases in key indicator parameters such as total iron, dissolved iron, ferrous iron, COD, DOC, total alkalinity, dissolved solids, and TOC. These results indicate that the molasses amendment used in this in-situ treatment program is an appropriate additive for this site and can result in the production of a reductive subsurface environment that will enhance the degradation of CAHs. A brief summary of the performance data for the pilot study is presented as Table 5.

Both hydrogeologic observations made during the study and field and analytical test results suggest that the most limiting factor affecting the success of this treatment technology is the ability to adequately distribute the nutrient solution within the impacted water-bearing zones. As previously discussed, the initial schedule for the pilot study was extended because early observations indicated little or no change had occurred in the nearby monitoring wells. Both field and analytical data indicate that significant changes were not observed in the monitoring wells until the final two to three months of the study.

The most significant changes were observed in the upper water-bearing zone in Well DWP-4-6, located 22 feet downgradient from the injection well, and to a lesser extent, in Well DWP-4-17, located 45 feet downgradient from the injection well. As previously discussed, samples from these wells generally indicated significant attenuation of TCE, decreases in ORP, increases in daughter products, and increases in total iron, dissolved iron, ferrous iron, COD, DOC, TOC, and total alkalinity. The data suggests that the IRZ had extended over 45 feet in the upper water-bearing zone, downgradient of the injection well by the end of the pilot study.

Less significant changes were observed in monitoring wells completed in the lower water-bearing zone. Well DWP-4-DW-3, located 11 feet downgradient from the injection point indicated some attenuation of TCE over time. And concentrations cis-1,2-DCE, methane and ethylene increased significantly over time. However, the geochemical parameters did not show any significant changes over time. There was also no clear effect to the lower water-bearing zone near wells DWP-4-DW-1 and DWP-4-DW3, located further from the injection point. Based on the analytical results, distribution of the nutrient solution in the lower water-bearing zone appears to be more limited than in the upper water-bearing zone. This is consistent with the data collected from the aquifer tests, which indicate that groundwater in the upper waterbearing zone travels faster than that in the lower water-bearing zone. Analytical data suggests that during the pilot study, the induced IRZ extended a little over 11 feet downgradient of the injection well in the lower water-bearing zone.

TABLE 5. SUMMARY OF PERFORMANCE INFORMATION FOR PILOT SYSTEM

Enhanced In-Situ Biotransformation Remediation Pilot Study	
Types of samples collected	Groundwater samples
Sampling frequency and protocol	Samples were collected using low-flow sampling techniques Field parameters were measured monthly Laboratory samples were collected semi-annually and analyzed for VOCs and extensive suite of geochemical parameters
Quantity of material treated	Pilot study area encompasses groundwater in an area of about 2000 ft ² Upper water-bearing zone varies in thickness from approximately 5 to 10 ft Lower water-bearing zone varies in thickness from approximately 0 to 3 ft
Untreated and treated contaminant concentrations	ORP concentrations decreased significantly, indicating that the treatment successfully produced a reducing environment. Significant changes in groundwater VOC concentrations were measured during the final quarter of the study Some significant decreases in TCE, combined with increases in its daughter products, were observed, especially during the final quarter of the study Increases in dissolved gases (especially methane, ethene and hydrogen) demonstrate enhanced microbial activity
Cleanup Objectives	No specific cleanup goals were identified for the field demonstration
Method of Analysis	VOCs were analyzed by GCMS Geochemical parameters were analyzed using various methods
Quality assurance and quality control (QA/QC)	ARCADIS Geraghty & Miller Level III data validation criteria as described in the February 1999 QAPP
Other Residues	Decontamination Fluids, Drill Cuttings Purge water

Overall it appears that the desired biogeochemical IRZ reactions have been stimulated in the pilot treatment area. In addition, these reactions have been successful in degrading impacting CAHs. However, the transport properties in the pilot treatment zone are poor. This means that with increased time of treatment it is likely that larger areas in the pilot treatment zone could be remediated, although, hydrogeologic conditions in the pilot area are not be ideal for the application of the IRZ technology.

Based on the pilot study data, it is anticipated that similar biogeochemical reactions could be stimulated in other areas at the Dallas facility. At locations where there is a reasonable groundwater gradient and a more laterally homogeneous stratigraphy, the IRZ technology should work very effectively.

4.4 PERFORMANCE DATA QUALITY

Data validation was performed on ten percent of the analytical laboratory data, as specified in the work plan. Two sets of groundwater data were validated: Group 9904920 and Group 20003459. These data packages contain four samples (plus one duplicate) collected July 22, 1999 and five samples (plus one duplicate) collected May 17, 2000 and all the associated trip, field, and equipment blanks. The samples were submitted to and analyzed by Gulf Coast Analytical Laboratories located in Baton Rouge, Louisiana. The samples were analyzed for the following parameters:

- Volatile organic compounds (USEPA Method 8260);
- Iron (total and dissolved) (USEPA Method 6010);
- Iron (ferric and ferrous) (Standard Method 3500-Fe D);
- Manganese (total and dissolved) (USEPA Method 6010);
- Biochemical Oxygen Demand (Standard Method 5210-B);
- Chemical Oxygen Demand (HACH8000);
- Chloride (USEPA Method 352.2);
- Dissolved Organic Carbon (Standard Method 5310-B);
- Nitrite (USEPA Method 353.2);
- Nitrate (USEPA Method 353.2);
- Ammonia Nitrogen (USEPA Method 350.3);
- Phosphorus (USEPA Method 365.1);
- Sulfate (USEPA Method 375.4);
- Sulfide (USEPA Method 376.2);
- Total Alkalinity (USEPA Method 310.1);
- Total Dissolved Solids (USEPA Method 160.1); and
- Total Organic Carbon (Standard Method 5310-B or USEPA Method 9060).

The results of the above referenced analyses were evaluated according to quality assurance/quality control (QA/QC) criteria described in the Quality Assurance Project Plan and Sampling and Analysis Plan (ARCADIS Geraghty & Miller, 1999b), guidelines established by the USEPA (USEPA, 1994 and 1999); and by following ARCADIS Level III data validation criteria.

The results of the data review are presented in the following two sections. A checklist is provided for each of the following categories: documentation, wet chemistry, metals, and volatile organics. At the end of each section is a summary of the samples and constituents that were qualified. Multiple qualifications on the same constituent in the same sample may result in a further reduction in validation level. The qualifiers used in this data assessment are:

“J” The contaminant was positively identified and the associated value is an estimated concentration below the method detection limit but above the regulatory required detection limit.

“UJ” The contaminant was analyzed for but was not detected. The reported quantitation limit is an estimate and may be inaccurate or imprecise.

“R” The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet the quality control data. The contaminant may, or may not, be present.

“U” The contaminant was analyzed for but was not detected. Parameters not assigned any qualifier are considered to be quantitative.

4.4.1 Accuracy

Accuracy was evaluated by assessing the results of holding times, field and laboratory blanks, initial and continuing calibrations, surrogate spike recoveries (organic analyses), serial dilution analyses (metals), laboratory control samples recoveries, and matrix spike analyses.

The holding times were met for all the evaluated samples. Qualifications were made as a result of contamination found in field and equipment blanks, unacceptable initial and continuing calibrations, unacceptable serial dilution analyses, and unacceptable matrix spike recovery.

4.4.2 Precision

Precision was evaluated by assessing the results between Matrix Spike (MS) and Matrix Spike Duplicate (MSD) analyses and between field and laboratory duplicate analyses. Precision was evaluated as the relative percent difference (RPD) between duplicate sample results.

Data was qualified based on unacceptable RPDs for field and laboratory duplicate analyses. The precisions of the MS and MSD analyses were acceptable.

4.4.3 Sensitivity

Sensitivity was addressed by ensuring that the reporting limits provided by the laboratories met those as required by the work plan. The detection limits outlined in the QAPP were not met on some of the project samples for the BOD or the xylene analyses.

4.4.4 Completeness

Completeness is an evaluation of the overall sampling program with respect to data generated that is usable versus data that may have been rejected. The required level of completeness for the project is 95 percent complete. Completeness is calculated as

$$\% \text{ completeness} = \text{number of valid results} / \text{number of possible results}$$

All results not qualified with an R\Rejected flag are considered valid. A total of nine samples and two duplicates (excluding trip, field and equipment blanks) with 66 parameters (volatile organics, metals and wet chemistry parameters) were included in the validation set. A single data point was rejected during the data validation process. The completeness requirements were met for all target analytes on this project.

5.0 COST OF THE TECHNOLOGY SYSTEM

5.1 PROCUREMENT PROCESS

The IRZ technology uses molasses as an electron donor source. The molasses is a commercially off-the-shelf component, and molasses was considered as the electron donor source for this very reason. The molasses is readily available from animal feed stores, it is an inexpensive product and it is routinely delivered in bulk quantities from suppliers.

The grade of molasses required for the IRZ implementation can be selected based on the intended remediation. Molasses grades containing higher amounts of sulfur may be chosen for remediation projects targeting metal precipitation. Other commercially off-the-shelf components of the IRZ technology include:

- Standard type wells or injection points are used to introduce the molasses into the aquifer.
- Standard drilling or direct push methodologies are used to install the injection points.
- Automated delivery systems can be designed and fabricated from standard industrial components (i.e. tanks, valves, tubing and controllers).
- Manual batch loading systems use standard water delivery equipment (i.e. tanks, pickup trucks, hoses, and filters).

- Monitoring equipment and instruments may not be available locally, but are standard supplies that can be purchased through any major environmental or laboratory supply company.

5.2 COST DATA

The costs for conducting the pilot study were tracked throughout the pilot study and are summarized on Table 6. This pilot project was conducted and billed on a lump sum basis and each of the major elements of the project was billed on a lump sum basis. Therefore, the profit for the pilot study is accounted for within each cost element.

TABLE 6. COST SUMMARY FOR PILOT SYSTEM

Cost Category	Total Cost for Pilot System
1. Capital Cost for Technology	
Technology mobilization, setup, and demobilization	\$10,113
Planning and preparation	
Historical Data Review, site -Visit and- meetings	\$13,963
System Design	\$8,034
Work Plans and Permitting	\$15,606
Site Work	
UXO Survey	\$8,733
Pumping Test	\$15,814
Equipment and Appurtenances	
Labor for Construction of Delivery System	\$17,598
Structures	\$5,292
Process Equipment	
Injection Wells (includes materials and labor)	\$13,765
Monitoring Wells (includes materials and labor)	\$43,985
Startup and Baseline Testing	
2. O&M for Technology	
Labor for O&M	\$10,664
Supplies and Equipment for O&M	\$4,821
Labor for Sampling	\$16,111
Supplies and Equipment for Sampling	
Analytical Fees	\$27,010
Data Management, validation and evaluation	\$13,954
3. Other Project Costs	
Reporting	\$11,657
Project Management	\$15,437
Project Total	\$306,557

Notes:

Utility costs were not tracked for the pilot study. Utility usage included electricity for climate control (air conditioning) within control building and for the air compressor for pneumatic pump. Water usage was minimal and only occurred during monthly O&M and sampling events. Because the automated system was not used throughout the test, total utility costs for the pilot system are estimated to be less than \$300 total for the duration of the test.

Costs for disposal of drill cuttings and purge fluids were not tracked for this pilot study. These residual wastes were managed by ENSAFE. Some of the labor shown for installation of monitoring wells and injection wells was incurred to contain the drill cuttings from the wells. Some of the labor shown for sampling was incurred to contain purge liquids. The actual cost for disposal of these residual wastes was not documented by ARCADIS Geraghty & Miller. However, disposal costs for the pilot study are estimated to be less than \$5,000.

The *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* suggests that wherever possible, unit costs be presented in terms of the amount of contaminant removed during the remediation. This type of unit cost was not calculated for the pilot study. Since this is an in-situ treatment technology, the volume of water treated cannot be accurately estimated. Because of the nature of this program, some ongoing positive affect from the pilot study may occur for a period of three to six months after completion of the pilot study. Furthermore, because of the limited schedule and scope of the pilot study, as well as fluctuations observed in the groundwater conditions, the mass of contaminants removed cannot be accurately measured.

The *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* also suggests that wherever possible, the cost of a fullscale remediation system be projected based upon pilot study costs. The costs for a full-scale system were not projected for this site because the cost of such as system would depend on the size and location of the system. For example, a system installed in the area of the pilot study may be much more expensive to install and operate than a system installed in an upgradient location where the injection well spacing and volume of injection fluids is expected to be lower.

Some comparison can be made, however, between the costs of the pilot system and a hypothetical full-scale system. The costs for planning, preparation, mobilization, permitting and set-up for the pilot system was approximately \$47,000, which represents a significant portion of the overall cost of the project. These costs are expected to be similar for a full-scale system (i.e. not proportional to the size of the system). This is because, although additional design, planning, preparation, and permitting will be required for a full-scale system, much of the historical data review, planning, and preparation has already been conducted as a result of the pilot study. The cost for the UXO survey, the injection well and monitoring well installations and the costs associated with groundwater sampling for a full-scale system are expected to be generally proportional to the cost incurred for the pilot system and would depend on the size and location of the full-scale remediation project. As previously discussed, a full-scale system installed in the area of the pilot study would cost more than one installed in an upgradient location where the injection well spacing and volume of injection fluids is expected to be lower.

Annual operation and maintenance costs, data management and evaluation, and reporting for a full-scale system are expected to be higher, but not proportionally higher than the costs incurred for the pilot-scale system. Some economy of scale can be expected for these elements.

6.0 REGULATORY/INSTITUTIONAL ISSUES

Potential regulations that affect an IRZ program are limited to those addressing *in-situ* remediation technologies. There are no unusual issues involving the transport, storage or disposal of wastes and treatment residuals. A permit is required from the Class V Injection Well section of the TNRCC. Based on our experience with this permitting process, the injection well permits are relatively easy to acquire. The amount of interaction with regulatory agencies required to execute an IRZ remediation program is generally greater than with traditional technologies. However, full-scale IRZ remediation programs have now been implemented at a number of sites within Texas and many of the TNRCC staff are familiar and agreeable with this technology.

7.0 TECHNOLOGY APPLICABILITY AND ALTERNATIVES

The ability to stimulate indigenous bacterial populations to degrade CAHs through the creation of an IRZ is not in doubt at the site. Technical limiting factors are the complex hydrogeologic conditions and extremely flat groundwater gradients that prohibit adequate delivery of the nutrient solution. As tested, the IRZ technology is limited by slow groundwater velocities and the impact of the in-situ lifetime of the injected soluble carbon substrates is particularly sensitive to the native groundwater velocity. Given those limitations, the use of the IRZ technology at the site is still likely to be the most cost effective technology for remediation, because these same technical issues would also have a negative impact on any *in-situ* remedial technologies that could be applied at the site. Table 7, represents estimated unit costs for groundwater remediation system components for a site-wide IRZ technology. In addition, the use of carbon substrates with slower degradation kinetics would decrease the sensitivity of the IRZ technology to slow groundwater velocities.

TABLE 7. ESTIMATED UNIT COSTS FOR GROUNDWATER REMEDIATION SYSTEM COMPONENTS

Item	Estimated Unit Cost
Monitoring Wells (labor and materials for installation and development)	
Shallow (2-inch diameter PVC wells, 25' deep)	\$1,800
Deep (2-inch diameter PVC wells with isolation casing , 45' deep)	\$3,200
Injections Points (labor and materials for installation)	
Shallow (1-inch diameter PVC points, 25' deep)	\$1,500
Deep (1-inch diameter PVC points, 45' deep)	\$2,800
Injections (labor and materials for each injection event for each point)	\$650
Groundwater Sampling (labor and equipment for sample collection)	\$300
Analytical Fees (includes analytical cost plus 15% customary mark up)	
Volatile Organic Compounds (USEPA Method 8260)	\$160
Dissolved Gases (AM 20 GAX)	\$490
Metals	
Ferrous and Ferric Iron (6010 B, 200.7 & 3500 -FeD)	\$40
Total and Dissolved Manganese (6010 B)	\$25
Other Geochemical Parameters	
Ammonia (350.3)	\$20

Alternatives that could overcome the problems encountered during the pilot study include:

- Tight injection well spacing and the pressure injection of greater volumes of injection solution. Injection pressures cannot exceed those that would induce hydrofracturing, but given that limitation, the use of higher injection pressures and greater volume would exploit the preferential transport pathways present in the heterogeneous geologic matrix underlying the pilot study area. The injected solutions will migrate into adjacent less permeable zones by the natural groundwater flow or through diffusion. The high transport zones can be envisioned as extensions of the sand pack of the injection well. Injection volumes need to be appropriately increased using this mode of injection. Under these conditions the solutions will follow preferential pathways, which are likely the same pathways that are supporting CVOC laden groundwater flow. An option that was not pursued during the pilot study was the installation of additional monitor wells to evaluate possible transport and stimulation of the IRZ in zones other than those within the monitor well array.

- Design of a treatment system that takes into account the greater time required due to the flat groundwater gradients. This could include the use of carbon substrates that act in a slow release fashion or the use of alternate carbon substrates (such as solubilized vegetable oil) that may offer slower kinetic reactivity and have greater life expectancy (and subsequent transport potential) in the treatment zones.
- Installation of an IRZ treatment system in other areas across the site that are expected to have steeper hydraulic gradients and to exhibit more laterally homogeneous stratigraphy. The IRZ technology is generally predicated on the exploitation of natural groundwater flow systems. Areas of more stable flow would allow for the more reliable manipulation and creation of IRZs. In the case of the pilot area the best way to exert influence would be to move 20 to 30 feet upgradient onto the concrete pad. An infiltration trench could be installed so that larger volumes of molasses amended water (either in a pulse or continuous mode) would allow for a greater impact on the hydraulic regime in the pilot area. Since the recent changes in RCRA concerning the use of treated groundwater, it may be possible to use groundwater from the existing pump and treat system as the infiltrate. The amended groundwater would follow the existing groundwater flow pathways through this highly complex area. This approach would also likely be enhanced through the use of a carbon substrate with a longer life expectancy.

Other technologies that could be implemented include pump and treat, chemical oxidation, or the use of reactive iron walls.

- Pump and treat would be subject to the heterogeneous conditions observed during the pilot study. Pump and treat is not expected to effectively remediate the groundwater plume within a reasonable timeframe, but could be used for hydraulic control in critical areas of the plume. Given the size of the dissolved plume, pump and treat is not expected to be a cost-effective approach for this site.
 - A more effective, but significantly more expensive option, would be the use of a vacuum enhanced groundwater recovery system. The radius of influence of a given extraction point would be increased, as would groundwater recovery rates. However, the groundwater treatment, vapor treatment, and vacuum inducement equipment would be costly per unit volume of groundwater treated.
- Chemical oxidation using injected Fenton's reagent or permanganate salts would have the same transport problems as those found during the pilot study. The use of pressure injection may overcome some of those problems (as it would with the IRZ technology). However, the cost and reactivity of chemical oxidants can be prohibitive. This type of technology is most effective when applied to CAH source areas rather than the distal portions of a plume.
- A reactive iron wall offers a relatively passive treatment option. Two forms of reactive iron walls could be applied: trench based systems or a system based on in-situ injection.

- At this location depth is an inhibiting factor. The cost to install a trench-based iron wall would go up almost exponentially at depths greater than 20 to 25 feet. In addition, iron walls installed using trenches are highly susceptible to CAH breakthrough when installed in situations where there is a high degree of heterogeneity within the water-bearing zones. Installation of a wall that is thick enough to treat the “worst case” CAH concentrations would likely be cost-prohibitive.
- A recent development in reactive iron wall technology is the use of the direct injection of nano-scale elemental iron (in some cases with catalyst added) colloids. This process is implemented using injection wells, so that depth is not as much as a limiting factor (compared to trenching). In addition, colloids injected into highly heterogeneous geology will naturally follow the most permeable and dominant transport pathways in the waterbearing zone being treated, minimizing the potential for CAH breakthrough. It should be noted that this application is newer than the molasses injection, and has only been applied at a few sites nationwide.
- Other possible in situ technologies include air sparging, various types of circulating wells, and heat enhancement of those systems. The problem in their application placement of the treatment points in appropriate locations. Just as an IRZ system is dependant upon downgradient flow to spread the reactive reagents, these other in situ systems are dependant upon groundwater flow to bring impacted groundwater to and through the treatment zone. Geologic uncertainties would impact this design process.

8.0 OBSERVATIONS AND LESSONS LEARNED

- The molasses solution is susceptible to molding and this problem may be exacerbated by the relatively mild climate in the Dallas area. As a result, an automated injection system is not feasible at this site. Any full-scale system using this technology would require that batches of solution be prepared and periodically injected to prevent fouling. Injections of molasses in an installed vertical array of injection wells would be performed on a bi-weekly basis for the first quarter, there after on a monthly basis. The use of alternate carbon substrates could ultimately allow bi-monthly to quarterly injections. Based on the results of the pilot study, during which the molasses concentrations in the injection fluids were varied from 2% to 20%, initial injections would be at 20% molasses. If a monthly injection regime is established concentrations will likely be cut back to 10%. If it is found that a bi-monthly or quarterly injection program can be implemented, injection concentrations would remain at 20%.
- The potential impact of ferric iron reduction on the inducement of a reductive dehalogenating IRZ would appear to be minimal. The ferrous iron concentrations generated during the pilot test indicate that the majority of iron minerals in the soils of the pilot area are not bio-available. Sulfate, could be more of an issue. During the pilot test complete consumption of sulfate did not take place, although the CVOC results indicate

that dehalogenating conditions did exist. A full-scale system would ultimately reduce the native sulfate concentrations.

- The indigenous *in-situ* bacterial populations demonstrated that they were capable of being stimulated into the desired modes of activity through the addition of the carbon substrate present in the injected molasses solutions. The stimulated bacteria consumed available native electron acceptors at increasingly lower redox conditions and then drove the sequential reductive dehalogenation of TCE through all potential halogenated daughter products and ultimately to innocuous ethene gas.
- A full scale IRZ to treat the area between the pilot study and Cottonwood Bay would require the injection of 10 to 20 tons of molasses per year (at this scale molasses is available at a price less than \$100 per ton).
- Flat groundwater gradients and reversing groundwater gradients in the pilot study area, complicated by heterogeneous hydrogeologic conditions inhibited the distribution of the nutrient solution in the water-bearing zones. Because of the difference in groundwater flow velocities, distribution of the nutrient solution was more effective in the upper water-bearing zone than in the lower water-bearing zone.

9.0 REFERENCES

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