Environmental Security Technology Certification Program

(ESTCP)

In-situ Substrate Addition to Create Reactive Zones for Treatment of Chlorinated Aliphatic Hydrocarbons: Vandenberg Air Force Base

Contract #41624-99-C-8032

December 17, 2004
Final Technical Report

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December 17, 2004

Under Contract #41624-99-C-8032
ESTCP Project CU-9920

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List of Acronyms and Abbreviations

1,2-DCE	1,2-Dichloroethene
1,2-DCA	1,2-Dichloroethane
1,1,1-DCA	1,1,1-Dichloroethane
1,1,1-TCA	1,1,1-Trichloroethane
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
bgs	below ground surface
BOD	Biochemical Oxygen Demand
BRAC	Base Realignment and Closure
CAH	Chlorinated Aliphatic Hydrocarbons
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CF	Chloroform
COC	Constituents of Concern
COD	Chemical Oxygen Demand
COTS	Commercially Off-The-Shelf
CT	Carbon Tetrachloride
DCE	Dichloroethene
DNAPL	Dense, Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DoD	Department of Defense
DTSC	Department of Toxic Substance Control
EARP	Enhanced Anaerobic Reductive Precipitation
ECS	Engineering Consulting Services
ERD	Enhanced Reductive Dechlorination
ESTCP	Environmental Security Technology Certification Program
GC	Gas Chromatograph
H_2	Hydrogen
IRP	Installation Restoration Program
IRZ	In-situ Reactive Zone
K	Hydraulic Conductivity
L	Liters

MC	Methylene Chloride
MCL	Maximum Contaminant Level
mg/L	milligrams per liter
MNA	Monitored Natural Attenuation
MS	Mass Spectrometer
NAS	National Academy of Science
ORP	Oxidation Reduction Potential
PBC	Performance Based Contract
PCE	Tetrachloroethene
PCP	Pentachlorophenol
psig	pounds per square inch gauge pressure
PVC	Polyvinyl Chloride
RCRA	Resource Conservation and Recovery Act
Redox	Reduction-oxidation potential
RWQCB	Regional Water Quality Control Board
STL	Severn Trent Laboratories
TBP	Tributyl Phosphate
TCA	Trichloroethane
TCE	Trichloroethene
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbon
TVOC	Total Volatile Organic Compound
ug/L	micrograms per liter
UIC	Underground Injection Control
U.S. EPA	United States Environmental Protection Agency
VAFB	Vandenberg Air Force Base
VC	Vinyl Chloride
VOC	Volatile Organic Compound

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ACKNOWLEDGEMENTS

We gratefully acknowledge the hosting of this demonstration Amena Atta of Vandenberg AFB. We greatly appreciate the guidance and support of ESTCP (Cathy Vogel and Andrea Leeson) and AFCEE for this work. The guidance of the AFCEE lead Jerry Hansen and of the ESTCP reviewers Hans Stroo and Dr Marvin Unger was vital. Numerous ARCADIS employees contributed to the work including C. Lutes, D. Liles, V. D'Amato, A. Frizzell, B. Molnaa, T. Teeple, J. Burdick, M. Hansen, A. Warren, B. Comstock, D. Singer, L. Hall, J. Friedman, B. Lu, D. Kidd, G. Fiol, M. Flaugher, S. Cullen, D. Springer and R. Hames. The excellent field work of Tim Teeple and David Springer is especially appreciated.

PREFACE

ARCADIS is the owner of Contractor Patented Technology for the in-situ addition of carbohydrate substrate material to create reactive zones for the removal of chlorinated hydrocarbons from groundwater as set forth in U.S. Patent Nos. 6,143,177 and 6,322,700.

To discuss application of this technology at government sites please contact:

- Van Sands at ARCADIS in Denver CO 720-344-3792 regarding legal and contractual matters and
- Chris Lutes of ARCADIS in Durham, NC at 919-544-4535 or clutes@arcadis-us.com regarding technical information, or
- Jerry Hansen at AFCEE 210-536-4353 or jerry.hansen@brooks.af.mil.

For commercial application please contact ARCADIS only, at the above listed phone numbers.

EXECUTIVE SUMMARY

This final technical report documents the demonstration of an innovative groundwater remediation technology performed at Vandenberg Air Force Base (VAFB) Site 35 by ARCADIS G&M, Inc. (ARCADIS). The general purpose of the demonstration program was to evaluate the efficacy of the In-Situ Reactive Zone (IRZ)/Enhanced Reductive Dechlorination (ERD) technology in removing chlorinated aliphatic hydrocarbons (CAHs) from impacted groundwater in a range of geologic conditions and CAH concentrations. This site provided an opportunity to evaluate IRZ at a site that was initially highly aerobic with minimal evidence of CAH natural attenuation.

Ultimately, the objectives of the demonstration were to demonstrate the ability to remediate contaminants in the subsurface over a relatively short time period (from one to five years in typical full-scale applications) and to gather information that can be used to estimate long term treatment effectiveness, life span and costs. Also important in this demonstration was to show that the degradation of CAHs does not “dead-end” at undesirable by-products such as cis-1,2-dichloroethene (cis-DCE) and/or vinyl chloride (VC).

The primary benefits of IRZ technology include its ease of regulatory acceptance, its in-situ nature and its relatively low cost. Potential limitations to the application of the IRZ technology using soluble carbohydrates can include the following:

- Intermediate degradation products such as VC can be formed; however, proper system design can ensure their further degradation.
- Production of reduced gases or secondary water quality impacts from byproduct organic compounds, fermentation byproducts or mobilized metals is possible. The effects of these constituents usually do not extend beyond the reactive zone, but they should be monitored and addressed during implementation.
- ERD’s effectiveness on dense, non-aqueous phase liquid (DNAPL) has not been conclusively proven and is not the subject of this report. However other publications suggest potential effectiveness; see for example Jacobs (2003), Mowder (2004), Cope (2001) and Sorenson (2003).

Scope and Location of Demonstration

The demonstration area is at VAFB Site 35, downgradient of a missile silo where TCE was historically used. TCE is thought to have flowed downslope into a series of channels, infiltrated vertically through the soil profile and impacted the underlying groundwater. No definitive soil source had been clearly delineated prior to the demonstration. The TCE plume has been investigated since 1994, and has exhibited TCE concentrations up to 6,200 ppb. TCE degradation products were not present in high concentration. Site 35 groundwater is unconfined and occurs within the Orcutt formation sands, which overly the less permeable Sisquoc formation. The highest TCE concentrations occur within the bottom 10 feet of the Orcutt formation.

Groundwater conditions are aerobic (DO>1 mg/L) and oxidizing (ORP>300 mV), with pH values above 6.0 prior to treatment. Subsurface investigations conducted during the demonstration pointed to a TCE source area downgradient of the utility building that was previously unknown. In addition, the pilot test installation narrowed the delineation of the southern and northwestern edges of the plume.

The active treatment phase of the demonstration was from February 2001 to April 2003. A total of 31 injections were conducted in three injection wells. Over this time, a total of 683 gallons of raw blackstrap molasses, 6,830 gallons of dilution water, 1,500 gallons of push water, 7,718 grams of potassium bromide tracer and 669 pounds of $NaHCO_3$ buffer were injected into the system. To stabilize pH at the injection wells, the buffer was added to the injectate during the final five months of active treatment, which allowed for a substantial increase in carbon dosing. Monitoring was conducted during the demonstration to gauge technology effectiveness, describe changes in biogeochemical conditions and gather process monitoring feedback.

Summary of CAH Treatment Results

The two monitoring wells that received the most substantial and sustained doses of molasses substrate were 35-MW-20 and 35-MW-16. At 35-MW-16, 25 feet downgradient from the injection wells, an 85% reduction in TCE concentration had been achieved as of July 2003, with treatment apparently ongoing. These values are computed without correction for the observed variance in the upgradient concentration or dilution effects by the reagent, which however was minimal. Enhanced TCE degradation and cis-DCE production occurred 20 to 27 months after the first injection, including a travel time of approximately 4 months. VC also appeared during the 20-27 month interval at 35-MW-16, so the lag time between TCE and cis-DCE degradation was short – a few months - or nonexistent. The pH level at this well during active treatment was slightly higher than at 35-MW-20, usually between 4.5 and 5 s.u. The beginning of enhanced treatment appeared to occur during the phase of buffered injections, and continued through the most recent post-treatment monitoring round in July 2003.

Well 35-MW-20 was close to injection well 35-I-2 and would have been directly and nearly immediately affected by injections. 35-MW-20 thus represents an observation point near the upgradient edge of the reactive zone. A 49% reduction in TCE had been achieved at 35-MW-20 as of July 2003 without correction, and treatment appeared to be ongoing 3½ months after the last injection. The lag time experienced at this well from the first injection until enhanced TCE degradation and cis-DCE production occurred was 8 to 14 months. The first appearance of VC occurred 27 months into treatment, after the phase of buffered injections began. Low pH, between 4 and 4.5 standard units (s.u.), was observed here and can inhibit methanogenesis, and thus may have suppressed dechlorination. After active injections ended, the pH level rose to 4.7 s.u., and VC and ethene levels increased to their highest levels to date, suggesting that pH played a role in this system’s performance in this area.

Other wells in the reactive zone received lower and less consistent TOC doses, and thus less complete treatment would be expected. At wells 35-MW-7 and 35-MW-11, enhanced cis-DCE production occurred five to twelve months after the arrival of elevated TOC, but VC has not been detected at 35-MW-11. 35-MW-7 data showed an 80% decrease in TCE over average pretreatment levels, without correction, by the post-demonstration period. Long-term data for 35-MW-7 show that IRZ technology has enhanced cis-DCE and VC production as TCE byproducts.

The other wells that did not get substantial, consistent doses of substrate experienced much less complete treatment or no treatment at all. This, along with the appearance of byproducts and bromide tracer data, strengthens the conclusions that substrate availability is linked with improved biodegradation and that contaminant removal was attributable to enhanced biodegradation rather than displacement.

Analysis of CAH Data: Conditions Required for Enhanced Biodegradation

The Vandenberg demonstration has shown that IRZ can be successfully applied to accelerate treatment of TCE under initially aerobic, low-alkalinity conditions. Up to 85% removal of TCE has been achieved in the reactive zone to date. The most recent monitoring data indicated that treatment was ongoing several months after the last injection of carbon solution. The methanogenic zone of the IRZ continued to expand well into the second year of operation. The estimated size of the reactive zone for one injection well, under a dosing rate similar to that used in the demonstration, might eventually match the methanogenic zone if elevated TOC levels were sustained. However, the furthest point at which complete dechlorination was demonstrated was 25 feet, or 4 months' travel time, from the injection wells. The length of the zone of groundwater chemistry impact was at least 120 feet, which should be taken into account during the design phase to protect any potential receptors.

Active process monitoring and application of controls (water pushes and buffer addition) were key factors in overcoming "stalling" of this sensitive system. In part due to the aerobic and low buffering characteristics of the aquifer, the system required a relatively long acclimation period to achieve complete dechlorination, but production of vinyl chloride and ethene were seen in the final full monitoring round, after approximately 20 months of treatment. No single variable – TOC, DOC, pH, methane, or starting TCE concentration – appeared to be able to predict CAH treatment at all of the reactive zone wells. However, the most complete treatment occurred after a high dosing rate, buffered injection was adopted, and highly reducing conditions were established.

Comparison of Results with Primary Objectives

During the 26-month period of active treatment, and for as much as ten months after the last injection, the treatment system demonstrated slow but effective TCE removal by biodegradation in a dissolved phase plume that showed very limited TCE degradation before treatment. Multiple lines of evidence of complete treatment – production of ethene, reduction in *cis*-DCE and no accumulation of VC, were seen in the most effectively treated downgradient wells. Effective treatment was seen only where substantial substrate (molasses and its breakdown products) and anaerobic conditions were observed in downgradient monitoring wells. The rate of treatment was significantly affected by the low buffering capacity of the aquifer, which initially limited the carbon dosing rate, thereby slowing the performance of the treatment system. Addition of a buffer to the injectate starting in October 2002 allowed a nearly four-fold increase in the dosing rate and resulted in improved CAH biodegradation. Treatment was also somewhat uneven within the targeted zone due to non-homogeneous groundwater flow patterns; however, a substantial zone was established with a limited number of injection wells.

Primary qualitative performance criteria included technology evaluation and prevention of "stalling." Performance of the technology evaluation criterion at Vandenberg was clearly fulfilled by the collection of extensive system performance data from an array of 11 monitoring wells downgradient from the three injection wells. Although the ERD process was initially slow due to the low buffering characteristics of the aquifer, addition of a buffer to the reagent allowed the system to overcome any apparent "stalling" during active treatment. Active process monitoring and application of controls (water pushes and buffer addition) were key factors in overcoming or avoiding "stalling" of this sensitive system. In part due to the aerobic and low buffering characteristics of the aquifer, the system required a relatively long acclimation period to achieve complete dechlorination, but production of vinyl chloride and ethene were seen in the final full monitoring round at some monitoring locations.

Primary quantitative performance criteria included reduction of remediation time and percent reduction of contaminants. The performance goal for remediation time was 5 years in a typical full-scale application. The 26-month pilot system achieved significant contaminant reductions and ethene production, including an initial 20 months under sub-optimal operating conditions. Thus it is expected that a full-scale system would reach ethene production sooner; under these operating conditions, a remediation time of 5 years or less may be attainable at Vandenberg, although the demonstration did not proceed far enough to make this determination quantitatively. The 80% target contaminant reduction for total CAHs was not met within the target time of one year, though TCE reductions of ≥80% were reached at specific wells by the post-treatment period. Molar concentrations of total CAHs for the four most highly treated reactive zone wells fell by 12 to 66% during active treatment, a range which includes desorption peaks and production of daughter products late in the demonstration. TCE concentrations for the same wells fell by 42 to 74% during active treatment. However, 85% TCE reductions were achieved within the post-treatment period at 35-MW-16 (29 months after the first injection; three months after the last injection), and 80% TCE reduction was achieved at 35-MW-7, also within the post-treatment period (36 months after the first injection; 10 months after the last injection; based on an average pre-treatment concentration of 997.5 ug/L calculated from September through December 2000). These reductions include possible natural attenuation effects. Cis-DCE and VC were minimal before treatment, and were produced during treatment. The concentrations of these constituents are expected to decline with further treatment.

Comparison of Results with Secondary Objectives

Secondary qualitative criteria included system performance optimization, reliability, ease of use, maintenance, versatility, and scale-up constraints.

- An anaerobic environment was successfully created in response to continuous "tuning" of the system. Frequent performance monitoring, conducted immediately before injection events, allowed for timely adjustment of reagent delivery rates. Injection rates ranged from 120 to 240 pounds of molasses per month (per injection well) during the most effective treatment period at the end of the demonstration.

- No reliability issues were anticipated, and only minor maintenance and corrective actions were required to keep the system running reliably. Field implementation of a properly designed ERD system is relatively straightforward, requiring an environmental technician with appropriate safety training, with office support from degreed scientists or engineers. However, system design and operation oversight should only be conducted by scientists or engineers experienced in ERD technology.

- IRZ technology has been shown to be effective for many other contaminants in addition to CAHs. It has also been used at a wide variety of geological and hydrogeologic conditions and configurations.

- Scale-up issues were anticipated to be efficacy of the manual batch injection mode and determination of area of influence. Batch injection was proven successful at Vandenberg; area-of-influence was not closely defined in the demonstration due to the continued growth of the reactive zone beyond the monitoring well network.

Secondary quantitative criteria were established for geochemistry manipulation, contaminant mobility, contaminant reduction (rate), and hazardous materials:

- The goals of DO less than 1 mg/L and ORP less than 50 mV were generally met within the reactive zone at Vandenberg. It is noted that the even distribution of substrate is a significant factor in creating a geochemically effective reactive zone. Treatment was somewhat uneven spatially and temporally within the targeted zone due to non-homogeneous groundwater flow patterns and buffering issues. However, a substantial zone of geochemically favorable conditions was established with a limited number of injection wells.

- The Vandenberg plume was primarily a dissolved phase plume, and not much would be expected in the way of contaminant “spikes” upon desorption. However, in some wells, modest spikes were observed in TCE concentrations after active treatment began.

- Calculated degradation rates for TCE at Vandenberg were slow compared to other ERD applications, partly due to the long acclimation period when unbuffered reagent was used, but compared well with typical natural attenuation rates previously observed in the field at other sites.

- Potentially hazardous materials were limited to soil cuttings from well borings and purge water.

Lessons Learned

The application of ERD to treat CAHs in groundwater at many varied sites has provided a valuable knowledge base that has taught many lessons for future applications of the technology both at the pilot-and full-scale. Some specific lessons learned from the Vandenberg demonstration are included below.

<u>Substrate Dosing Required for Successful Treatment.</u> Successful treatment at Vandenberg was associated with a wide range of TOC values above 10 and as high as 3,000 mg/L. In comparison to observations at many other sites that 50-200 mg/L TOC in monitoring wells is sufficient for complete degradation, the demonstration illustrated the wide variability of site responses to dosing rate. Methanogenic conditions as indicated by methane concentrations in excess of 1,000

µg/L were generally associated with rapid, complete treatment. The use of a clean water push to disperse the injected TOC and addition of a sodium bicarbonate buffer were required to be able to substantially increase the molasses injection rate at Vandenberg without deleterious pH drops at the injection wells.

Optimization Time Required. Most ERD pilot systems are operated for a period of 6 to 18 months to gather the information needed to determine whether and how to scale up the system. At Vandenberg, a 26-month program, optimization time was prolonged primarily by buffering issues. The Vandenberg experience, as well as other applications, has led to the recommendation for presumptive use of a buffer for any aquifer with low buffering capacity. The effort of optimization should primarily be expended during the pilot phase to minimize any costs associated with delays or system modifications at larger scale.

Microbial Acclimation / The Role of Bioaugmentation. ERD systems can be subject to apparent stalling or long lag times that are attributable in part to the time required for substrate delivery, microbial acclimation, and in some cases, implementation of system modifications such as buffer additions to optimize the geochemistry of the system. At Vandenberg, a period of 20 months was needed to achieve the first evidence of complete dechlorination.

An alternate approach that has been suggested to reduce microbial acclimation time is bioaugmentation. While it may in some cases reduce lag times, bioaugmentation systems also require substrate addition to establish proper environmental conditions, and time for operational adjustments such as dosing level and buffer addition. Moreover, engineered recirculation systems must be designed and installed, and the regulatory permitting burden is often more time consuming for bioaugmentation than for biostimulation.

The practicality of bioaugmentation for cost-effective treatment of large areas has not yet been widely shown (Suthersan and Payne, 2003). Any consideration of the incremental cost/benefit of bioaugmentation must include not only the relatively modest cost of the culture, but also the very high cost of dense recirculation well networks and operation of a pumping system. Small differences in lag time are most likely to be critical at sites warranting urgent remedial action, unlike Vandenberg Site 35. Therefore, the added costs of bioaugmentation are likely to outweigh the potential benefit of reduced acclimation time at the demonstration site.

Long Lag Times to Complete Dechlorination. The lag time to complete dechlorination can be significant. Compared to many ERD sites, Vandenberg represents a relatively long lag time, both because it was initially aerobic and because of buffering issues. Remedies for both conditions are discussed in this report. During the pilot testing phase, it is important to define and address any conditions that may delay the onset of complete dechlorination. At Vandenberg, a scale-up design for ERD would incorporate a buffer in the reagent from start-up, which would be expected to cut the acclimation time significantly.

Vinyl Chloride Production. The formation of VC was not sufficiently extensive to be of concern at this site. Furthermore, reductive dechlorination of VC to ethene should occur with the ERD process (and has occurred in this demonstration); VC is also quickly biodegraded by aerobic microorganisms. For these reasons, the production of VC or other intermediate products is considered a temporary situation and does not represent a major impediment to the technology, but should be monitored during application of the technology.

Fermentation and Byproduct Formation. The formation of secondary byproducts including the ketones acetone and 2-butanone has been observed at some ERD sites. The occurrences of these byproducts are generally limited in space and time, and often sporadic. It is expected that they are utilized by microbes in the IRZ. Almost all of the ketones are aerobically degradable as well and so are expected to degrade on the downgradient edge of the reactive zone. Furthermore, almost all have higher risk-based limits than ERD target compounds. However, the possibility of production of these byproducts needs to be accounted for in the project planning stage. Careful and regular monitoring of groundwater should be provided to ensure that pH levels are not depressed and TOC levels are not excessive. In addition, the remedial plan should be flexible enough to allow for modification of both the delivery frequency and mass of organic carbon delivered, and in the case of poorly buffering aquifers, addition of a buffer.

Secondary Water Quality Impacts. Secondary water quality impacts (including metals mobilization and high COD/BOD) were observed during this demonstration, but as expected were limited to the area of the reactive zone and did not appear to be significant downgradient. Although ketones were generated as metabolic byproducts of molasses biodegradation, they did not appear to pose an appreciable risk.

Groundwater Chemistry Impacts. As seen at Vandenberg, the geochemical impacts of the IRZ may extend farther downgradient than the zone of effective treatment. Effective treatment at this site was limited to the first line of monitoring wells, but the zones of redox, TOC and bromide impacts extended approximately 120 feet downgradient. One of the goals of pilot testing is to determine the extent of such impacts so the design for the full-scale system spaces injection wells at an appropriate distance from potential downgradient receptors.

Cost Analysis

Cost comparisons provided in the report are based on a plume-wide application to a dissolved plume with sorbed material in a source area. Applied under appropriate conditions, ERD provides significant cost savings over conventional pump and treat technology, and compares favorably with other more innovative technologies in a comparison including ex-situ substrate-enhanced bioremediation with recirculation, a zero valent iron barrier and natural attenuation. Estimated unit costs will be provided at the conclusion of the project in the cost and performance report when complete financial information is available.

1. Introduction

This final technical report documents the demonstration of an innovative groundwater remediation technology performed at Vandenberg Air Force Base (VAFB) Site 35 by ARCADIS Geraghty and Miller (ARCADIS). The general purpose of the demonstration program was to evaluate the efficacy of the In-Situ Reactive Zone (IRZ) technology in removing chlorinated aliphatic hydrocarbons (CAHs) from impacted groundwater in a range of geologic conditions and CAH concentrations. VAFB was one of two locations at which the technology was applied for demonstration purposes. Data from the work at Hanscom AFB has been separately reported (Lutes, 2003). The work reported here was performed in accordance with the demonstration plan for VAFB (ARCADIS, 2000).

The demonstration has been completed as originally designed, and additional work performed at the site by some cooperative groups has been included in this report. However, additional results are expected from cooperative work performed on the site in 2003 by the U.S. Environmental Protection Agency (EPA)/Office of Research and Development (ORD)/National Risk Management Research Laboratory (NRMRL)/Subsurface Protection and Remediation Division (SPRD), AFCEE and the Army Corps of Engineers (COE). This work is expected to:

- Allow the potential for abiotic degradation of chlorinated solvents by minerals formed within the anaerobic zone to be evaluated
- Further characterize the downgradient fringe of the reactive zone (known as the redox recovery zone).

1.1 Background

Chlorinated solvent contamination of groundwater is a widespread problem at many military and civilian facilities. This class of compounds includes widely used industrial CAHs such as carbon tetrachloride (CT), methylene chloride (MC), 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 such diverse products as aircraft engines, automobile parts, electronic components and clothing. Contamination of groundwater by mobile metals (e.g., hexavalent chromium, lead, arsenic, nickel, mercury and cadmium) is also widespread at military facilities due to the use of these metals in ordnance, armament, armor, and as components of corrosion prevention coatings on vehicles. Because of the integral nature of CAHs and metals in efficient military operations, it is not surprising that the Unites States Armed Forces are often faced with widespread, costly remediation problems related to these compounds.

The conventional remedy for CAH contamination in groundwater is groundwater extraction and ex-situ treatment, typically with air stripping or carbon adsorption, also known as pump and treat or in-situ air sparging. An alternative to these conventional technologies that has already been used at over 140 commercial and 13 Federal sites is IRZ technology for the remediation of CAHs and metals. IRZ involves the addition of a food grade carbohydrate substrate, which serves as a supplemental energy source for microbiological processes in the subsurface. This substrate is typically molasses, but other substrates can also be used, including high fructose corn syrup, whey, etc. Through this subsurface molasses injection, the existing aerobic or mildly anoxic aquifers can be altered to highly anaerobic reactive zones. This creates suitable conditions for the biodegradation of CAHs and/or the precipitation of selected metals in insoluble forms. Thus this technology can be more specifically referred to as Enhanced Reductive Dechlorination (ERD) or Enhanced Anaerobic Reductive Precipitation (EARP). Other available innovative remedies for CAH contamination in groundwater include chemical oxidation, phytoremediation and vacuum enhanced recovery.

The primary benefits of this technology include its ease of regulatory acceptance, its in-situ nature and its relatively low cost. The benefits of ERD technology include its record of successful application under the following conditions:

- *At Various Constituent Concentrations* – Areas containing dissolved CAH concentrations in excess of 160 milligrams per liter (mg/L) have been successfully treated. Much more dilute plumes with concentrations of target constituents in the 10 – 100 micrograms per liter (µg/L) range have also been treated successfully.
- *In Varied Geologies* – The ERD technology has been applied at sites with widely differing geologic and hydrogeologic settings, from low permeability silts and clays, to high permeability alluvial deposits, to bedrock settings and with groundwater velocities ranging from a few feet per year to several feet per day. However, as discussed in Section 2, there are permeability and velocity limits beyond which the technology cannot be implied.
- *Under Multiple Regulatory Programs* – The ERD technology has been applied under multiple regulatory programs, including Comprehensive Environmental Response Compensation and Liability Act (CERCLA) and Resource Conservation and Recovery Act (RCRA), and under the jurisdiction of politically sensitive regulatory agencies such as the California Regional Water Quality Control Board. It has also been applied in several countries outside the U.S.

1.2 Objectives of the Demonstration

1.2.1 Objectives

The general purpose of this demonstration program was to evaluate the efficacy of the ERD technology to remove CAHs from the impacted groundwater in a range of geologic conditions and CAH concentrations. Ultimately, the objectives of the demonstration were to demonstrate the ability to remediate contaminants in the subsurface over a relatively short time period (from one to five years in typical full-scale applications) and also to gather information that can be used to estimate long term treatment effectiveness, life span and costs. The primary goal of this technology demonstration is to use the results to develop a protocol for use of ERD technology for CAHs at Department of Defense (DoD) facilities (this document, soon to be released, is formally titled “Technical Protocol for Using Soluble Carbohydrates to Enhance Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons” [Suthersan, 2002]). Performance objectives are discussed in more detail in Section 3.1. The demonstration helped determine the rates of mass removal of CAHs present in the groundwater at the demonstration sites. Also important in the demonstration was to show that the degradation of CAHs does not “dead-end” at undesirable by-products such as *cis*-DCE and/or VC.

To meet these objectives, a pilot test of the technology was conducted at Vandenberg Air Force Base (VAFB). VAFB is located near Lompoc, California, on the Pacific coast. The area selected for the demonstration was comprised of Sites 32 and 35 at VAFB (Figure 1-1). A TCE plume at Sites 32 and 35 has been investigated since 1994, and has exhibited TCE concentrations up to 6,200 ppb. The site met qualifying criteria for the IRZ demonstration including the following:

- The depth of the contaminated aquifer (about 31-41 feet bgs) was reasonably shallow. There are cost implications as the depth increases.
- CAH concentrations exceeded treatment standards by more than an order of magnitude.
- The hydraulic conductivity of site soils (1 ft/day) met the desired level (above 10^{-4} cm/s or approximately 0.3 ft/day).
- Sufficient site investigation information was available.
- No dense, non-aqueous phase liquid (DNAPL) was known to be present. This was a criterion for the demonstration but not for the technology in general.
- The available sulfate concentration (200-300 milligrams per liter [mg/L]) met the desired limit (<700 mg/L; though evidence has been accumulated at other sites suggesting that the technology can be applied at high sulfur sites).

1.3 Regulatory Drivers

Groundwater impacts by CAHs at DoD sites are regulated under the RCRA and CERCLA programs. Ongoing work at Installation Restoration Program (IRP) Sites 32/35 is overseen jointly by the California Environmental Protection Agency, Department of Toxic Substance Control (DTSC) and the California Central Coast Regional Water Quality Control Board (RWQCB) under a 1991 Federal Facilities Site Remediation Agreement (FFSRA), which addresses cleanup of IRP sites at VAFB. The FFSRA is a cooperative agreement that recognizes that, provided cleanup of IRP sites continues under DTSC and RWQCB oversight, enforcement actions will not be taken against VAFB. The Remediation Project Manager (RPM) for DTSC Southern Region is Quang Than; the RPM for the RWQCB is Mr. Bill Meese; and the VAFB RPM is Ms. Amena Atta.

ARCADIS is aware of no current cleanup standard negotiated between VAFB and regulatory agencies. In the absence of an existing negotiated cleanup goal, the default primary goal would likely be to clean up groundwater impacts to within drinking water standards, in accordance with the Regional Water Quality Control Board - Central Cost Region’s Basin Plan. For the CAHs at the site, these goals would default to primary maximum contaminant levels (MCLs).

1.4 Stakeholder/End-User Issues

Stakeholders and end-users of ERD technology are concerned foremost with the issue of CAH cleanup. Under appropriate conditions, ERD offers significant advantages over conventional pump and treat technology, including lower cost and reduced treatment time. The advantages and limitations of the technology are discussed in detail in Section 2.4. The production of intermediate products is a potential concern to stakeholders and regulatory agencies. The ERD process converts more highly chlorinated CAHs to less chlorinated and eventually non-chlorinated end products. The cascading reactions can result in the production of VC. This product is more carcinogenic than the parent compound. Reductive dechlorination of VC should also occur with the ERD process, and it is also quickly biodegraded by aerobic microorganisms. For these reasons, the production of VC or other intermediate products is considered a temporary situation and does not represent a major impediment to the technology but should be monitored during application of the technology.

Another stakeholder/regulatory issue can be the production of gases such as methane, hydrogen sulfide, and carbon dioxide, and the migration and potential accumulation of these gases in the vadose zone. Concentrations of these gases can accumulate in the subsurface during the treatment period, when structures in the vicinity do not allow for passive diffusion of these gases. For this reason, vapor-phase concentrations of these compounds are monitored when a potential concern exists to ensure that safe conditions are maintained. If required, venting of subsurface gases or a modified donor injection routine will be used to protect against exposure or accumulation. This issue is not considered to be a major impediment to technology implementation, but must be considered.

Secondary water quality impacts from ERD can occur due to the formation of generally transient by-products of substrate consumption as measured by parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), taste, odor, and sulfides. However these impacts are typically limited to the reactive zone itself. These byproducts, which are typical of many natural processes in which bacteria consume a food source, are generally rapidly consumed when the conditions become more aerobic on the edges of the reactive zone. Secondary water quality impacts can also occur from mobilization of metals naturally occurring in the solid phase into the groundwater. Although enhanced anaerobic in-situ bioremediation processes will, in general, reduce the mobility of many metals (indeed it has been successfully used for the treatment of many), it will solubilize some other naturally occurring metals in the reactive zone (e.g., iron, manganese, and arsenic). However, even in solubilized form under anaerobic conditions, metals such as arsenic are substantially retarded by adsorption to the aquifer matrix. Furthermore, it is generally believed that they will be reprecipitated/ immobilized downgradient of the reactive zone when the conditions return to their preexisting state (which, for the purposes of this discussion, is assumed to be aerobic). Similarly, reprecipitation/immobilization will occur within the IRZ area some time after system shutdown. These reducing conditions are by no means unique to IRZ systems – they occur, for example, at sites of total petroleum hydrocarbon (TPH) releases and landfills as well.

Molasses itself has been mentioned as a potential source of metals. Available analyses of metals in typical molasses-water mixtures used in IRZ applications have shown concentrations below regulatory standards. Injected metals did not produce secondary water quality issues in this demonstration (see Section 4.3.5). However, this is a potential issue that should be considered in the design phase for IRZ projects. The paucity of available data suggests that further work should be done to explore the metallic content of different sources of molasses.

Thus the potential for secondary water quality impacts needs to be fully identified and addressed during design and in consultation with all applicable regulatory agencies and the public.

As discussed in Section 4.3.5, secondary water quality impacts (including metals mobilization, high COD, BOD, TDS and sulfide) were observed but as expected were limited to the area of the reactive zone and did not appear to be significant downgradient. Although ketones were generated as metabolic byproducts of molasses biodegradation they did not appear to pose an appreciable risk. Gas production was not an issue at this site since the demonstration was conducted in an open pasture area, far from buildings or other structures where gases could accumulate.

2. Technology Description

2.1 Technology Development and Application

IRZ technology as used in CAH remediation is described in detail in a technical protocol document written under the demonstration program (Suthersan et al., 2002; soon to be available on government web sites).

2.1.1 General Technology Description and History

ERD technology is intended to facilitate and expedite the biological reductive dechlorination of CAHs through the well-documented mechanisms pictured in Figure 2-1. The ERD technology stimulates indigenous microbiological organisms through the engineered addition of electron donors, which contain degradable organic carbon sources.

The general mechanism behind the application of ERD technology relies on enhancing or inducing the bioremediation of CAHs through periodic subsurface injection of a soluble electron donor solution (typically comprised of a carbohydrate such as molasses, whey, high fructose corn syrup, lactate, butyrate, or benzoate). Through periodic subsurface substrate injection, the ERD technology alters existing aerobic or mildly anoxic aquifers to anaerobic, microbiologically diverse, reactive treatment zones. Within such zones, conditions are conducive for the bioremediation of CAHs.

ERD technology facilitates and expedites the degradation of CAHs through biological reductive dechlorination. Chlorinated compound reduction can be a biologically mediated reaction that entails transferring electrons to the substrate of interest from various initial electron donors. The more oxidized the chlorinated compound is, the more susceptible it is to reduction.

Reductive dechlorination occurs when aquifer bacteria utilize chlorinated solvent molecules as electron acceptors in the oxidation of their carbonaceous food source (electron donors). The reduction of chlorinated solvent molecules that are used as electron acceptors cleaves one or two of their chlorine atoms, leading to the sequential dechlorination pattern observed in many contaminated aquifers. Several bacterially mediated anaerobic processes that lead to reductive dechlorination are discussed in detail in Section 1.3 of the protocol document (Suthersan, 2002). By injecting a degradable carbon source into the aquifer, the rate and extent of bacterial reductive dechlorination can be enhanced to levels that provide a cost-effective remedial method. These reductive dechlorination processes include dehalorespiration (in which reductive dechlorination is used for growth with CAHs serving as the electron acceptor) and cometabolic anaerobic biodegradation (in which the degradation does not yield a metabolic benefit to the bacteria). These cometabolic processes typically occur under either sulfate reducing or methanogenic conditions

In practice, ERD can be operated as an in-situ bioreactor that forms downgradient from a line of degradable substrate injection wells placed in a line perpendicular to groundwater flow. If sufficient carbon substrate is injected, methanogenesis and reductive dechlorination zones form near the injection line, while sulfate reduction, nitrate and oxygen metabolism dominate farther downgradient. The technology operates most effectively when groundwater is passing through the sulfate-reducing zone, still bearing a degradable carbon load that will support methanogenesis and reductive dechlorination.

A conceptual design of this process has been provided as Figure 2-2. This technology can be implemented in a variety of ways, including fixed, automated systems and mobile, manually controlled systems (See also Sections 4 and 6 of the protocol document [Suthersan, 2002]). The particular system used in this demonstration was truck-mounted (see Figures 2-3 and 2-4 for a schematic and photograph of this system).

ERD technology developed from ex-situ biological reactor and precipitation technology, which has been routinely used for decades to treat a broad range of inorganic and organic compounds. However, some of these ex-situ processes involve addition of reagents, such as sulfide salts, which would be controversial to use in-situ. Efforts over the last 15-20 years have demonstrated that similar treatment approaches can be engineered in-situ. CAH biotransformation under anaerobic conditions has been studied for two decades at various scales (Vogel and McCarty, 1985; Parsons and Lage, 1985; Bouwer, 1993; and references cited therein). Researchers and remediation practitioners at ARCADIS recognized that biochemically-induced changes could be achieved without the need to inject potentially controversial reagents, and that naturally occurring mechanisms of attenuation could be enhanced.

In early 1994, when an innovative remedial solution for chromate-impacted groundwater was requested at a CERCLA site in Pennsylvania, ARCADIS chose molasses as a reagent to enhance these processes. In this case we avoided the technical, regulatory, safety and economic concerns associated with sulfide injection by using molasses to achieve reducing conditions. The Pennsylvania project clearly demonstrated that molasses IRZs could effectively produce controlled conditions required to remediate heavy metals. Subsequent projects have demonstrated the effectiveness of IRZs for remediation of CAHs and other organic and inorganic contaminants. Our experience has shown that molasses is not the only carbohydrate material that can be used for this purpose; other carbohydrates such as high fructose corn syrup and whey can also be effective. This approach has been accepted by regulators and has since been demonstrated in a wide variety of geological conditions with both high and low groundwater velocities. Enhancing CAH degradation using ERD has become an accepted practice in the last several years, but additional work remains to improve the design and optimize performance of ERD systems under varying conditions.

In addition to CAHs, ERD processes have demonstrated or potential application to a wide spectrum of contaminants and co-contaminants such as:

- Chlorinated cyclic hydrocarbons, e.g., pentachlorophenol (PCP)
- Chlorinated pesticides, e.g., chlorinated propanes, lindane
- Metal precipitation, e.g., Cr^{+6} to Cr^{+3}; metal sulfide complexes of nickel and copper; metal-humic complexes of beryllium and other metals
- Other halogenated organic contaminants

- Energetics such as perchlorate, TNT and RDX

2.1.2 Design Criteria

The key parameters that go into an IRZ/ERD system design include:

- Formation geochemistry (including the concentrations of electron acceptors such as dissolved oxygen (DO), nitrate, sulfate, pH and buffering capacity)
- Site-specific hydrogeology (including depth to water, saturated thickness, and hydraulic conductivity)
- Contaminant mass and form (dissolved, sorbed and free phase).

These parameters are discussed thoroughly in Sections 2 and 4.1 of the protocol document (Suthersan, 2002).

Ultimate design goals include contaminant removal rates and closure requirements (see Sections 1.2 and 3.1 of this report and Section 6.5 of the protocol document [Suthersan, 2002]). Interim design goals are set to ensure the creation of appropriate conditions for CAH biodegradation and may typically include these ranges for various field parameters (in this context, "monitoring wells" refers to wells 1 to 3 months downgradient of the injection wells):

- pH - > 4.0 s.u. in the injection wells; > 5.0 s.u. in the monitoring wells
- DO - < 1.0 mg/L in both monitoring and injection wells
- Oxidation-reduction potential (ORP) - > -400 mV and < -250 mV in the injection wells; < -100 mV in the monitoring wells. Note, however, that these ORP values should not be taken as absolutes since ORP is pH dependent. For sites where reducing environments are identified in the groundwater prior to initiation of reagent injections, a target goal of lowering the ORP by 200 mV in the injection wells and 100 mV in the monitoring wells should be employed.
- Total organic carbon (TOC) - >500 mg/L and < 9,000 mg/L in the injection wells and > 50 mg/L in the monitoring wells
- Specific conductance – order of magnitude increase in the injection wells; 20 to 50% increase in monitoring wells

To achieve those goals parameters that must be specified during system design include:

- Substrate to be used and initial dose rate
- Intended radius of influence/injection well spacing
- Injection and monitoring well layout (which may be a barrier, source zone or plume treatment system)
- Injection system type (manual vs. automated, conventional well vs. direct push etc.)
- Systems to handle byproducts (which may include the injection of buffers or the use of ventilation systems under structures).

These design considerations are discussed at length in Sections 4-6 of the protocol document (Suthersan, 2002). Pilot testing is usually required and adjustment or "tuning" of the system during operation is critical. These topics are discussed in Sections 5 and 6 of the protocol document.

2.2 Previous Testing of the Technology

As of September 2002, ARCADIS has been involved with more than 130 IRZ sites, across eight countries and 32 U.S. states. Forty-seven of these sites are full-scale implementations, five of which have achieved closure. The other sites are ongoing pilot applications, or Interim Remedial Measures, or they are completed pilot projects that are now in the full-scale design phase. The technology has successfully been applied to the following chlorinated compounds, energetics and metals:

- TCE, DCE, VC, CT, chloroform (CF), chlorinated propanes, PCP, pesticides, trichlorofluoromethane, and perchlorate;
- Hexavalent chromium, nickel, lead, cadmium, mercury, and uranium
- TNT, RDX and perchlorate.

Appendix A to the IRZ Protocol (Suthersan, 2002) includes a comprehensive table with information on ARCADIS IRZ sites for CAHs, as well as 15 case studies. Appendix A-1 of this document is an extensive bibliography of papers and book chapters published on this technology.

2.3 Factors Affecting Cost and Performance

Although application of IRZ using soluble carbohydrates can occur in a variety of hydrogeologic settings, there are certain conditions that are better suited for cost effective use of the technology. Existing conditions that are anaerobic or borderline aerobic/anaerobic but with insufficient TOC can be most rapidly treated. Conditions that are anaerobic and already have sufficient degradable TOC may not be aided substantially by addition of soluble carbohydrates. One of the most important criteria is hydraulic conductivity. Generally, hydraulic conductivity of the aquifer needs to be greater than 1 ft/day and when coupled with hydraulic gradients, groundwater velocities on the order of 30 ft/year, or greater, are desirable. Another important criterion is the pH, which needs to be initially in the range of about 5 to 9 in order to have an active microbial population. Site screening criteria and methods are discussed more fully in Section 2 of the protocol document (Suthersan, 2002).

The implementation of an IRZ project is a dynamic process which requires a detailed understanding of the site geochemistry and hydrogeologic conditions before implementation and as it changes as a result of pilot or full-scale implementation. This technology is most likely to be successful when there is considerable process monitoring during the initial deployment of the pilot test that allows for adjustment of reagent deliverability (strength and frequency). Where ERD has failed, or has required longer than expected treatment periods, it is usually the result of improper monitoring (the wrong parameters or the wrong frequency) or data evaluation in the early stages of the pilot test. 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 (or a buffering agent added), if pH levels drop too quickly.

Similarly, the effects of reagent injections must be reviewed in the context of how the addition of aqueous solutions affects hydraulic gradients (i.e., mounding) and flow directions. Groundwater flow directions and gradients should be viewed both in a macro and micro scale before and during the demonstrations.

Once a preliminary determination has been made that IRZ is an appropriate technology option to consider for the site, a more detailed data set needs to be gathered. Information required to fully review a site for IRZ includes:

- Site specific geology and hydrogeology, including: fraction of organic carbon (F_{oc}) in the aquifer matrix, boring logs, predominant aquifer lithology, aquifer hydraulic characteristics, horizontal and vertical hydraulic gradient, groundwater velocity, and depth to water
- CAH concentrations and distribution, both current and historical, if available
- If available, data on general groundwater quality such as TDS, specific conductance, pH, dissolved organic carbon (DOC), carbonate and bicarbonate alkalinity, and general cations/anions [calcium, magnesium, sodium, potassium, chloride, sulfate, and nitrate]
- Any previously gathered biogeochemical data, including ORP, nitrate, sulfate/hydrogen sulfide, ferric/ferrous iron, dissolved oxygen, trace gases (including methane, hydrogen, carbon dioxide, ethane, and ethene)
- The site's situation (regulatory drivers, stage in the investigation/remediation process, clean-up goals and time frames, future plans for the site)
- Some brief historical information on the site (source of CAH, estimated date of release, and duration of release events)
- Maps showing the relationship of active operational areas (buildings, etc.) and impervious surfaces (roads and parking lots) to the contaminant plume(s).

Table 2-1 provides a comprehensive overview of cost elements associated with an ERD project.

In a general sense, with an IRZ system, the cost of the reagent material itself is relatively insignificant. When using reagents such as carbohydrates, the cost per pound of TOC delivered is as outlined on Table 2-2. The selection of a carbon substrate(s) will be primarily driven by overall reaction rates, which are in turn controlled by the site conditions. A goal should be to minimize overall project cost by minimizing the number of required injection points, the number of injection events, and reagent cost (Harkness, 2000). The physical characteristics of the substrate (i.e., phase and solubility) may also make certain substrates more suitable than others in particular applications.

The majority of the costs related to reagent injection include the labor associated with preparing the reagent mixture and injecting the material into the wells/points along with related costs (mobilization to the site, record keeping, preparation, etc.) Temporary equipment required for the injections includes a solution mixing/holding tank, a portable mixer, a transfer pump, and injection piping/hose. This equipment should be sized and consistent with use at the pilot test site and can be mobilized to each site in a conventional pick-up truck or by trailer. The mixer can be as simple as a paddle, or agitation of the tank through truck movement. A nontoxic, non-reactive tracer or pH buffers may also be included in the reagent solutions. Permanent equipment at the various injections wells includes a removable well seal for the injection wellhead, removable perforated diffuser tubing (to assure even reagent distribution along the screened interval of the well), and quick-disconnect fittings to allow easy attachment of the injection piping/hose to the diffuser tubes for the injection itself.

Budgetary limitations can often directly or indirectly affect design decisions such as source reduction versus plume-wide treatment. Appendix A of the IRZ Protocol (Suthersan, 2002) contains specific information regarding the technology application cost (capital and operation and maintenance) at a variety of sites at which ERD has been successfully applied. Based on our experience and analysis, the two largest cost factors for ERD implementation are the injection well installation and the O&M associated with reagent injections. Three other factors that need to be given special consideration during design in order to develop the most cost effective approach for site remediation are:

- Plume Size to be Treated – This is the primary factor driving the cost of the technology, as the larger the plume area to be treated, the more wells are needed (drilling costs) and the more time it takes for reagent delivery.
- Depth of Target Zone – Drilling costs are the primary factor affecting overall technology cost. Therefore, deep contaminant settings and/or those requiring specialized drilling techniques (bedrock drilling, multiple conductor casings, etc.) can significantly increase costs. The depth to groundwater will define well design and contribute significantly to the capital cost of a full-scale system. The saturated thickness can also have an influence on cost, since there are practical limits on the maximum screened interval that can effectively be used in an injection well. Based on our experience, a 25-foot screened interval represents a practical limit for an injection point. Of course, this limit will be impacted by the heterogeneity of the subsurface lithology, hydraulic conductivity, and the resulting effects on groundwater flow characteristics. For example, if the lithology and resultant groundwater flow characteristics are such that there are variations in the flow characteristics within the target saturated interval, the use of multiple screened zones or multiple well points should be considered – even if the interval is less than 25 feet.
- Groundwater Flux through Zone of Treatment – Reagent injections also play a large role in overall technology costs. At sites in which there is a high groundwater flux, more substrate will be required, thereby increasing costs. In faster groundwater flow systems, the limited transverse dispersion in groundwater can limit the extent of the reactive zone created by an individual injection point. This is of particular importance in settings where drilling costs may be high, as with deep settings or complex geology. In such cases, an in-situ recirculation well can yield considerable cost savings over use of direct injection wells. The in-situ recirculation well concept aims primarily at delivering reagents in a cost effective manner while remediating larger, deeper contaminant plumes at sites with relatively high groundwater velocities.

2.4 Advantages and Limitations of the Technology

As late as 1998, conventional remediation options for sites contaminated with CAHs were considered to be air stripping, granular activated carbon adsorption, and ultraviolet oxidation (Nyer, 1998). Most of these technologies are the ‘treat’ portions of conventional pump-and-treat systems where impacted groundwater is removed to the surface for treatment and discharge. Pump-and-treat is known as a conventional technology with limitations due to long term operations and maintenance costs, which can be prohibitively expensive. These limitations stem from the fact that many contaminants partition preferentially to aquifer solids rather than the water carrier fluid. This results in moving vast quantities of groundwater while removing increasingly smaller portions of contaminant mass with time. Established remediation methods for metals removal also employ groundwater extraction followed by ion exchange or chemical precipitation. Like pump-and-treat for CAHs, these remedial techniques are costly and require long periods of time to complete.

The primary advantages for IRZ using soluble carbohydrates can be summarized as follows:

- The *in-situ* process 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 and co-contaminants
- No ex-situ waste is generated
- The process usually uses electron donor sources that are typically easily accepted by regulators and the public
- The biologically mediated reactions involved can generally be driven by indigenous microflora
- The technology is flexible in application, yielding a spectrum of contaminant mass treatment options from passive/containment barrier applications to aggressive source area applications
- The technology promotes reduction of residual contaminant mass through desorption and disruption of the contaminant phase equilibrium
- The technology enhances natural attenuation processes
- The technology is applicable to various geological settings and aquifer conditions
- The electron donor source is highly soluble and can move through both diffusive and advective processes into difficult lithologies such as fractured bedrock
- Systems can be designed with flexible operation approaches ranging from automated systems to manual bulk application
- IRZ can be used in tandem with existing remediation systems to optimize performance (discussed below)
- IRZ 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 using soluble carbohydrates. This can be compensated for to a great extent by a complete understanding of the geochemical and hydrological conditions of the aquifer system to be treated. A good conceptual model of the aquifer will produce a more effective IRZ design. Potential limitations to the application of the IRZ technology using soluble carbohydrates can be summarized as follows:

- Excessive depth of contamination tends to raise costs
- Low permeability aquifers require more injection points
- High permeability aquifers with high groundwater flows 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 substrate
- Limited porosity of contaminated media such as fractured bedrock minimizes the propagation of the treated area
- Biological fouling of injection wells or aquifers from reagent injection is theoretically possible but rarely constitutes a major problem in practice (see “System Maintenance” under Section 3.5.1)
- Systems with large amounts or influxes of electron acceptors such as oxygen, nitrate or soluble iron can require large doses of substrate; however, substrate cost is typically a small fraction of the total project cost. For such systems, frequent injections may add to project costs, or may warrant an automated injection system. In addition, the duration of treatment may be relatively long, also adding to total project costs.
- Potential production of excessive quantities of reduced gases such as methane can be problematic in the vicinity of confined structures. Also, production of byproduct organic compounds containing reduced sulfur or nitrogen, including hydrogen sulfide, is possible.
- Molasses in its pure form contains concentrations of several metals. In a dilute mixture, as is typically used in IRZ applications, the concentrations have been below regulatory standards. Injected metals did not produce secondary water quality issues in this demonstration (see Section 4.3.5). However, this is a potential issue that should be considered in the design phase.
- Longer lag times prior to effective treatment are noted in low concentration plumes
- Intermediate products such as VC can be formed; however, proper system design can ensure their further degradation
- Highly brackish aquifers can pose problematic microbial ecology
- The effectiveness of ERD on DNAPL has not been proven and is not the subject of this report. However other publications suggest potential effectiveness; see for example Jacobs (2003), Mowder (2004), Cope (2001) and Sorenson (2003).
- If not carefully controlled, fermentation effects of excessive molasses loading can create conditions conducive to formation of aldehydes, ketones and mercaptans, which, however, can then be further degraded biologically. Excessive fermentation can also decrease pH and potentially mobilize naturally occurring metals.

These potential limitations are general guidelines to be considered when evaluating potential sites for ERD treatment. Site-specific constraints should be considered for all remediation technology options.

Other innovative alternatives for the treatment of chlorinated aliphatic hydrocarbons in the saturated zone include chemical oxidation with permanganate or Fenton's reagent as well as various forms of reductive iron barriers.

2.4.1 Alternate Electron Donors

Alternate electron donors are also available for ERD. Commercially available carbon substrates vary in phase, degree of solubility, the speed with which the material becomes bio-available and is degraded, compositional complexity and cost. Examples of carbon substrate products for widespread field application include:

- Hydrogen (gas, very rapidly used)
- Butyrate, lactate, etc. (soluble, pure compounds, rapidly used)
- Corn syrup (soluble, readily consumed)
- Molasses (soluble, readily consumed)
- Vegetable oils (partially soluble, readily consumed)
- Yeast extract (partially soluble, readily consumed)
- Whey or other milk solids (in solid form, which can be dissolved in water and then is readily consumed, or liquid, slowly-to-readily consumed)
- Soluble humates (soluble, slowly consumed)
- Chitin (partially soluble, slow-release)
- Organic mulches (partially soluble, slowly-to-readily consumed)
- Hydrogen Release Compound™ (partially soluble, slow releasing)

A detailed discussion of the advantages and disadvantages of these various substrates is beyond the scope of this report. However, information comparing various substrates can be found in the protocol document prepared under this project (Suthersan 2002, Sections 1.1, 4.3, 4.5). The reader may also refer to Suthersan 2002B, section 4.2.1.4 "Electron Donors". Finally, these issues will also be the subject of a forthcoming document under preparation by a Tri-service group coordinated by AFCEE, tentatively entitled "*Principals and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents" (available August 2004).*

2.4.2 Use of IRZ with Other Technologies

IRZ has often been used in conjunction with other remedial technologies. Typical pairings of technologies would include

- IRZ used to supplement an existing pump and treat system until concentrations can be reduced to a level allowing the pumping system to be discontinued.
- IRZ in a high-concentration portion of a plume with pump-and-treat (or another containment or chemical/physical barrier technology) used to contain downgradient edge of the plume
- chemical oxidation for fast reduction of a limited source area with IRZ as a barrier or zone application in other portions of the plume
- IRZ in the highest-concentration portions of a dissolved plume with monitored natural attenuation in downgradient areas

- recirculation systems to hydraulically enhance the distribution of the IRZ substrate
- bioaugmentation with an ERD system to shorten lag times at sites showing no VC or ethene production, after a suitable period of biostimulation.
- aerobic approaches such as air sparging/SVE at the downgradient fringe of the reducing IRZ where VC production may impact a potential receptor

Reductive IRZ technology may be hampered by previous applications of chemical oxidation and may benefit in these cases from recirculation of groundwater from other areas of the plume. However it should be noted that several studies have suggested that biological populations rebound surprisingly quickly following chemical oxidation. Also, ongoing pump and treat systems in the IRZ area, if not consistent in their extraction patterns, may affect the even distribution of substrate.

3. Site/Facility Description

3.1 Performance Objectives

This demonstration is the second of a series of ESTCP/AFCEE funded demonstration projects that aim to evaluate the efficacy of the IRZ/ERD technology to remove CAHs from the impacted groundwater in a range of geologic conditions and CAH concentrations. A companion demonstration project at Hanscom AFB has been reported in a separate document (ARCADIS, 2003).

Primary and secondary performance objectives, as established and discussed in the demonstration plan, are presented in Table 3-1.

3.2 Selecting Test Site

The site chosen for this demonstration was selected and proposed based on ARCADIS' review of obtainable site characterization data. Most existing DoD-wide databases of sites are limited in the depth of information available, i.e., (1) they treat bases as a whole but do not provide information specific to each site or operable unit or (2) types of contaminants are listed but not concentrations or closure standards. Thus, candidate sites were obtained in a non-systematic, networking-based approach. Information on candidate sites was solicited from ARCADIS, AFCEE, ESTCP and the Army Environmental Center staff. The qualifying criteria used during this initial site review included the following:

- Depth (size) of the contaminated aquifer requiring treatment – generally, this is of little technical significance; however, there are cost implications as depth increases
- CAH concentrations preferably exceeding 10 times the treatment standard or 3 times the treatment standard AND 10 times the detection limit to allow easy detection of the effect of the treatment
- Site must exhibit at least moderate hydraulic conductivity ($K>10^{-4}$ cm/sec or 0.3 ft/day)
- Site should have completed an initial investigation, or be in the remedy selection process or have an operating pump-and-treat system in place
- Site should have no DNAPL present or DNAPL remedy selected/successfully implemented with ERD implementation as a polishing remedy. This was suggested just as a requirement for the initial demonstration site. The presence of DNAPL would represent a continuing source of dissolved CAHs that would complicate efforts to monitor the progress of the IRZ technology in a short-term demonstration.
- Available sulfate mass must correspond to the microbiology that is appropriate for the type of ERD desired. At the time the site was selected, there was concern that aquifers that are high in sulfate may not be conducive to developing microbiology that is appropriate for CAH remediation. More recent results suggest that the technology can be applied under high sulfate conditions.

During the review, site hydrogeology and other data were examined. Existing data on CAH contaminant and intermediate breakdown product concentrations and the site's current regulatory status were considered during the initial site screening. Candidate sites were chosen from a grouping of approximately 25 DoD sites with CAH impacts. These 25 sites do not constitute an exhaustive list of DoD sites that could benefit from the implementation of the ERD technology. Sites were selected based on a combination of factors. One important factor was adherence to technical constraints of ERD technology discussed above. ARCADIS also considered the economic issues that impacted our ability to provide a cost effective demonstration program at a number of DoD sites. Thus, factors such as depth to the water table and geographical location (proximity to one of ARCADIS' offices) were important in site selection. Geographical factors and depth to the water table are not typically involved in choosing to implement the ERD technology from a technical prospective. Lastly, the sites were judged as to whether they were good "field laboratories" in which ARCADIS could implement the ERD technology and interpret the results in a manner consistent with the goals of an ESTCP/AFCEE demonstration project. Sites with extremely low groundwater velocities were eliminated as incompatible with a short-term field program, although the technology can be applied at sites with low velocities as long as the aquifer hydraulic conductivity is reasonable.

Site selection criteria for ERD systems have been broadly described in Section 2 of the protocol document (Suthersan, 2002). Although application of ERD using soluble carbohydrates can occur in a variety of hydrogeologic settings, there are certain conditions that are better suited for cost effective use of the technology. One of the most important criteria is hydraulic conductivity. Generally, hydraulic conductivity of the aquifer needs to be greater than 1 ft/day and when coupled with hydraulic gradients, groundwater velocities on the order of 30 ft/year, or greater, are desirable. Another important criterion is the pH, which needs to be initially in the range of about 5 to 9 in order to ensure the presence of a microbial population suitable for microbial activity. Other general site selection criteria include:

- No large quantities of pooled DNAPL, or DNAPL remedy selected/implemented but a polishing step needed. (Note that the application of this technology for moderate amounts of, for example, emulsified or sorbed free product is an area in which initial results are promising. However, treatment in these situations is not as rapid as applications for dissolved/sorbed CAH contamination. Thus, we preferred to conduct this demonstration in a dissolved phase plume). Elevated concentrations of solvents may act as toxic inhibitors to biodegradation as well, especially for sites where the release is relatively recent (i.e., within 1 to 3 years) and the in-situ biological community has had little time to adapt and diversify.
- Sites that show some evidence of slow biodegradation, including those "stalled" at DCE and VC are desirable. The Vandenberg site, however, was challenging because it showed little evidence of biodegradation before treatment.
- The depth of the plume is also a factor in determining the cost effectiveness of an in-situ approach. The capital expense related to installing multiple injection wells in deep settings (greater than 50 feet below ground surface [bgs]), or in installing recirculation wells across thick homogenous settings needs to be compared to the costs associated with competing technologies.

Existing redox conditions that are anaerobic or borderline aerobic/anaerobic but with insufficient TOC can be most rapidly treated. Conditions that are anaerobic and already have sufficient degradable TOC may not be aided substantially by addition of soluble carbohydrates.

Table 3-2 summarizes evaluation criteria for implementing IRZ technology at Vandenberg per established site screening parameters.

Based on the available geologic/hydrogeologic and groundwater chemistry data, the ability to successfully implement ERD technology at Vandenberg appeared favorable. Calculated groundwater velocities and aquifer hydraulic conductivities (the ability to deliver reagents) at the site both appeared to be within acceptable ranges.

Field tasks for the pilot demonstration at Vandenberg were handled by the ARCADIS office in Fullerton (Los Angeles), California. The Los Angeles office had experience implementing ERD technology.

In summary, upon initial review, Vandenberg AFB provided a fairly standard site for IRZ implementation. In retrospect, several factors complicated its use as a demonstration site, including the low buffering capacity of the aquifer and a non-homogeneous flow field. However, a successful demonstration was conducted.

3.3 Test Site Description

3.3.1 Site/Facility Description

Sites 32 and 35 are located on San Antonio Terrace in the northern part of VAFB. Together, these sites comprise about 156 acres between El Rancho Road and El Rancho Oeste Road. The two sites share a common boundary composed of sections of Astral Road and Astro Road (unpaved section) (Figure 3-1). Due to their shared biological, geological, and hydrological settings, and their similar designs and histories, Sites 32 and 35 have been treated and studied as a “site cluster.” Reports prepared by Dames & Moore and the Air Force referred to Sites 32 and 35 as an Atlas F facility. Dames and Moore also reported that the silo facility at Site 32 served primarily as a training facility for actual operations at Site 35 and that the facilities at Site 32 were designed and constructed simultaneously with those at Site 35 with only minor differences in construction. Atlas F facilities reportedly used "dry pad" technology for launches. Dry pad facilities typically generated waste during missile launches, such as TCE, mixed solvents, lubrication oils, and hydraulic fluids (Reynolds, 1985). Seven Atlas missiles were launched from the Site 35 facility between 1962 and 1965, while two launches occurred at Site 32 in 1963 and 1964.

Based on the records search and site personnel interviews during the Resource Recovery and Conservation Act (RCRA) Remedial Investigation (RI), the primary contaminant sources at Site 35 included the silo facility and the waste dump. The primary release mechanisms at the silo facility involved pre-launch, launch, and post-launch activities, potential leakage from USTs, and potential leaching from the waste dump. Detailed descriptions of launch-related activities that may have affected groundwater quality are provided in the demonstration plan (ARCADIS, 2000).

Site 35 facilities include a missile silo, a control center, an instrument building, and a utility building (Building 1930), all within a barbed-wire fence. The only current onsite occupants of Site 35 are in Building 1930, which is a staging facility for the 1) Corrosion division, 2) Refurbishing division, and 3) the Equipment/Cranes division of the Missile Refurbishment Squadron. SIC codes 9711 and 3443 are applicable.

Surface features include five drainage channels (Channels A through D), each lined with concrete, and an unlined direct runoff away from the silo facility and control center (Figure 3-1). Except for Channel A, all channels at the site generally direct water from the northeast to the southwest. Channel A directs water to the northwest. These channels are hypothesized to be the original source of CAH contamination.

3.3.2 Site/Facility Characteristics

3.3.2.1 Topography

Topography within the Site 35 boundary slopes gently southwestward toward El Rancho Oeste Road from El Rancho Road. Topographic elevation across the site cluster varies from approximately 520 feet above mean sea level (msl) at the northeast boundary to approximately 290 feet msl at the southwest boundary. The average slope is 0.06 feet per foot.

3.3.2.2 Geology

Site 35 is located on the northeast margin of the San Antonio Terrace, a broad, flat platform formed in Pleistocene time. The stratigraphy of the site includes Orcutt Formation sediments at the surface, deposited unconformably on Sisquoc Formation shale and mudstone. The Orcutt Formation consists of loosely consolidated lenticular beds of sand, gravel, and clay of predominantly continental origin, with the upper zone representing eolian and beach sand (SAIC, 1990). The thickness of the Orcutt formation is approximately 40 feet in the demonstration area.

Soils at the site cluster consist of Tangair and Narlon type sands. Highly permeable Tangair type sands are found on the northeastern two-thirds of the site, while low permeability Narlon type sands are found on the southwestern third (cited as personal communications, Shipman, 1972 in Tetra Tech, 1999).

Bedrock beneath the site consists of the late Miocene Sisquoc Formation, which is "white to cream-white, punky diatomaceous claystone and clayey diatomite" interlayered with "light gray claystone and slightly diatomaceous or siliceous clay shale" (Dibblee, 1989). The contact between the Sisquoc Formation and the surficial sediments is an erosional surface and therefore tends to be irregular and unpredictable. Bedrock bedding planes strike north-northwest and dip to the southwest, approximately parallel to the topographic slope.

A series of marine transgression and regression episodes during the mid- to late-Pleistocene (Upson, 1949) may have caused significant erosion of the bedrock surface. The bedrock surface appears to be similar to, but gentler in slope than the topographic surface, and generally slopes from northeast to southwest with an average gradient of 0.07 feet per foot. The only bedrock outcrop observed in the immediate vicinity of Site 35 was near the pond on the southwest side of

Site 32. A spring was observed above the outcrop, suggesting that the bedrock is relatively impermeable and likely acts as an aquitard to the shallow groundwater zone. The flow rate of the spring was estimated to be 1 to 2 gallons per minute (Tetra Tech, 1999).

3.3.2.3 Hydrogeology

Site 35 is located immediately south of the drainage divide between San Antonio Creek Basin to the south, and the Shuman Canyon Basin to the north. Drainage of surface water is to the southwest, toward San Antonio Creek. A spring located just south of the intersection of El Rancho Oeste Road with Astro Road and a man-made pond south of the spring are the only perennial surface water features at the site. Storm water is routed through five drainage channels (Channels A through D), each lined with concrete, and an unlined direct runoff away from the silo facility and control center (Figure 3-1). Except for Channel A, all channels at the site generally direct water from the northeast to the southwest. Channel A directs water to the northwest.

Groundwater is unconfined and occurs within the Orcutt formation sands. Depth to groundwater varies from approximately 50 feet below ground surface (bgs) along the northeastern boundary of the site, to ground surface at the spring discharge to the southwest. Beneath the demonstration area at Site 35, the depth to groundwater is approximately 10 to 15 feet bgs, and the depth to bedrock is approximately 40 feet bgs. The predominant direction of groundwater flow is to the southwest (Figure 3-2), following the topography of the Sisquoc Formation bedrock, with a local hydraulic gradient of approximately 0.041 ft per ft (calculated between Site 35 wells 35-MW-7 and 35-MW-8), and a Site 35 hydraulic gradient of approximately 0.043 ft per ft. The layer of clayey weathered bedrock (Tetra Tech, 1999) reported at the Sisquoc/Orcutt formation contact and the low permeability Sisquoc shale are interpreted to prevent the flow of shallow groundwater into underlying bedrock.

Estimates of hydraulic conductivity (K) made before the demonstration ranged widely (Table 3-3). Based on aquifer slug tests and K tests of soil core samples collected from borings at Site 35, reported K values ranged from 2.1×10^{-5} feet/day to 111.5 feet/day (Tetra Tech, 1999). In the vicinity of the demonstration program, at well 35-MW-7, slug tests gave a K value of 1 ft/day. ARCADIS’ step drawdown test in August 2000 (reported in Section 4.3.2.1) yielded a K estimate of 0.92 to 3.83 ft/day, which is consistent with a silty sand material characteristic of the Orcutt formation at Site 35.

Before ARCADIS’ step test, groundwater velocity was calculated using the earlier K estimate for well 35-MW-7. Using the relationship $v = KI/n$, where I is the hydraulic gradient (0.041 as presented above) and n is porosity (estimated at 0.35 for silty sand), the average linear groundwater velocity was initially calculated to be approximately 0.12 ft/day. Using ARCADIS’ range of K values, average linear groundwater velocity was 0.11 to 0.46 ft/day.

3.3.2.4 Biotic Setting

A three-strand barbed-wire fence surrounds Site 35. The area within the fenceline at Site 35 consists of weathered pavement, free-standing structures, unvegetated areas, and areas that support iceplant or disturbed annual grasses. No permanent surface water is on site; however, a freshwater spring and a cattle pond exist within Site 32, west of El Rancho Oeste Road.

ARCADIS observed surface water in topographic depressions along the northeastern margin of El Rancho Oeste Road, near the southwestern Site 35 margin, during site reconnaissance in March 2000. A row of eucalyptus trees is located to the west of Site 35, presumably planted as a windbreak for the missile silos. The area surrounding Site 35 is dominated by annual grassland scrub habitat. A “waste” dump is located southeast of Site 35 in the grassland between Sites 32 and 35. Construction debris (e.g., broken concrete) is the primary waste observed in this dump.

3.3.2.5 Climate

The climate at VAFB near Site 35 remains relatively mild and constant throughout the year. The prevailing wind direction is from the west and northwest. The climate is categorized as subtropical (Mediterranean), receiving modest precipitation during the winter months (December through March), and little or no precipitation the rest of the year.

The VAFB 30th Weather Squadron compiles climatic data at various sites on base, including the Base Airfield, which is geographically similar to the site cluster in its altitude and distance from the Pacific Ocean. From 1952 through 1997, the annual rainfall at the airfield ranged from 4.00 inches to 28.40 inches, with an average of 14.16 inches per year (Tetra Tech, 1999). During California's drought period of 1984 through 1990, the annual rainfall at the airfield averaged 9.93 inches. During the IRZ demonstration, annual precipitation was close to average in 2001 with 14.68 inches, low in 2002 with 9.21 inches and slightly lower than average with 8.59 inches to date in October 2003.

The average annual temperature at the airfield from 1952 to 1997 was 57 degrees Fahrenheit (°F). Recorded temperature extremes from 1952 through 1998 were 25°F and 100°F.

3.4 Pre-Demonstration Testing and Analysis

The nature and extent of the dissolved CAH plume was characterized prior to the IRZ demonstration in an RI (Tetra Tech, 1999), in pre-demonstration sampling and analysis by ARCADIS and in a round of baseline groundwater sampling by ARCADIS. Additional Tetra Tech data, originally collected for evaluation of natural attenuation, was used by ARCADIS to determine site suitability for IRZ.

3.4.1 Distribution of CAHs in Groundwater

Chlorinated solvent impacts to groundwater at Site 35 consist primarily of TCE, and to a lesser extent degradation daughter products cis-DCE and trans-1,2-DCE (trans-DCE). TCE-impacted groundwater is present at its highest concentrations immediately southwest and downgradient from the Site 35 facilities. The suspected source of chlorinated solvents to Site 35 groundwater is the former use of solvents at the missile silo. Based on the area of highest TCE impact to groundwater, the likeliest transport mechanism is surface water drainage from the missile silo area to the channels, discharge to surface soils, and subsequent infiltration to groundwater. However, despite numerous soil CAH analyses in this area, no obvious elevated chlorinated hydrocarbon source in soils had been identified before the demonstration project. Depth-discrete groundwater sampling within the saturated zone has indicated that the highest TCE concentrations are found in groundwater flowing at the base of the Orcutt formation aquifer, near the interface with the underlying Sisquoc Formation. The maximum TCE concentration reported from Site 35 in groundwater prior to our work was from 1996 Hydropunch^{TM} sample 35-B-9 at a depth of 39 feet bgs (bottom of saturated zone), which had a TCE concentration of 6,200 ug/L (Figure 3-3 and Table 3.5-9 in Appendix B of ARCADIS, 2000). Well 35-MW-7, subsequently installed adjacent to 35-B-9, exhibited 2,900 ug/L TCE in 1998. Based on the pre-demonstration groundwater data, well 35-MW-7 was at the area of highest TCE groundwater impacts at Site 35.

In 2000, ARCADIS installed wells 35-MW-11 through 35-MW-20 in the vicinity of 35-MW-7 for the pilot IRZ test (Figures 3-4 and 3-5). Four wells were installed with conventional drilling techniques in August 2000; the Site Characterization and Analysis Penetrometer System (SCAPS) was used in September 2000 to install seven wells, three piezometers and five temporary well points. In October 2000, two additional injection wells were installed and two additional monitoring wells were installed with conventional techniques at locations where the SCAPS was not able to reach the desired depth. The wells installed and their characteristics are detailed in Table 3-7. The maximum pre-demonstration TCE concentration among the new wells obtained using an on-site hydrosparge technique was 4,000 ug/L at 35-MW-12.

ARCADIS and cooperators also drilled several additional borings to the east of the demonstration area in an effort to locate the source of the TCE plume. These borings were drilled near an existing transect of wells, just downgradient from the Site 35 buildings and drainage ditches. A groundwater sample collected by direct push and hydrosparge field analysis methods at a point almost directly east of the demonstration area (see 35-H-1C and 35-H-1B in Figures 3-4 and 3-6) had a concentration of 5,000 ug/L. This result identified a previously unknown area of high-concentration groundwater near the suspected source, between existing wells 35-MW-1 and 35-MW-6, both of which were nearly clean. If the CAHs in the demonstration area are related to the source at 35-H-1C, a westerly component of groundwater flow is implied between the two locations. In Figure 3-6, it is also notable that the CAH compound mix detected in the westernmost well, 35-MW-18, is substantially different from that in the other wells. This could possibly indicate a somewhat different source for this side of the plume.

The size of the TCE plume, estimated prior to the demonstration based on concentrations greater than 100 ug/L, was approximately 1,000 feet long, with a maximum width of approximately 425 feet. The plume was interpreted to extend from a distance of approximately 300 feet upgradient of well 35-MW-7, downgradient towards the area between wells 35-MW-8 and 35-MW-10.

3.4.2 Distribution of Metals in Groundwater

Metals were reported in Site 35 groundwater samples from 1996-1998, some at concentrations exceeding background threshold values (BTVs) and California Drinking Water Primary Maximum Contaminant Levels (see Table 3.5-6 in Appendix B of ARCADIS, 2000). However, filtered groundwater samples contained far lower concentrations; only nickel was reported in well 35-MW-1 at concentrations exceeding the MCL of 100 mg/L.

3.4.3 Natural Attenuation Parameters and Site Type Category

Selected wells at Site 35 were tested for natural attenuation parameters in 1994, 1996, 1998 (see Table 3.7-1 in Appendix B of ARCADIS, 2000). The additional monitoring parameters included chloride, nitrate, sulfate, fluoride, alkalinity, total organic carbon (TOC), total sulfide, carbon dioxide (CO_2), total dissolved solids (TDS), light hydrocarbon gases, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and ferrous iron. The wells selected for natural attenuation monitoring (35-MW-1 through 35-MW-8) represented areas with the highest measured CAH concentrations (e.g., monitoring wells 35-MW-7 and 35-MW-8) and down-plume or edge-of-plume areas with lower CAH concentrations. Background concentrations of chloride, total alkalinity and CO_2 were obtained from upgradient well 35-MW-5.

An RI Report for the site (Tetra Tech, 1999) concluded that, in general, groundwater conditions were not favorable for intrinsic bioremediation (natural attenuation): high DO (>0.5 mg/L), relatively high nitrate (>1 mg/L), low ferrous iron (<1 mg/L), high sulfate (>20 mg/L), non-detectable sulfide in the contaminated zone, non-detectable methane (<0.5 mg/L), moderately high oxidizing ORP (>50 mV), low TOC (<20 mg/L), low temperature (<68 °F [20 °C]), and non-detectable ethene/ethane (Tetra Tech, 1999). However, the presence of degradation daughter products including both cis-DCE and trans-DCE in groundwater beneath the site suggested that some limited reductive dechlorination had already naturally occurred. Of note was the apparent lack of a carbon source in groundwater. Since it is a relatively simple means with which to augment the carbon supply, and in turn drive the aquifer anaerobic through bacterial consumption, ARCADIS concluded that induced reductive dechlorination at Site 35 was feasible. This was supported by the moderate groundwater velocity (estimated at 0.12 feet/day in the area between wells 35-MW-7 and 35-MW-8), the limited thickness of the contaminated aquifer, and the limited TCE concentrations in groundwater, which were not expected to be inhibitory to microbial growth.

Microbial counts conducted on Site 35 groundwater samples in September 2000 established the numbers and types of bacteria present before the demonstration. Phospholipid Fatty Acid (PLFA) analysis suggested the existence of an actively dividing, gram negative bacterial community in a non-toxic environment. Denaturing Gel Electrophoresis (DGGE) analysis showed a bacterial community dominated by facultatively anaerobic gram negative bacteria. Microcosm tests performed by EPA ORD/NRMRL/SPRD on saturated soil samples before treatment were inconclusive, and are discussed further in Lutes (2002).

The behavior of chlorinated solvent plumes with respect to reductive dechlorination has been categorized into three types (USEPA, 1998). Type 1 behavior occurs in the presence of anthropogenic carbon, and results in the rapid degradation of the more highly chlorinated solvents, provided that anaerobic conditions and an adequate supply of carbon substrate exist. Type 2 behavior is similar to Type 1, but is driven by a relatively high concentration of biologically available natural organic carbon rather than an anthropogenic carbon source. Biodegradation is generally slower with Type 2 than with Type 1 conditions. In both cases, the role of competing electron acceptors and the fate of VC are variables to be considered. Type 3 behavior dominates where little carbon is available and conditions are aerobic, or where the microbial community is incapable of chlorinated solvent biodegradation. Reductive dechlorination does not occur under Type 3 conditions, but VC may be oxidized in an aerobic environment.

At Vandenberg, only trace components of petroleum hydrocarbons have been detected in groundwater, and pre-demonstration TOC levels (presumably of natural origin) were limited, ranging from 4 to 6 mg/L. Background DO levels above 1 mg/L indicate an aerobic setting. However, the first stage of TCE degradation to DCE was observed to a very limited extent before treatment. Plume behavior at Vandenberg thus has characteristics of both Type 2 (natural carbon source, slow biodegradation) and Type 3 (low carbon, aerobic) behavior. However, in spite of the evidence of partial biodegradation, the biochemistry suggests that Type 3 behavior predominates at Vandenberg. Complete and efficient degradation would not be expected under these pre-existing circumstances – that are probably not methanogenic or sulfate reducing but rather probably predominantly aerobic or possibly denitrifying or iron reducing. As shown in Table 1-1 of Suthersan, 2002 (reprinted from various ITRC sources), TCE degradation under denitrifying and iron reducing conditions has been observed, but DCE and VC treatment has not. Thus, we have an internally consistent picture of the starting conditions that is also in agreement with our overall theoretical understanding of these processes developed based on experience at other sites and in the literature (Suthersan, 2002).

3.4.4 Soil Sampling and Analysis

Two soil samples, one blank and one duplicate were obtained in August 2000 during well installation (35-I-2 and 35-MW-11). Results showed that TCE in soil ranged from 13-61 ug/kg, and the TOC concentration was <2,000 mg/kg. The soils were classified based on sieve tests as “silty sand” or “poorly graded sand with silt”.

3.4.5 Conceptual Site Model

Based on discussions presented in the above sections and further developed in the RI Report (Tetra Tech, 1999), TCE historically used at the missile silo at Site 35 has flowed downslope into a series of channels, infiltrated vertically through the soil profile and impacted the underlying groundwater. Although no definitive soil source has been clearly delineated, an area of high TCE impact, centered downgradient from the point at which the lined portion of Channel B discharges onto surficial soils, is consistent with such a release model. Another area of high TCE impact, identified during pre-demonstration drilling, is downgradient from the Utility Building.

Site 35 groundwater is unconfined and occurs entirely within the Orcutt formation sands, which unconformably overly the diatomite and diatomaceous siltstone of the Sisquoc formation. This aquifer configuration affords an effective bottom to the unconfined aquifer and is thought to restrict vertical migration of groundwater contaminants. The aquifer is characterized by moderate velocities (estimated as 0.12 feet/day in the area of highest impact). Groundwater conditions are aerobic, and the magnitudes of TCE concentrations reported were not indicative of a DNAPL source (based on a rule of thumb of 1% of solubility indicating the presence of DNAPL).

The hydrogeology and chemistry of the Site 35 TCE plume afforded a high degree of control for the technology demonstration:

- The flow path was linear to the southwest
- The nature of the TCE-impacted groundwater was adequately defined and limited in thickness
- TCE degradation products were not present in high concentration
- Groundwater baseline data were available to measure subsequent changes in groundwater conditions

In addition, the depth to groundwater beneath the site was shallow, at about 15 feet below grade in the area of highest impacts. These conditions lent themselves well to engineering design of a remedial strategy. Given the high levels of DO in the Site 35 plume, efforts to induce reductive dechlorination were expected to work due to the limited thickness, reasonably permeable sediments, and moderate groundwater flow rates.

3.5 Testing and Evaluation Plan

Operational and experimental methods for the ERD demonstration from system start-up through demobilization are discussed in this section.

3.5.1 Demonstration Installation and Startup

The pilot system was comprised of a truck-mounted substrate delivery system that was transported to the site for each injection event. Injections of the dissolved molasses solution were initially delivered at a design dosing rate calculated on the basis of subsurface physical and biogeochemical characteristics. Subsequently, the dosing was altered as needed at individual injection wells based on process monitoring data (primarily TOC and pH). At VAFB, since low pH was a limitation on the carbon dosing rate, a “clean water push” was occasionally used to disperse the injected carbon further into the formation immediately following an injection. This allowed the molasses injection rate to be increased without further pH drops at the injection well. A sodium bicarbonate buffer was eventually added to the injectate to help stabilize the pH. Permission for buffer additions was granted by the RWQCB and DTSC in a letter dated October 15, 2002.

Physical setup for the VAFB system was minimal. Permanent equipment was limited to injection and monitoring wells. Injection wells were supplied with removable well seals with fittings to allow for connection of supply hoses. Utility requirements were limited to a source of potable water for mixing of the molasses solution. The demonstration area, including pre-existing wells and new sample locations, is shown in Figures 3-4 and 3-5.

The temporary equipment required for the injections included the following: a solution mixing/holding tank, a gasoline powered transfer pump, and an injection hose. A schematic of the injection system is presented in Figure 2-3. Start-up testing of the injection system involved filling the tank with water to check for leaks. The tank and associated pumps generally functioned without difficulty. Temporary equipment, molasses, and reagents (sodium bicarbonate buffer, bromide tracer), were stored in an existing site building. A conventional pick-up truck was used to transport the equipment to the injection well for each injection event.

Injection events generally involved first testing the pH in the injection wells and consulting guidance provided by the project manager as to what injections to make depending on the observed pH. Then the reagent solution was mixed manually, and the injection system was connected to the injection wells, and the solution was pumped into wells. During some events, the solution injection was followed by an injection of clean water. A single batch of reagent solution (for one injection well) consisted of 10 gallons of food-grade blackstrap molasses, 100 gallons of potable water, and 113 grams of potassium bromide as a conservative tracer. Mixing of the reagent solution was accomplished by partially filling the solution tank with water, adding molasses and potassium bromide to the tank, stirring the tank manually for several minutes with a polyvinyl chloride stir rod, and then filling the tank to the desired volume with clean water. Injection volumes for individual wells typically ranged from 5 to 20 gallons of molasses.

Once mixed, the solution tank and injection equipment was transported in a pickup truck to the injection wells. Hoses were connected between the solution tank, transfer pump, and injection well. The system valves were then opened, the pump was operated until all of the reagent solution had been transferred to the well. If a double injection was planned, a second batch of reagent solution was mixed and injected using the same procedure. Following the injection of reagent solution, if a water push was to be injected, the solution tank was filled with 100 to 200 gallons of clean water, which was injected using the same procedure.

The reagent solution injection proceeded at a rate of approximately five gallons per minute at observed well head pressures of approximately 18 to 20 pounds per square inch gauge pressure. Labor required for each event at the initial injection rate was approximately four to six hours for a single batch injection, with an additional and one to two hours for a double injection.

System Maintenance

Very little maintenance or repair work was required during the demonstration. The system required occasional replacement or adjustment of fittings, repair of the molasses injection pump, and redevelopment of two injection wells (35-I-1 and 35-I-3) early in the demonstration. The redevelopment was undertaken after it was noted that well 35-I-2 had much greater rates of TOC consumption /dilution than the other two injection wells, which was attributed to its use in the aquifer test.

Given the enhanced biological nature of the in-situ remedy being used, there is some chance of biological fouling developing in and around the reagent injection wells (i.e., the well screen itself or possibly the well filter pack). However, given that the biological growth is anaerobic in nature, the actual mass of biological growth is typically minimal (as compared to biomass related to aerobic processes commonly observed in other remediation areas such as pumping wells or above-grade water treatment). In the case of reagent injection well fouling or plugging, a typical remedy would be to surge the well using a surge block to induce turbulence in the well and break up the biological mat. Well fouling can lead to difficulty in conducting subsequent injections and may ultimately lead to loss of the well for injection purposes. However, injection well fouling was not an issue at the VAFB demonstration. None of the injection wells had increased pressure requirements for injection.

Safety issues were limited to those associated with handling equipment (vehicles, pumps, hoses, fittings) in the field, and working with contaminated groundwater from wells. No hazardous materials were used in the injection solution or generated during operation of the system, with the exception of purge water from the wells.

3.5.2 Period of Operation

Dates of major events relevant to the demonstration are summarized in Table 3-4. A total of 31 injections were conducted between February 2001 and April 2003, for a total of 27 months of active system operation. In addition, data collected in July 2003 by US EPA, and in February

2004 by Tetra Tech, indicates that the treatment system was still effective at that time; thus 30 to 36 months of enhanced biodegradation were observed.

3.5.3 Amount/Treatment Rate of Material Treated

During the 27 months of active system operation, a total of 683 gallons of raw blackstrap molasses, 6,830 gallons of dilution water, 1,500 gallons of push water, 7,718 grams of potassium bromide and 669 pounds of $NaHCO_3$ were injected into the system. The average molasses injection rate for the three injection wells combined was 48 lbs/week before the buffer additions, and 123 lbs/week after the buffer additions. Rolling average loading rates over the period of treatment are shown in Figure 3-7.

The volume of molasses injected varied for the three injection wells. The total volumes injected were 195 gallons at 35-I-1, 333 gallons at 35-I-2 and 140 gallons at 35-I-3. Rolling average loading rates per injection well are shown in Figure 3-8.

3.5.4 Residuals Handling

No hazardous waste was generated during the setup and operation of this demonstration, except for soil (drill cuttings) generated during injection well and monitoring well installation, and purge water generated during well development and sampling. Purge water was treated in a wastewater treatment process and disposed. Soil cuttings were stored in 55-gallon drums, characterized and disposed of at a licensed hazardous materials disposal facility.

3.5.5 Operating Parameters for the Technology

A description of operating procedures and labor requirements for the ERD demonstration is given in Section 3.5.1. Carbon dosing was variable during the demonstration, as was the use of water injections to disperse the substrate. These parameters were determined on the day of the injection event based primarily on the pH measurement in the injection well, but also on more detailed process monitoring conducted at regular intervals during the demonstration. Section 4.3.3 contains a discussion of process monitoring parameters and process control throughout the project.

Performance monitoring (to assess technology efficacy) for this demonstration was conducted using a high level of quality assurance analysis during three full sampling rounds and four abbreviated sampling rounds. Analytical parameters, methods and analysis locations/ organizations are specified in Table 3-5. Furthermore, records were kept of the color, odor and other readily apparent characteristics of the sampled groundwater.

3.5.6 Experimental Design

The experimental design for the project was established in the demonstration plan (ARCADIS, April 2000). In brief, the types of measurements made are listed below. Discussions on the methods and outcomes of each type of data collection are provided elsewhere, as cited.

- Soil characterization – Section 3.5.7.1.5 – Soil samples were collected during well installation and analyzed for the parameters listed in Table 3-6.

- Process monitoring – Sections 3.5.7.2, 4.3.3 – In 29 periodic events, measured DO, pH, ORP, specific conductance, temperature and water level. In addition, used field test kits to analyze for hydrogen sulfide and ferrous iron, and laboratory analysis for bromide and TOC.
- Full and abbreviated groundwater monitoring – Sections 3.5.7.1.3, 4.3.4, 4.3.5 - three full and four abbreviated sampling rounds were conducted, with analysis for the parameters listed in Table 3-5.
- Process control – Sections 4.3.3.1 – Varied carbon dosing and water pushes in 31 injection events based on continuous evaluation of groundwater monitoring data.

3.5.7 Sampling Plan

The project sampling plan was developed on the basis of ARCADIS' previous experience at commercial ERD sites and existing site data for the Vandenberg demonstration area. The sampling plan is detailed in the project's demonstration plan (ARCADIS, April 2000), which also contains the project QAPP.

3.5.7.1 Sample Collection

Field methods are described in this section for well installation, aquifer testing, and sampling of saturated soils, groundwater and dissolved gases.

3.5.7.1.1 Well Installations

Four wells were installed using conventional HSA drilling techniques in August 2000. These wells were used for initial aquifer testing and to obtain soil and groundwater samples for pretreatment analyses and lab-scale treatability studies. In September 2000, seven additional wells and three piezometers were installed by the COE (Kansas City, MO) using a Site Characterization and Analysis Penetrometer System (SCAPS) rig. In October 2000, two additional injection wells were installed using conventional techniques to complete the demonstration zone well layout, and two monitoring wells were installed at locations where the SCAPS rig was not able to reach the desired depth. A total of three injection wells and eleven monitoring wells (two upgradient, nine downgradient of the injection wells) were used for the demonstration project (Figure 3-5). Table 3-7 summarizes well construction data.

In addition to installing wells for the demonstration test, the SCAPS rig was used to drill temporary borings in an attempt to locate a CAH source area. At five borings east of the demonstration area, temporary well points were constructed similarly to the demonstration area wells (total depth approximately 40 ft bgs, 10 feet of pre-packed 0.75-in ID well screen). A groundwater sample in the casing was hydrosparged to collect volatile gas samples for direct sample ion trap mass spectrometer analysis for CAHs. These borings are identified on Figure 3-4 as hydrosparge locations.

3.5.7.1.2 Aquifer Test

ARCADIS conducted a step-drawdown test on August 29, 2000 on injection well I-2 to determine the hydraulic conductivity of the target zone for the pilot test. Drawdown monitoring was conducted at I-2 and monitoring wells 35-MW-7, 35-MW-11, 35-MW-14 and 35-MW-20. Groundwater drawdown measurements were collected at three pumping rates: 1.0, 1.5 and 1.7 gpm, and during the recovery phase.

3.5.7.1.3 Groundwater Sampling

Groundwater sampling methods used by ARCADIS at VAFB Site 35 during the IRZ demonstration were of three types:

- Full monitoring events included field and biogeochemical parameters as well as CAHs. These events were intended to evaluate the effectiveness of the technology and to provide a complete picture of the microbial processes ongoing.
- Abbreviated monitoring events included CAHs and a limited set of field and biogeochemical parameters. These events were intended to evaluate the effectiveness of the technology.
- Process monitoring events included field parameters and occasionally TOC and/or bromide, but not CAHs. These events were used to control system operation.

In addition, EPA (Robert S. Kerr Environmental Research Center, Ada Oklahoma) collected groundwater samples on July 22-23, 2003 as part of an ongoing investigation of CAH degradation mechanisms. During this round, the standard operating procedure RSKSOP-214 rev 2 was used for inorganic analyses, RSKSOP-122 rev 2 was used for volatile organics, and RSKSOP-148/1 headspace GC/MS was used for the chlorinated VOCs. RSK-SOPs 194 and 175 were used for the light hydrocarbon gases and hydrogen. Additional work using a SCAPS rig is expected to be performed at the demonstration site by AFCEE and the COE Kansas City district SCAPS team. The EPA data (a similar but more abbreviated list of parameters than ARCADIS' full monitoring list) are incorporated into the attached graphics.

Sampling methods used in ARCADIS monitoring events were as follows:

Full Monitoring Events. Three full monitoring events were conducted, in November 2000 (pre-treatment), April 2002 (judged to be the mid-point of treatment) and May 2003 (at the end of active treatment). Groundwater samples were collected using low-flow methods with a peristaltic pump and an FC5000 flow cell, with one exception. Well 35-MW-7 initially contained a dedicated QED bladder pump. During the first full monitoring event, this well was purged and sampled with the bladder pump, a QED controller and related equipment. Analytical methods are listed in the VAFB Demonstration Plan (ARCADIS, 2000). Laboratory analyses included the following:

- Volatile organic compounds (VOCs)
- 23 Metals (total and dissolved [field filtered] Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Th, V, Zn)
- Dissolved gases (methane, ethane, ethene, carbon dioxide, hydrogen, nitrogen, oxygen)
- Water quality parameters (alkalinity, ammonia, nitrate, nitrite, sulfate, chloride, bromide, COD, BOD, TOC, DOC)
- Microbial tests (performed infrequently; included phospholipid fatty acid [PLFA] analysis, denaturing gradient gel electrophoresis [DGGE] profiling, volatile fatty acids [VFAs] analysis and targeted gene detection for *Dehalococcoides* ethenogenes [DHE] detection)

Analytical methods are listed in the VAFB Demonstration Plan (ARCADIS, 2000). Parameters measured with a field meter in the flow cell included initial water level, pH, temperature, specific conductance, DO and ORP. Hach® test kits were used to measure hydrogen sulfide and ferrous iron (plus total iron and manganese in November 2000 only) before laboratory samples were collected. An in-line hydrogen stripper/sampler was used with the flow cell for hydrogen sampling. Samples for DOC, dissolved TOC and dissolved metals were field-filtered with a disposable 50-micron in-line water filter. Field blanks, duplicates and MS/MSD samples were also collected during these events.

Abbreviated Monitoring Events. Four monitoring events conducted in August 2001, October 2001, January 2002 and October 2002 targeted an abbreviated list of analytes. Groundwater samples were collected using low-flow methods with a peristaltic pump and an FC5000 flow cell. Hach® test kits were used to measure hydrogen sulfide and ferrous iron before laboratory samples were collected. Selected samples were field-filtered with a disposable 50-micron in-line water filter. No duplicates or MS/MSD samples were collected during these events, but field blanks and trip blanks were collected.

Process Monitoring Events. Twenty-nine process monitoring events conducted between March 2001 and May 2003 targeted field measurements and, as needed, TOC and bromide. (Bromide was added to the injectate as described in Section 3.5.1 as a conservative tracer to account for effects of dilution.) Several sampling and measurement methods were used, depending on well diameter and well type. At injection wells 35-I-1, 35-I-2 and 35-I-3, down-hole pH readings were collected before injections to determine molasses injection volumes. In the 2" diameter monitoring wells, down-hole measurements were made with the FC5000 sonde, and samples for TOC or TOC/bromide were collected with a disposable bailer. In the ¾" monitoring wells, low-flow methods were used with a peristaltic pump and an FC5000 flow cell to collect measurements and samples.

3.5.7.1.4 Dissolved Gas Sampling

ERD processes produce gases that can provide useful information about the process. Additionally, in some cases, the gases produced may need to be managed for health and safety reasons. The evaluation of the potential for problems with gas generation is generally done as part of engineering design of a system. The depth to the zone of interest, likely paths for vapor migration, proximity of structures and other receptors and potential volumes of gases produced are assessed in this context. For the Vandenberg demonstration program, it was determined that there were no causes for concern about gas generation hazards or nuisances since no structures lay over the demonstration zone, which was located in a pasture.

Standard low-flow sampling techniques are used as the basis for sampling groundwater for dissolved hydrogen analysis as hydrogen is an extremely volatile gas that can easily be lost to the atmosphere if exposed to air particularly under turbulent conditions. The use of a flow-through cell increases the protection of samples/measurements against atmospheric loss or contamination. As such, Chapelle et al. (1997) describe a gas stripping method (also known as the “bubble strip” method) for dissolved hydrogen sampling of groundwater monitoring wells. The gas stripping sampling method and associated analysis (Wiedemeier, et al., 1996) has been incorporated by analytical laboratories performing dissolved hydrogen analysis (in this case

Vaportech). They have developed relatively straightforward sampling kits and instructions which draw heavily on the gas stripping sampling method, and were employed here.

Other essential dissolved gas parameters monitored during the demonstration included light hydrocarbons, namely methane, ethane, and ethene. These samples were collected in glass bottles provided by the analytical laboratory using low-flow methods.

3.5.7.1.5 Saturated Soil Sampling

During the HSA drilling program, soil samples were collected from within the saturated portion of the aquifer that was targeted for treatment. Samples were collected by driving a split spoon into formation using a 140 pound weight. Two field-composited samples were collected: one from within the saturated zone at injection well I-2, and one from within the saturated zone at monitoring well 35-MW-11. One duplicate sample and one field blank were also collected. Soil analytes were CAHs, TOC and grain size.

3.5.7.1.6 Sample Shipment and Labeling

Sample sets were accompanied by a chain-of-custody form. Prior to shipment or transfer of custody, all samples were maintained in the custody of the field manager. Upon transfer of custody, the field manager verified the information on each sample label and assured that each container was intact and sealed using custody tape. He/she then signed and dated the chain-of-custody form. The individuals receiving the samples also signed, dated, and noted the time that they received the samples on the chain-of-custody form. This form documents transfer of custody of samples from the field investigator to another person, to the laboratories, or to other organizational elements.

Samples were properly packaged for shipment and delivered or shipped to the designated laboratory for analyses. Because common carriers (Federal Express, Airborne Express, etc.) will not sign chain-of-custody records, the original chain-of-custody form and one copy of the form was placed in a plastic bag inside the secured shipping container when samples were shipped. One copy of the record was retained by the task field manager.

Shipping containers were secured shut using nylon strapping tape and custody seals. A custody seal was placed over the lid of the sample cooler to indicate whether the cooler had been opened during shipment prior to receipt by the laboratory. The original chain-of-custody form was transmitted to the project manager after samples were accepted by the laboratory. This copy then became a part of the project file.

A sample identification system was used to enable the field personnel to establish unique and appropriate identifications for each sample collected. This system incorporated identifiers for the site, sample matrix, the sample location, and the sample number. Field duplicates were designated by the sample code DUP, while equipment, field, and trip blanks were designated with the sample matrix codes EB, FB, and TB, respectively.

The site identification code for Vandenberg was VAN. The matrix codes included:

- SS – Soil

- GW – Groundwater
- SG – Shipped ground water sample for hydrogen analysis

Location codes were assigned in the field. Sample numbers were assigned in the field. Thus, for example, a groundwater sample at Vandenberg might have been coded: VAN-GW-35-MW-13. A duplicate of that sample would then have been coded: VAN-GW-35-DUP-1. A trip blank for groundwater would be coded: VAN-GW-35-TB-1.

3.5.7.2 Sample Analysis

ESTCP demonstration sites are subjected to rigorous performance monitoring. Performance monitoring (to assess technology efficacy) for this demonstration was conducted using high quality assurance, low-flow groundwater sampling techniques and analysis during three full sampling rounds and four abbreviated sampling rounds. Analytical parameters, methods and analysis locations/organizations for groundwater and soil samples are specified in Tables 3-5 and 3-6. Furthermore, records were kept of the color, odor and other readily apparent characteristics of the sampled groundwater.

The results of routine process monitoring were used to modify injection protocols and make other process control decisions, in an effort to maintain reducing conditions while avoiding overly depressing pH. Process monitoring was conducted using portable field instrumentation (e.g., Horiba U-22) and varies from relatively low QA (e.g., using down-the-well sondes) to relatively high QA (e.g., using flow-through cells) to measure DO, pH, ORP, specific conductance, and temperature. In addition, field test kits are used to analyze for hydrogen sulfide and ferrous iron, and samples are periodically submitted for laboratory analysis of bromide and TOC. Twenty-nine process-monitoring events were conducted at Vandenberg. Table 3-8 is a week-by-week summary of the demonstration including injections and sampling events. The only groundwater sampling rounds not listed in this table are the initial full sampling round conducted in November 2000 and site-wide monitoring performed by Tetra Tech throughout the demonstration.

Finally, one soil sample per installed well was analyzed for the parameters listed in Table 3-6, which also summarizes the laboratory used, sample size, preservation, holding time, etc. Further details of these methods are contained in the final demonstration plan.

3.5.7.3 Experimental Controls

Experimental controls included the use of background wells 35-MW-14 and 35-MW-15, and other wells outside of the treatment zone in the groundwater monitoring program. Results for these control samples are discussed in Sections 4.3.4.3.1 and 4.3.3.3.4.

3.5.7.4 Data Quality Parameters

Representativeness, completeness, comparability, accuracy and precision of the demonstration data are addressed in the data validation memoranda in Appendix A-2. Relatively few data quality problems were identified, and most of these were judged inconsequential or were resolved by re-sampling or relying on alternate measurements of the same parameter.

3.5.7.5 Data Quality Indicators

Validation of the demonstration data were performed using the QA/QC criteria set forth in the "USEPA Contract laboratory (CLP) National Functional Guidelines for Organic Data Review," revised in June 2001. The data validation memoranda in Appendix A-2 describe the methods used to calculate data quality, and their results.

3.5.7.6 Calibration Procedures, Quality Control Checks, and Corrective Action

Calibrations of laboratory analytical equipment are addressed by the data validation memoranda in Appendix A-2, which also describe the use of blanks, surrogates, matrix spikes and laboratory control spikes.

Procedures used to calibrate field equipment are described in the project's demonstration plan (ARCADIS, 2000). Relatively few problems were encountered, and many of these were able to be resolved by re-sampling or relying on alternate measurements of the same parameter.

3.5.8 Demobilization

Following the final injection event, reagent solution mixing and injection equipment was rinsed with potable water to remove residual molasses. No other above ground equipment or facilities were used during this demonstration, so no further demobilization was required. Underground equipment utilized during this demonstration was limited to the injection well and monitoring wells which were installed for this demonstration. These wells were left in place for future use.

3.6 Selection of Analytical/Testing Methods

Analytical methods used in the demonstration are listed in Tables 3-5 and 3-6. Field instruments used in the program were identified in ARCADIS SOPs, in the project demonstration plan (ARCADIS, April 2000).

3.7 Selection of Analytical/Testing Laboratory

The locations or laboratories where analyses were performed are indicated in Tables 3-5 and 3-6. The majority of analyses were performed either by ARCADIS in the field or at Severn Trent Laboratories (STL) in Arvada, Colorado. Specialized analyses for dissolved gases in groundwater were performed by Vaportech Services, Inc. of Valencia, Pennsylvania; and microbiological tests were performed by Microbial Insights, Inc. of Rockford, Tennessee. In addition, although it was not planned in the demonstration plan, numerous additional rounds of analyses at 35-MW-7 were provided courtesy of Tetra Tech of Santa Barbara, California, the Base's contractor. Grain size testing of soil samples was performed by Engineering Consulting Services, Inc. (ECS) of Research Triangle Park, North Carolina.

4. Performance Assessment

4.1 Performance Criteria

Performance criteria are listed in Table 4-1. Criteria were based primarily on performance objectives agreed upon by ESTCP/AFCEE and ARCADIS in the planning stages of the project (see demonstration plan, ARCADIS, April 2000). Other criteria are included in an effort to conform with new reporting guidance issued during the implementation of the demonstration (ESTCP, October 2002).

4.2 Performance Confirmation Methods

Performance confirmation methods and brief summaries of results are listed in Table 4-2. Because of the complexity of the demonstration (including the nature of the geology and the biology of CAH biodegradation), results are not easily presented fully in the requested table format. Moreover, the temporal and spatial relationships of the multiple lines of evidence cannot be fully conveyed in this summary table. Therefore, references to relevant text are included as needed. A comparison of demonstration results with objectives is given in Section 4.3.7.

Data collection methods and data analysis procedures used in this demonstration, including the Quality Assurance Project Plan, were established in the project demonstration plan (ARCADIS, April 2000; see especially, Section 3.2, Pre-Demonstration Sampling and Analysis; Section 5.4, Sampling Plan; and Section 9.0, Quality Assurance Plan).

4.3 Data Analysis, Interpretation and Evaluation

4.3.1 Performance Overview

The demonstration-scale system at Vandenberg AFB was operated for approximately 26 months, between February 2001 and April 2003. During that time, the findings discussed below demonstrated slow but effective TCE removal by biodegradation in a dissolved phase plume that showed very limited TCE degradation before treatment. Overall, percentage removals of initial TCE concentrations varied from modest to strong within the reactive zone (Table 4-17a), depending on the consistency of TOC delivery, with the highest reduction being 85%. Evidence of complete treatment – production of daughter products *cis*-DCE, VC and ethene, was seen in the most effectively treated downgradient wells. Effective treatment was seen only where substantial substrate (molasses and its breakdown products) was observed in downgradient monitoring wells. The rate of treatment was significantly affected by the low buffering capacity of the aquifer, which initially limited the carbon dosing rate, thereby slowing the performance of the treatment system. Addition of a buffer to the injectate starting in October 2002 allowed a nearly four-fold increase in the dosing rate and resulted in improved CAH biodegradation. Treatment was also somewhat uneven within the targeted zone due to non-homogeneous groundwater flow patterns; however, a substantial zone was established with a limited number of injection wells.

4.3.2 Test Data

4.3.2.1 Aquifer Test Results

ARCADIS' step drawdown test in August 2000 yielded a K estimate of 0.92 to 3.83 ft/day, which is consistent with a silty sand material characteristic of the Orcutt formation at Site 35. Using ARCADIS' range of K values, a hydraulic gradient of 0.041, and a total porosity of 0.35 for silty sand, groundwater velocity was calculated to be 0.11 to 0.46 ft/day.

4.3.2.2 Soil Sample Results

Soils were classified on the basis of sieve analysis as "silty sand" or "poorly graded sand with silt," confirming the field descriptions on boring logs for I-2 and 35-MW-11. VOC analysis (Table 4-3) found 13 to 61 ug/Kg TCE in the saturated soils, and <2,000 mg/Kg of TOC was detected. This would suggest a relatively low potential for sorption of volatile to aquifer solids outside of the source area.

4.3.2.3 Groundwater Flow Direction and Velocity

Water level data collected during groundwater sampling events (prior to injections) were mapped to monitor the direction of groundwater flow in the demonstration area. A representative map of conditions on January 23, 2002, during the active treatment period, is shown in Figure 4-1. The water level data shown in the figure were collected just before that day's injection, and approximately two weeks after the previous injection. In general, the data were consistent with previous reports of flow to the southwest, and little variation from the homogeneous flow field shown in Figure 3-2 was seen in the potentiometric data during the course of the demonstration. This suggests that the injections did not have a long-lasting effect on the flow field. (Frequent measurements conducted during an initial injection event at piezometers near the injection wells showed that water levels returned to within a few tenths of a foot of pre-injection levels within a few hours of the injection.) However, some mounding of groundwater, up to approximately 0.75 feet, was often seen in the area of the injection wells, most often at 35-I-2, both before and after the injections began. Note that 35-I-2 was the well that, because of pH considerations, received the greatest volume of injection. At injection well 35-I-3, though interpretation is affected by its location at the edge of the monitoring array, flow usually appeared to be deflected to the west or even to the west-northwest. This slight difference in flow direction, possibly attributable to the mounding effect at 35-I-2, may have been the cause of the separate, small northern lobe of the reactive zone. Note also that since the water levels were measured routinely with water level meters (as opposed to pressure transducers), a density effect from the dilute molasses (most concentrated at the injection well) would be likely to make the hydraulic head at the injection wells even higher than the measured water levels. As discussed more thoroughly later in this report, the arrival times of TOC and bromide at monitoring wells suggests the existence of preferential flow paths that were not observable in the potentiometric data.

On January 23, 2002 (Figure 4-1), near the midpoint of the demonstration, the hydraulic gradient between 35-I-2 and 35-MW-19A was approximately 0.034 ft/ft, somewhat lower than the value of 0.041 ft/ft reported by Tetra Tech. Under the January 23 gradient, with a porosity of 0.35 and a K ranging from 0.92 and 3.83 ft/day, average linear groundwater velocity would be 0.09 to 0.38 ft/day. This range is in agreement with estimates derived from the August 2000 aquifer test (Section 4.3.2.1), ranging from 0.11 to 0.46 ft/day. Gradients between most studied well pairs were relatively stable during the demonstration (data not shown for brevity).

4.3.2.4 Geological Cross-Sections

Geologic logs from new and pre-existing well borings were used to construct the cross-sections in Figures 4-2a and 4-2b. The aquifer consisted predominantly of poorly graded sand with silt, both vertically and horizontally across the demonstration area. In the vicinity of 35-MW-7 and 35-B-9, an area of slightly coarser material characterized as well to poorly graded sand was found at the base of the aquifer. The coarser material very likely influenced the flow of groundwater through the demonstration area. However, the density of well points, even in this demonstration program, was not sufficient to fully delineate this coarser material and thus predict localized preferential flow paths.

4.3.2.5 Groundwater Sample Results

Analytical results for the three full groundwater monitoring events are summarized in Tables 4-4, 4-5 and 4-6. Results of these and other sampling events, including EPA's data from July 2003 and several rounds of data collected by Tetra Tech, are represented graphically in the figures presented later in the discussion of results. The results are discussed at length in Section 4.3.

Results for the pretreatment hydrosparged groundwater samples from temporary SCAPS borings are summarized in Table 4-7 and Figure 3-6. TCE detections at 35-H-1B and 35-H-1C were of note, because the pre-existing adjacent wells 35-MW-1 and 35-MW-6 had almost no CAH detections. Thus, the hydrosparge detections were indicative of a source area that had not previously been located, downgradient from the Utility building. This area is approximately due east of the demonstration area, where similar TCE concentrations were found. The constituents at the hydrosparge locations generally match those found in the 35-MW-7 area, suggesting a connection between the two areas which is also suggested by the potentiometric data.

In addition to identifying the source area to the east, the baseline groundwater sampling and hydrosparge results served to narrow the CAH plume delineation to the south (at 35-H-2B) and west (at demonstration area wells such as 35-MW-18, where concentrations were substantially lower than at 35-MW-7). With this new data, the gross direction of plume propagation was more closely defined.

A summary of metals results for samples collected at the end of active treatment (May 2003) is provided in Table 4-8. The metals results are discussed with respect to secondary water quality issues in Section 4.3.5.

4.3.3 Process Monitoring Results and System Operational Adjustments

4.3.3.1 Injection History

Section 3.5.2 gives a broad outline of the injection period and total volumes of materials injected. A more detailed history log is presented in Table 3-8. Injection histories differ for each of the three injection wells, due to the varying performance of process monitoring parameters at each well (chiefly pH). Although the three wells were constructed identically in the same formation, they exhibited very different rates of TOC consumption/dilution. It is possible that this is attributable in part to the use of well 35-I-2 in the aquifer test, which may have enhanced its development.

Three phases of project monitoring are noted for discussion purposes: first, the 20 months of un-buffered injections (beginning February 2001), followed by 7 months of buffered injections (beginning October 2002), followed by a 3½ month period of post-treatment monitoring (beginning in April 2003).

4.3.3.2 Injection Rates and Field Parameter Observations

The two active phases of the demonstration were characterized by dramatically different carbon loading rates (mass of carbohydrate substrate injected per week). The initial design loading rate was cut back early in the project due to a decrease in pH to undesirable levels.

Average molasses loading rates for the system as a whole and for individual injection wells are shown on Figures 3-7 and 3-8. Injections of aqueous molasses solution were successful in quickly achieving reducing conditions, as evidenced by depressed DO and ORP measurements in downgradient wells in a short period of time (Figures 4-3 and 4-4). Figures 4-5, 4-6 and 4-7 show that TOC in the injection wells (typically measured immediately prior to injection events) was favorably elevated after the initial injections at design loading rates. However, pH levels in injection wells markedly decreased from background levels (6 to 6.5 s.u.) to near the bottom of the acceptable range for injection wells (4 s.u.).

A detailed discussion of the causes of pH drop in IRZ systems and its management are given in the protocol document (Suthersan et al., 2002). In brief, the pH of groundwater generally decreases during the injection of degradable organic substrates. The magnitude of the pH decrease depends on the dose of substrate and the natural buffering capacity of the system (both the groundwater and the aquifer solids). The VAFB site exhibited low buffering capacity, and pH was initially controlled by careful carbon dose control and injection of an occasional clean water "push" to disperse dissolved carbon away from the immediate vicinity of the well. The low buffering capacity was observed despite alkalinity levels in groundwater that appeared to be potentially adequate (95-143 mg/L during baseline sampling and higher during treatment). However, buffering capacity is also dependent on the alkalinity of the aquifer solids; thus, the observed low buffering capacity may be attributable to the mineralogy of the aquifer matrix at Vandenberg.

Thus, to control pH, the initial injection frequency was decreased as illustrated in Figures 4-5 through 4-7. This revised dosing regime was necessary to avoid further drops in pH, but negatively affected the consistency of the TOC level in the injection wells (Figures 4-5 through 4-7) and monitoring wells (see variable TOC levels observed during unbuffered phase of demonstration in 35-MW-11 and 35-MW-7, for example, in Figure 4-8) and the reactive zone. TOC levels were favorably high during this period at the most effectively treated monitoring wells (35-MW-16 and 35-MW-20; see Figures 4-8 and 4-9), but were associated with pH levels below the desired range of 5 to 9 s.u. TOC was low or sporadically elevated at other wells in the reactive zone (35-MW-11, 35-MW-7; see Figure 4-10) where pH remained within an acceptable range. As shown in Figures 3-7 and 3-8, average loading rates gradually declined until October 2002, when buffer additions commenced.

Addition of the buffer starting in October 2002 (20 months into the demonstration) allowed the carbon loading rate to be roughly quadrupled. In this phase of the demonstration, stabilization and mild recovery of pH was observed at downgradient monitoring wells (Figure 4-10). Post-treatment pH trends have been upward toward initial levels over a period of months. DO, ORP and TOC levels in monitoring wells were sustained approximately at previous levels (Figures 4-3, 4-4, 4-8 and 4-9). The bar chart for individual wells (Figure 4-9) shows that elevated TOC levels were sustained through the active phases of the project at wells 35-MW-20, 35-MW-11, 35-MW-7 and 35-MW-16. In addition, elevated TOC levels at these wells lasted at least five months beyond the last injection (through July 2003). At one well for which more data is available, 35-MW-7, TOC concentrations held constant at a modestly elevated level through February 2004, ten months after the last injection.

4.3.3.3 Measures of Reactive Zone Influence

Several measures can be used as indicators of reagent delivery and the consequent creation of the reactive zone: the arrival of geochemical changes in such parameters as DO, ORP, TOC and the tracer bromide; the development of redox zones; and visual and visual/olfactory changes in the groundwater. The progression of the reactive zone throughout the treatment period was tracked as a series of plots showing zones in which various electron acceptor processes were predominant and in which TOC/bromide levels were elevated and reducing conditions were observed. The first indication in downgradient monitoring wells of influence by the carbon injections was a decrease in DO and ORP, followed by an increase in TOC and bromide. In the time series provided by Figures 4-11 through 4-15, these parameters are seen to have affected the monitoring wells closest to the injection points within 2 months of the first injection. The zones of DO/ORP and TOC/bromide influence continued to grow at least 20 months into the demonstration. After 20 months, the length of the zone had gone beyond the demonstration-specific dense array of monitoring points, so further growth of the length of the zone could not be observed in detail. (Planned AFCEE/COE SCAPS work may provide further insight on this). Over the course of the demonstration, some fluctuation of the zone of influence was seen in the small northern lobe of the reactive zone, although the southern lobe continuously expanded.

The development of redox zones, i.e., areas of altered redox conditions dominated by methanogenic, sulfate reducing, or less reducing conditions, is interpreted in Figures 4-16 through 4-19. The different zones are characterized by the dominance of one of these states, and may include more than one type of reducing behavior, such as sulfate-reducing behavior in a methanogenic zone. For the purpose of this evaluation, methanogenesis was defined by a methane concentration in groundwater of greater than 1,000 µg/L. By eight months into the demonstration, three zones, including methanogenesis, had developed downgradient from the injection points. By 14 months, the methanogenic zone extended to well 35-MW-13, and sulfate reducing conditions had developed in a separate, northern lobe of the reactive zone. The zone continued to increase in size and become more reducing through 27 months of operation.

Visual and olfactory observations were recorded periodically when groundwater samples were extracted from monitoring wells. Color, odor, turbidity, and other qualitative observations about the samples were documented. These observations were standardized during data entry into numbers rating the observed level of reagent impact implied by the sample characteristics in an effort to present the qualitative data graphically. The numeric rating system utilized a scale from 0 to 5, with 0 (actually 0.1 so that the measurement would show up graphically) corresponding to no impact whatsoever and 5 corresponding to undiluted molasses injection solution. The numerical ratings were as follows:

0.1	No Influence	No color, odor, turbidity or other qualitative observations to suggest an impact
1	Slight Influence	One of the following: slight color, slight odor, or turbidity
2	Significant Influence	Two or more of the following: slight color, slight odor, or turbidity
3	High Influence	One or more of the following: moderate-to-strong color, odor, and/or turbidity
4	Very High Influence	Strong color and odor
5	Molasses Solution	Theoretical maximum. Of course, there will always be some dilution; thus this rating was never assigned to a sample.

The qualitative observation ratings are plotted in Figure 4-20. The data are generally in agreement with other indicators, showing reagent influence within 6 to 8 months of the first injections at the nearest downgradient monitoring wells, and within 20 months at the furthest downgradient well, 35-MW-19A. Given the low cost of obtaining and recording this data, it is recommended as a useful check, especially in instances where the same field personnel can consistently be utilized.

4.3.3.4 Groundwater Flow Characteristics

The shape of the reactive zone and the variable influence of the injections on downgradient wells are indications that groundwater flow was characterized by preferential flow pathways. The formation of two lobes of the reactive zone were due in part to variable carbon loading at three injection wells (see Section 4.3.3.1 and Figure 3-8). As discussed above, the most consistent loading, as well as highest overall volume of carbon loading occurred at well 35-I-2. Injections at wells 35-I-1 and 35-I-2 appear to have formed the main lobe of the reactive zone, where the best-treated monitoring wells are located (35-MW-20, 35-MW-16, 35-MW-11, 35-MW-7). Injection well 35-I-3 appears to have formed the smaller northern lobe. Based on potentiometric surface maps, the groundwater flow direction at this injection well may have been more to the west than the southwest, which may also explain the presence of a separate lobe. The substrate injections were shown in Section 4.3.2.3 not to have a significant long-term effect on the potentiometric surface. As discussed above, these preferential flow pathways could not have been accurately predicted from potentiometric or stratigraphic information.

The arrival of TOC, an indication of the presence of the molasses or its degradation products, was staggered with time, arriving within one month at 35-MW-20, after about four months at 35-MW-16, five months at 35-MW-11, and seven months at 35-MW-7. The bromide tracer arrival times were similar. These results also suggest some heterogeneity, since the arrival times were not in order of distance from the line of injection wells.

Variability indicative of preferential flow paths was also seen in the influence of the reactive zone on wells further downgradient. Even though monitoring well 35-MW-13 was apparently on a flow path between 35-MW-7 and 35-MW-19A, it was less strongly influenced (in terms of the measures of reactive zone influence discussed in the previous section; see Figures 4-11 through 4-19) than were 35-MW-7 or, eventually, 35-MW-19A.

4.3.3.5 Bromide Tracer Data

The bromide tracer data (Figures 4-21 and 4-22, and Tables 4-9 and 4-9a) show that:

- Bromide was detected in all wells in the November 2000 background monitoring round at levels of 1.2 mg/L or less.
- Bromide was not detected at levels appreciably above background concentrations at upgradient wells 35-MW-14 and 35-MW-15.
- Concentrations of bromide exceeded pre-treatment levels in reactive zone wells and generally coincided with other indicators of reactive zone influence such as TOC, DOC, BOD and COD (Figures 4-23 and 4-24, and Table 4-10). One possible exception is 35-MW-19A, where the sampling frequency did not allow resolution of elevated bromide levels.
- Elevated bromide concentrations were first observed at 35-MW-20, as would expected for a monitoring well located 8 feet from an injection well and within the injection mounding radius. Bromide levels remained high in this well throughout the active treatment period.

4.3.4 CAH Treatment

CAH data for the three full monitoring events are summarized in Tables 4-4, 4-5 and 4-6, and a summary of CAH reductions is given in Tables 4-17a through 4-17d. Graphical plots of the full CAH monitoring data set are discussed and referred to below.

4.3.4.1 Summary of CAH Treatment Results

The performance monitoring data in Tables 4-17a through 4-17d provides an overview of treatment in terms of percent reductions in CAHs. TCE reductions varied downgradient from the injection wells; no TCE reduction occurred where little or no TOC was delivered, but 42 to 85% reductions occurred at other locations where varying levels of TOC influence were achieved. Cis-DCE and VC concentrations generally increased in the reactive zone, having undergone the daughter product production phase, but not the subsequent degradation phase by the end of the demonstration. Detailed discussions of the conditions that led to this variable performance are presented in Section 4.3.4.3.

Trends in concentration and molar units are shown in Figures 4-25 through 4-33 for the four wells in the reactive zone that received the largest, most sustained substrate dose and show the best treatment – 35-MW-20, 35-MW-16, 35-MW-11 and 35-MW-7. Treatment was enhanced despite the initially highly aerobic conditions.

Enhanced DCE production occurred first at the closest monitoring wells (35-MW-20 and 35-MW-11, 8 to 15 months), then at more distant wells with consistently high TOC levels (35-MW-16 and 35-MW-7, 15 to 27 months). In most cases DCE appeared before the buffering phase began.

Vinyl chloride production occurred at 35-MW-16 (20 and 28 months), at 35-MW-20 (20 and 28 months) and 35-MW-7 (28 months). Accounting for travel time and the timing of sampling events, it appears that VC was first produced during the unbuffered phase at 35-MW-16, during either the buffering or post-treatment phases at 35-MW-20, and during the post-treatment phase at 35-MW-7. A trace of vinyl chloride was also observed at 35-MW-11 after 20 months. Results from VAFB/Tetra Tech data also show the appearance of vinyl chloride at 35-MW-7 after injections were completed.

Lag times to DCE and VC production were almost certainly prolonged by difficulties in managing pH levels during the initial 20-month unbuffered phase. The low pHs may have themselves reduced microbial diversity, and required reductions in the rate of carbon substrate addition. High substrate loadings have been associated with optimum performance in these systems (Suthersan, 2003). Recent practice within ARCADIS has shifted to a more presumptive use of buffering at sites similar to Vandenberg.

4.3.4.2 Methodologies Used in CAH Data Analysis

Several different approaches were used to understand the CAH data set from this demonstration. CAH data was available from three primary sources:

a) sampling conducted by ARCADIS using high QA/QC methods with GC-MS analysis by STL (one round pre-demonstration and six rounds during the demonstration)

b) one round of post-treatment sampling conducted by EPA-Ada

c) periodic compliance monitoring of 35-MW-7 conducted before, during and after the demonstration by the Base’s contractor, Tetra Tech.

Various approaches were used to graphically review and interpret the data:

a) plots of CAH concentration vs. time, with indications of the injection times

b) plots of CAH concentration on a molar rather than mass/volume basis

The significance of changes in concentration was determined primarily by comparisons to pretest concentrations, or in some cases, in comparisons to a baseline level that was observed before and for a period after injection, but before biodegradation evidently began (as indicated by both biogeochemical and CAH data).

In most cases, sufficient data was available that the presence or absence of trends in pre- and post- treatment concentrations could be readily discerned by inspection. Multiple lines of evidence were also sought to confirm that biodegradation was being enhanced (NAS, 2000):

a) evidence that biogeochemical conditions were appropriate for anaerobic biodegradation was obtained and reviewed

b) the trends and time sequence of product production (i.e., DCE, VC, and ethene) were sought to verify that observed decreases in target compounds were not due to dilution and fit with the current theoretical/laboratory understanding of CAH biodegradation

c) trends in historical and recent data were compared inside and outside of the reactive zone

d) tracer (bromide) corrections were used to verify that dilution was not the primary cause of observed trends

e) downgradient and side-gradient well data were reviewed to rule out displacement effects

More details about particular methods of data interpretation are provided in the sections that follow.

4.3.4.2.1 Dilution Calculations Using Tracer

We have assumed that bromide tracer used is indeed conservative and does flow along with and at the same rate as the injected aqueous phase. Thus the amount of dilution in a given well should be directly proportional to the amount of bromide that shows up in that well. For clarification, as an extreme example, if 180 mg/L of bromide were injected into the injection well and then 180 mg/L bromide were withdrawn a week later at a monitoring well located one-week downgradient of the injection well, we would surmise that the monitoring well contains only injection fluid. Likewise, if 0 mg/L bromide were measured in the monitoring well, none of the water from the injection well has made it to the monitoring well and there is thus no dilution.

Based on this logic, VOC measurements were corrected by calculating a dilution factor per the following equation:

$$DF = 1 - \frac{[Br]_{MW}}{[Br]_{Inj}}$$

Where:

DF = dilution factor (that is, the percentage of monitoring well sample that is not dilution water),

$[Br]_{MW}$ = the bromide concentration measured on a sample taken from a monitoring well on a given date, and

$[Br]_{Inj}$ = Injection fluid bromide concentration (an approximate running average of injection fluid bromide concentrations made around the assumed travel time of the injection well to the monitoring well). This takes into account both the molasses solution and the water “push” fluids.

Then, the VOC concentration for a given monitoring well sample was corrected by calculating its actual concentration per the following equation:

$$VOC_{actual} = \frac{VOC_{measured}}{DF}$$

As an example, consider the Br concentration measured on a sample from 35-MW-7 on February 5, 2003. The measured Br in 35-MW-7 was 2.0 mg/L, and the average injection concentration was determined to be 180 mg/L. Thus the dilution factor was: 1 - 2.0/180 = 0.979. The TCE concentration from this sample was measured to be 270 ug/L. Therefore, the actual, undiluted concentration should be 270 / 0.979 = 276 ug/L. Note that these calculations neglect the site’s background concentration of bromide, which was generally below 1 mg/l. This simplification makes the calculations slightly conservative.

Dilution-corrected TCE, cis-DCE and VC data are presented in Table 9A. The percentage dilution observed was:

- Always 2.5% or less at 35-MW-7
- Always 6% or less at 35-MW-11
- Ranged from 2-20% at 35-MW-16 suggesting a preferential flow path to this well
- Ranged typically from 10-20% at 35-MW-20, the closest-in well. However, on one occasion (8/2/01) the measured bromide value essentially matched the injected concentration, which would have caused a dilution correction to indicate that any measured TCE concentration in that well represented an essentially infinite TCE value. Thus, it would be reasonable to ignore that one day's data for that well[1].

In general, the effects of dilution in the reactive zone were thus small enough that evaluations of CAH results are not significantly affected, and that the data can be interpreted in the uncorrected form.

4.3.4.2.2 Rate Calculations

The methodology for the rate (kinetics) calculations is discussed in Section 4.3.4.5.

4.3.4.3 Detailed Discussion of Trends in CAHs and Other Indicator Parameters

Discussion of CAH treatment will focus primarily on the two monitoring wells that received substantial and sustained doses of TOC – 35-MW-20 and 35-MW-16 – and secondarily on wells that received lower doses – 35-MW-11 and 35-MW-7. Although reducing conditions were observed at other wells, we would not expect from our theoretical understanding to observe treatment in the absence of delivered substrate (Suthersan et al., 2002).

4.3.4.3.1 Treatment at Upgradient Wells 35-MW-14 and 35-MW-15

Wells 35-MW-14 and 35-MW-15, upgradient from the injection wells, served as background wells for the demonstration. Both wells showed significant reductions in concentrations during the demonstration (Tables 4-17a through 4-17d) that must be taken into account when evaluating the performance of the technology.

Baseline concentrations at the background wells were 450 and 1500 ug/L. Since the two wells are only 25 feet apart, the difference gives a sense of the potential variability of concentrations across the plume.

At 35-MW-14, after the first injection, the TCE concentration soon fell to about 90% of baseline and remained at that level throughout the demonstration (Figure 4-34). However, no similarly rapid concentration decrease was seen in any of the downgradient wells later during the demonstration, and downgradient concentrations remained well above the ~50 ug/L seen at 35-

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[1] However, the uncorrected value of TCE observed in the well on that occasion was only 50% different from sampling rounds immediately before and after, which has dilution factors of 12% or less. That suggests that the dilution correction may well be conservative at this site.

MW-14. Thus, there is some uncertainty as to whether 35-MW-14 is a reliable indicator of upgradient CAH concentrations flowing into the monitored portion of the demonstration. Molar concentration trends were examined at downgradient wells to check for dilution, as discussed in the following sections.

At MW-15, concentrations gradually fell to 30% of pre-test levels (Figure 4-35). Changes at 35-MW-15 should be considered in the performance of monitoring wells in the southern portion of the demonstration area. As a comparison, cross-gradient well 35-MW-12, south of the demonstration area, showed a 16% decrease in TCE between the baseline and midpoint sampling events. The TCE reduction at 35-MW-15 during the same period was 43%.

The falling concentrations in the background wells do not appear to have resulted from the IRZ itself. 35-MW-15 may have been modestly affected by radial flow during injections, as evidenced by changes after the first injection: slightly depressed DO and ORP values (Figures 4-3 and 4-4) and a slightly elevated TOC level early in the demonstration (Figure 4-8). However, bromide levels did not rise above pre-demonstration levels. Well 35-MW-14 showed no apparent effect from the carbon injections, as evidenced by relatively unchanged TOC and DO levels.

In addition, TCE/DCE ratios did not change appreciably at either well, and no increases in DCE or other byproducts were seen at either well, ruling out the IRZ or a boost in natural dehalogenation as explanations for the decrease. Thus it is likely that the concentration changes were not attributable to the injections but merely resulted from minor changes in flow direction. Both wells appear to be on the eastern, upgradient edge of the plume.

4.3.4.3.2 Treatment at Wells 35-MW-20 and 35-MW-16

The most reducing conditions and thus some of the best treatment results were obtained at wells 35-MW-20 and 35-MW-16, which were located 8 and 25 feet downgradient from the line of injection wells, respectively. Well 35-MW-20 was close enough to injection well 35-I-2 that it would have been directly and immediately affected by injections. Thus, MW-20 represents the upgradient edge of the reactive zone – a location where sufficient residence time for complete treatment may not be present. (A mounding analysis found that piezometers located up to 11 feet away from the line of injection wells [Figure 3-5] experienced increases in water levels of 6 to 7 feet during injection.)

CAH trends at 35-MW-20 are illustrated in Figures 4-25 and 4-26. Concentration reductions are summarized in Tables 4-17a through 4-17d. A 49% reduction in TCE had been achieved as of July 2003, and treatment appeared to be ongoing 3½ months after the last injection. The lag time experienced at this well from the first injection in February 2001 until enhanced TCE degradation and cis-DCE production occurred was 8 to 14 months. At the same time that enhanced cis-DCE production was demonstrated (April 2002, 14 months into treatment), ethene and methane levels rose above background levels. The ethane and methane results suggest that a low rate of complete reductive dechlorination (to the ultimate end product, ethene) was immediately achieved upon establishment of methanogenic conditions.

However, the first appearance of VC at 35-MW-20 occurred over a year later, in May 2003 (27 months into treatment). The appearance of VC was accompanied by a decrease in the TCE level and a decreased rate of cis-DCE production, perhaps signifying the start of a significant acceleration of reductive dechlorination. This enhanced performance was detected after the phase of buffered injections began (October 2002 through April 2003).

Throughout active treatment, pH was low at this well, frequently being in the range between 4 and 4.5 s.u. (Figure 4-10). Low pH can inhibit methanogenesis, and may have suppressed dechlorination. After active treatment ended, the pH level rose to 4.7 s.u., and VC and ethene levels increased to their highest levels to date, suggesting that pH played a role in limiting this well's performance.

A molar plot of the 35-MW-20 data (Figure 4-26) shows a fairly steady level of total moles of chlorinated ethenes throughout the active treatment period, when TCE conversion to cis-DCE occurred. The steady level suggests a conservation of moles of CAH as TCE was converted to cis-DCE, and no significant change in total moles due other effects such as dilution. The total molar concentration approximately doubled in July 2003, apparently due to the most recent VC detection, possibly due to desorption.

At 35-MW-16 (Figures 4-27 and 4-28), farther removed from the injection wells (25 feet), an 85% reduction in TCE concentration had been achieved as of July 2003 (Table 4-17a), with treatment apparently ongoing. The first sign of enhanced TCE degradation and cis-DCE production occurred between 20 and 27 months after the first injection (October 2002 to May 2003). This period included a travel time of approximately 4 months, based on the first appearances of TOC and bromide at this well (Figures 4-8 and 4-21). A low rate of complete dechlorination may have been occurring as early as April 2002 (14 months), based on an ethene concentration above background levels, but dominant methanogenesis (>1,000 mg/L methane) wasn't seen until 20 months (October 2002). The lag time for enhanced TCE degradation was therefore estimated at approximately 16 to 23 months.

VC also appeared during the 20-27 month interval at 35-MW-16, so the lag time between TCE and cis-DCE degradation was short – a few months - or nonexistent. The pH level at this well during active treatment was slightly higher than at 35-MW-20, usually between 4.5 and 5 s.u. The beginning of enhanced treatment appeared to occur during the phase of buffered injections (although sampling frequency doesn't allow a definitive date), and continued through the most recent post-treatment monitoring round in July 2003.

Total moles of chlorinated ethenes at 35-MW-16 (Figure 4-28) remained fairly steady after an initial reduction in the TCE level, which may be partially attributable to dilution as background concentrations decreased. A 34% loss of molar ethene concentration was experienced over the duration of the test.

A nearly one-to-one conversion of TCE to cis-DCE (and to a small extent VC) is seen into the post-demonstration period. The sharp changes observed in the ratio of TCE/DCE and the concentrations of tracer observed in these monitoring wells show that most of the change in TCE was attributable to biodegradation, not dilution or natural fluctuation. The molar plots (Figures 4-26, 4-28, 4-31 and 4-33) also provide strong evidence for biodegradation since they generally suggest a direct molar correlation between TCE removal and DCE appearance.

4.3.4.3.3 Treatment at Well 35-MW-7 and 35-MW-11

Wells 35-MW-7 and 35-MW-11 are 30 feet and 13 feet downgradient from the line of injection wells, respectively. Both wells experienced a pulse of TOC and bromide that arrived in August to October 2001 and trailed off throughout the rest of the active treatment period (Figures 4-8 and 4-21). Despite their different distances from injection wells, substrate travel times to both were approximately the same, further suggesting the presence of preferential flow pathways.

Groundwater quality data for well 35-MW-7 dates to 1996, about 4½ years prior to the demonstration. CAH trends are shown in Figures 4-29 through 4-31, although it should be noted that there were substantial variations in sampling technique during the pre-demonstration period, which included Hydropunch, micropurge, and standard peristaltic pump techniques performed by three different groups. The long-term data in Figure 4-29 in general show that IRZ technology has enhanced cis-DCE production as a TCE byproduct. TCE concentrations were reduced by 67% from the baseline level (Table 4-17a), or 80% from average pre-treatment levels (997.5 ug/L, averaged from September through December 2000).

Following the first injection, TCE concentrations rose slightly at 35-MW-7, possibly as a result of the surfactant effect that transfers adsorbed TCE to the dissolved phase (Suthersan 2002). Given the low TOC of the soils, this effect would be expected to be slight. The rise was approximately concurrent with the arrival of bromide in August 2001 and elevated TOC in October 2001, 6 to 8 months after the first injection (Figures 4-8 and 4-21).

The lag time experienced at this well from the arrival of elevated TOC in October 2001 until enhanced TCE degradation and cis-DCE production occurred in October 2002 was 12 months. The next transition, from cis-DCE to VC, was observed 28 months after treatment began. Production of ethene has not been demonstrated at this well.

A molar plot of 35-MW-7 CAH trends in Figure 4-31 shows an overall decline in chlorinated ethenes during much of the active treatment period due to factors other than biodegradation (including dilution as background concentrations decreased). An estimated 40% loss of molar ethene concentration was experienced before October 2002. However, the onset of biodegradation to cis-DCE is apparent in late 2002/early 2003. Total moles then stabilized somewhat, showing that the reduction in TCE thereafter was primarily due to dechlorination.

Levels of pH were consistently within a preferred range at 35-MW-7 (5 to 6 s.u.). Methanogenesis was indicated by elevated levels of methane starting in April 2002, several months before enhanced TCE degradation occurred. Therefore, pH and methanogenesis do not appear to be as directly predictive of dechlorination at this well as they were at 35-MW-16 and 35-MW-20.

CAH trends for 35-MW-11 are shown in Figures 4-32 and 4-33. Following the first injection, the TCE concentration rose to double its pre-demonstration level, likely as a result of the surfactant effect (see Suthersan et al., 2002 for a more thorough explanation). These effects are likely to be observed most dramatically near the upper end of the reactive zone, so this observation is reasonable. The rise was concurrent with the arrival of bromide and elevated TOC in August 2001, 6 months after the first injection (Figures 4-8 and 4-21).

The lag time experienced at this well from the arrival of elevated TOC in August 2001 until enhanced TCE degradation and cis-DCE production occurred in January 2002 was 5 months. Although no VC has been detected, ethene was detected by October 2002, 9 months after enhanced TCE degradation was observed (Figures 4-41 and 4-44). TCE concentrations were reduced by 42% from baseline levels (Table 4-17a).

The molar plot for 35-MW-11 (Figure 4-33) shows a gain in moles of total CAHs early in the demonstration (possible surfactant effect), followed by a loss as enhanced treatment began in late 2001. Some portion of the molar loss may be attributable to dilution as background concentrations decreased. Thereafter, the total molar concentration is fairly stable, confirming that further reductions in TCE were attributable to formation of byproducts.

Levels of pH were consistently within a preferred range at 35-MW-11 (about 5 to 6 s.u.). Methanogenesis was indicated by elevated levels of methane by April 2002, soon after enhanced TCE degradation occurred. Therefore, pH and methanogenesis do not appear to be as directly predictive of complete dechlorination at this well as they were at 35-MW-16 and 35-MW-20.

4.3.4.3.4 CAH Data at Other Monitoring Wells

Other wells in the reactive zone received lower and less consistent TOC doses than the four wells detailed above, and experienced less complete treatment.

35-MW-19A was the furthest downgradient well installed for the demonstration. It did show some elevation in TOC late in the demonstration. It was sampled infrequently but shows a substantial reduction in TCE, increase in cis-DCE, and thus change in the TCE/DCE ratio during the demonstration (Figure 4-36 and Tables 4-17a and 4-17b).

35-MW-13 is also located relatively far downgradient. It showed only a single instance of potentially elevated TOC. Concentrations of TCE decreased substantially at this well while DCE held nearly steady (Figure 4-37). The TCE/DCE ratio changed modestly, but probably to a statistically significant extent. The pattern of TOC and bromide data suggests that this well is somewhat isolated from the preferential flow paths within the IRZ. It is also possible that this well, being downgradient of at least some of the IRZ, reflects the influence of a pattern in which TCE has been treated by the reactive zone, but the products of that reduction have been degraded before reaching the well.

35MW-17 and 35-MW-12, although part of the same transect as 35-MW-7 and 35-MW-16, were completely uninfluenced by TOC. They show no change in the TCE/DCE ratio, and a gradual decrease in TCE and cis-DCE which is probably attributable to natural attenuation or variation (see 35-MW-17 data in Figure 4-38).

The northernmost well, 35-MW-18 (Figures 4-39 and 4-40), received a modest and short-term dose of TOC. Its trend shows a substantial increase in TCE and cis-DCE, despite the predominant decrease in background concentrations. The ratio of TCE to DCE shows a dramatic change, indicating that biodegradation has been enhanced at this well. It is possible, however, that the desorption effect of the IRZ predominated at this well. It is also possible that this well is influenced by a separate source and thus varies in concentration somewhat independently of other wells in the demonstration zone (see discussion for further evidence for this in Section 3.4.1. The molar plot (Figure 4-40) shows successive increases in total moles of chlorinated ethenes, primarily due to the increase in TCE.

4.3.4.3.5 Ethene and Ethane Production

Evaluation of ethene and ethane trends is made difficult by anomalously high levels in the baseline data set (Figure 4-41). However, four later rounds (Figures 4-42 through 4-46) show both ethene and ethane at reactive zone wells at above-upgradient background levels from the 14-month mark (April 2002) to the 25 month mark (May 2003). Ethene in the July 2003 EPA round was done in only a few selected wells, but showed some downward trends in the post-treatment period. Varying detection limits make the more extensive data set for 35-MW-7 collected by Tetra Tech difficult to interpret.

4.3.4.3.6 Acetylene Production

Acetylene, a possible indicator of abiotic degradation, was measured only once post-treatment (May 2003) and was detected in very low concentration at three reactive zone/fringe wells – 35-MW-16, 35-MW-18 and 35-MW-19A (Figure 47). These levels, though higher than observed in upgradient background wells, are probably not indicative of a large degree of abiotic degradation.

4.3.4.3.7 Methane Production

Methane monitoring data are shown in Figure 4-48. To control costs methane monitoring was not performed until other parameters showed that the IRZ was well established. However as with ethene and ethane, elevated levels of methane were being produced by 14 months into the demonstration (April 2002) and continued steadily through July 2003 (29 months into the demonstration). Figures 4-16 through 4-19 illustrate the growth of the methanogenic zone.

The methanogenic zone was small in size at 8 months. It gradually and steadily expanded in the 14 and 20 month data sets. It expanded considerably between 20 and 27 months.

4.3.4.4 Analysis of CAH Data: Conditions Required for Enhanced Biodegradation

Key questions in interpreting this data set are:

- Why was a relatively long lag time to complete reductive dechlorination observed at this site?
- Why were relatively modest treatment rates observed as compared to other enhanced biodegradation sites?
- What changes in conditions allowed the complete reductive dechlorination to VC and ethene to eventually occur in the VAFB system?

A relatively longer lag time is commonly expected at sites that are initially aerobic (like VAFB), since they require successive consumption of various electron acceptors. The sequential consumption of electron acceptors, in turn, requires successive changes in the microbial community before the desired sulfate reducing or methanogenic conditions are reached (Suthersan 2002). At this site, there was no apparent correlation between DCE or VC production and the establishment of desired levels of DO or ORP, so these parameters are not predictive of complete reductive dechlorination in this system. The same is true for TOC. The lag time between the arrival of elevated TOC and increases in DCE, even accounting for travel time to different monitoring wells, was substantially variable.

Much is known about the conditions required for enhanced biodegradation, but much more will surely be learned in the coming years. An extensive recent review by Paul Bradley of USGS (2003) deals primarily with the conditions required for biodegradation of CAHs. We also present enhanced reductive dechlorination conditions and microbiology in the protocol document prepared for this project, in sections 1.3, 4.1.2, 4.5, 5.3 etc. (Suthersan 2002). An extensive discussion of the conditions required for enhanced reductive dechlorination will also be provided in chapter 2 of a book about to be released by Lewis publishers: Suthersan, S.S. and F.C. Payne, 2004, *In Situ Remediation Engineering*, CRC Lewis Publishers. In this section, we draw on this literature to interpret the Vandenberg data set, recognizing that some of these interpretations cannot be definitive, because the demonstration was not designed primarily to determine the effect of biogeochemical conditions on degradation rates.

In this demonstration, a steady, sulfate-reducing zone was established fairly quickly (within 6-8 months as indicated by H_2S data). The relative importance of sulfate reduction, methanogenesis and dehalorespiration in the microbial consortium at this site at various points in space and time can only be estimated from the available data. However, methane concentrations increased, and the zone of methanogenesis expanded steadily, well into the second year of unbuffered system operation. The sulfate reducing and methanogenic zones both dramatically expanded in the buffered treatment period. Although the onset of methanogenic conditions does not appear to be a perfect predictor of complete CAH degradation at this site, a long period of highly reducing conditions is associated with complete degradation in this dataset.

At Hanscom AFB (Lutes, 2002) and at a commercial site in Ohio (Payne, 2001), methane has predicted complete degradation of CAHs in ERD systems. At VAFB, methane appears to be a better predictor of degradation than DO, ORP or TOC, but is not a perfect predictor by itself.

Great emphasis has been placed by some on the role of dehalorespiring species, especially *Dehalococcoides ethenogenes*, in CAH bioremediation. However, others have disagreed, for example Nelson (2004) writes “The total rate of dechlorination (dehalorespiration + methanogenic co-metabolism + dechlorination contributions of sulfate reducers and others) may be largely independent of the contribution of dehalorespirers.” Bradley (2003) states that

> *A number of observations suggest that reductive dechlorination of chloroethene contaminants in groundwater systems is often attributable to the activities of cooperative consortia of microorganisms rather than to a single species.” It is likely, even in groundwater systems populated by D. ethenogenes, that sequential reductive dechlorination results from the interaction of distinct microbial populations (Flynn et al., 2000). The fact that VC dechlorination evidently is not sufficient to support growth in D. ethenogenes (Maymo-Gatell et al., 1999), but apparently is a specialized, highly efficient,*

> *and energy conservative process in some mixed microbial cultures (Rosner et al., 1997; Loffler et al., 1999; Flynn et al., 2000; Cupples et al., 2003; He et al., 2003a, 2003b), further suggests the importance of established microbial consortia in facilitating complete reductive dechlorination of poly-chlorinated chloroethene contaminants. Thus, while the presence of D. ethenogenes in chloroethene contaminated ground water suggests the potential for complete reductive dechlorination of PCE or TCE to ethene, the absence of this organism does not appear to preclude complete reductive dechlorination (Loffler et al., 1999; Flynn et al., 2000; Cupples et al., 2003; He et al., 2003a, 2003b).*

Since no bioaugmentation was performed, and *Dehalococcoides ethenogenes* was eventually detected in several wells at this site, we conclude that the total absence of a particular organism or genetic capability does not explain the lag time and modest treatment rates observed at this site. Rather it seems likely that a particular set of biogeochemical conditions was required for a completely degrading bacterial consortium to thrive, and that this consortium was not established until late in the demonstration.

Presuming, as we believe, that the appearance of DHE between May and July 2003 (the post-shutdown interval) is not due to differences in sampling/analytical methods, it may be attributable to one or both of the following reasons:

1) A change in pH. pH levels recovered somewhat during this interval, and taken together with TOC, which did not change, this may be a result of the fermentative bacterial population dying off, ceasing to produce VFAs, thereby causing a rise in pH. The higher pH may be favorable for DHE growth.
2) A change in substrate. As the molasses supply wanes after injections cease, the dominant bacterial population runs out of food and stops making end products (VFAs), thereby causing a rise in pH. The subsequent die-off of bacteria contributes to the TOC content of groundwater so that the TOC doesn't change for a period after system shutdown. The new substrate (especially under higher pH) may be favorable for DHE growth.

We note that reducing conditions and moderate to acidic pHs (probably greater than pH 5) are required for Dehalococcoides ethenogenes (DHE), the most common organism used in bioaugmentation, to thrive. DHE is strictly anaerobic and depends on other organisms in an anaerobic consortium to provide hydrogen, acetate etc. (Bradley 2003, Major 2003). Thus, even if bioaugmentation with Dehalococcoides ethenogenes could be successfully and cost effectively performed at this site, these organisms would require suitable environmental conditions in order to thrive, survive and participate in biodegradation. In other words, bioaugmentation at aerobic sites is always preceded with biostimulation. Thus, a hypothetical bioaugmentation program at this site would have required a similar period for substrate distribution and substrate and pH optimization as was experienced in this demonstration.

Interpretation of Sequence of Events. Viewed in these terms, our interpretation of the sequence of events in the three phases of the demonstration is:

Un-buffered phase (0 to 20 months). During this period, a sulfate reducing zone formed rapidly, a methanogenic zone formed more slowly and dechlorination of TCE began. Degradation rates for cis-DCE and VC are slower than for TCE in both primarily cometabolic systems and in dehalorespiring systems (Bradley 2003). Rates are especially slow for VC at concentrations below 200 ppb (Bradley, 2003). Additionally, different microbial consortiums are primarily responsible for DCE degradation than for TCE degradation in many systems. Thus, it is not surprising that DCE and VC began to increase in concentration at this site as treatment progressed. This pattern is observed at many sites, but is typically transient (Suthersan 2002, Lutes 2003). Concentrations of DCE at this site at 35-MW-11 and 35-MW-7 have peaked and begun to decline. The low buffering capacity of the aquifer caused pH to quickly fall below the optimal range in 35-MW-20 and 35-MW-16, which also may have suppressed dechlorination.

Buffered phase (20 to 27 months). In response to the buffer, stabilization and mild recovery of pH was observed at downgradient monitoring wells allowing a 4x higher carbon loading rate to be delivered. This expanded the sulfate reducing and methanogenic zones further downgradient. We can infer that this new, more favorable microbial environment likely included a large zone of fatty acids and hydrogen production. During this phase, DCE concentrations were gradually building up to levels sufficient to allow the system to produce measurable amounts of VC by cometabolism, DHE or other dehalorespiring species.

Post-treatment phase. The pH showed clear evidence of recovery toward more neutral, pretest values during this phase, especially at the downgradient wells 35-MW-16 and 35-MW-7. From this pH observation and what is known about molasses substrate processing in these systems (Suthersan 2002, Nelson 2004) we can infer that fatty acid levels would likely be declining during this period, and fermentative organisms dying off. This in turn produces a different, secondary substrate of decaying biomass which is likely to select for a different microbial consortium. We observed a substantial increase in sulfate reduction at some wells during this period and steady methanogenesis. Other indicators of redox conditions such as DO and ORP remained strongly reducing. Levels of vinyl chloride increased during this phase, indicative of more complete biodegradation.

In summary we conclude that enhanced biodegradation at this site required that all of the following conditions be simultaneously sustained :

- Adequate metabolizable TOC
- Methanogenic conditions
- pH’s suitable for a diverse microbial community.

4.3.4.5 Calculated Biodegradation (Concentration Reduction) Rates

In order to quantify the rate of decrease of constituents of concern (COC) during the demonstration, first-order attenuation rates were calculated for TCE and cis-DCE using exponential regression methods. The first-order attenuation rate is described by the following relationship:

$$y = y_o e^{-kx}$$

where

y_o is the initial constituent concentration
y is the constituent concentration at time x
and k is the first-order degradation rate constant.

To account for decreases in concentration caused by dilution and dispersion, the data were normalized using bromide tracer data (see Section 4.3.4.2.1 for an explanation of dilution calculations). The use of a normalized data set results in a more conservative estimate of attenuation than would the raw data, and the resulting k can be attributed to concentration reductions via biodegradation and other mechanisms such as abiotic reactions and enhanced solubility (due to a biosurfactant effect). The primary mechanism represented by the rate constant is believed to be biodegradation, based on the observed occurrence of reductive dechlorination.

Rates were calculated at four well locations: 35-MW-7, 35-MW-11, 35-MW-16 and 35-MW-20. Initial concentrations were represented by an average of data collected within six months prior to the first molasses injection.

For each well, normalized concentration data were plotted versus time. An exponential regression was then fitted to a selected time interval, yielding an estimate of k and a correlation coefficient (R^2) for that interval. R^2 measures how well the regression equation represents the trend in the data. R^2 values range from 0 to 1; the closer to 1, the more accurate the representation. From the first-order rate constant, the attenuation half-life was calculated. Time intervals over which rates were calculated were selected to best represent periods of continuous and supportable biodegradation as follows:

- TCE biodegradation rates were calculated for the entire demonstration and post-treatment periods (Figure 4-49 through 4-52). This approach is conservative because it incorporates the initial equilibration, reagent advective distribution, and desorption phases.

- Since cis-DCE at this site is primarily a TCE degradation product, cis-DCE biodegradation rates were calculated from peak levels attained during treatment to the end of the post-treatment monitoring period. Since cis-DCE was still being produced due to dechlorination of TCE during this period, the rate calculation based on this period of activity is substantially conservative. Rates were calculated for cis-DCE at 35-MW-7 and 35-MW-11, both of which peaked in early 2001. No peaks were evident in data from the other locations considered.

- No biodegradation rates were calculated for vinyl chloride, since its production had only recently begun by the end of the demonstration period.

Degradation rates were also calculated for the pre-demonstration period using historical data from 35-MW-7 (Figure 4-29). These calculations generally suggest that biodegradation and other natural attenuation processes were occurring at a slow rate before the demonstration. The presence of a low concentration of TCE daughter product cis-DCE prior to the demonstration tends to confirm that biodegradation was taking place.

Results of the rate calculations are summarized in Table 4-11. Rates for the pre-demonstration phase at 35-MW-7 were not presented since a large variety of different sampling and analytical techniques complicated that dataset.

Rates for TCE were lowest at 35-MW-20, which was closest to the injection wells. Thus, CAH concentrations observed at this monitoring well represent a substantially shorter hydraulic residence time for treatment than other wells. This is also attributable in part to the repetition of injections. With repeated introductions of fresh substrate at the injection well (and rapid delivery to 35-MW-20), some biochemical conditions (e.g., highly reducing conditions including methanogenic) that are created with time or distance from the injection well are enhanced in downgradient locations relative to the substrate injection area.

Rates for other ERD sites where similar substrates have been used are provided for comparison. The sites for which data are listed are TCE sites, one with PCE as a parent compound, with degradation products including cis-DCE and VC. Total CAH concentrations at the sites ranged from 1.2 to 22 mg/L, under a variety of hydrogeologic conditions. Data for the Hanscom AFB companion site are listed last for all three compounds. The Vandenberg site produced slower TCE degradation rates than the other sites. However, cis-DCE rates for Vandenberg were within the range experienced at other sites. The slow TCE rates at Vandenberg are partly attributable to the long period over which they were calculated, including an 18-month period of unbuffered injections, when biochemical conditions were not optimal. The calculated rates are consistent with the observation of a long lag time. Thus, they may be overly conservative if used to extrapolate/estimate future treatment efficiency at this site, now that the lag time has been overcome.

The rates in Table 4-11 are also compared to rates given in Howard et al. (1991) for anaerobic, aqueous biodegradation. It is noted that the Vandenberg rates encompass a potential variety of concentration mechanisms including biodegradation, whereas Howard's laboratory-derived rates are for biodegradation alone. Calculated half-lives for TCE in the Vandenberg demonstration ranged from 404 to 859 days, as compared to the published range of 98 to 1,653 days given by Howard et al. (1991). Rates for cis-DCE were also consistent with and in the low end of the range of published rates of biodegradation.

4.3.5 Secondary Water Quality Issues

While the substrate injected (molasses) and its breakdown products are generally nontoxic, they may elevate certain parameters in the water within the reactive zone temporarily. For example, by definition, any degradable organic substrate used to enhance anaerobic bioremediation will elevate the BOD, a traditional measure of water quality. Furthermore, since IRZ intentionally creates reducing conditions within the reactive zone, this will necessarily alter the geochemistry of the reactive zone. This will make some soil mineral metals more mobile (more dissolved) and others less mobile (more inclined to the solid phase). Further information about these matters can be found in the protocol document (Suthersan et al., 2002). An additional potential water quality issue, i.e., the metals content of the injected molasses solution, is discussed below. Although the food grade injectate is not expected to introduce metals in harmful concentrations, the metals evaluations in this section also indirectly address this potential problem.

In general, it is believed that enhanced anaerobic in-situ bioremediation processes will reduce the mobility of many metals (indeed it has been successfully used for the treatment of many), but it will solubilize some other naturally occurring metals in the reactive zone (for example iron, manganese and arsenic). However, even in solubilized form under anaerobic conditions, metals such as arsenic are substantially retarded by adsorption to the aquifer matrix. Furthermore, it is generally believed that they will be reprecipitated/immobilized downgradient of the reactive zone when the conditions return to their preexisting state (which for the purposes of this discussion is assumed to be aerobic). Similarly, reprecipitation/immobilization will occur within the IRZ area some time after system shutdown. Finally, we note that these reducing conditions are by no means unique to IRZ systems – they occur, for example, at sites of TPH releases and landfills as well. It is noted that mentions of metals in this section and throughout this document also refer to the metalloid arsenic.

4.3.5.1 Metals in Molasses

Molasses in its pure form contains concentrations of several metals that may exceed water quality criteria. Published analyses of blackstrap molasses (US Sugar, 2001) and analyses of metals in a molasses/water mixture by ARCADIS are presented in Tables 4-12 and 4-13. The ARCADIS metals sample was from a different molasses source than was used at VAFB, but at the same dilution, so the results should be similar for VAFB. None of the metals detected exceeded available Federal MCLs. In addition, the site metals groundwater data discussed below encompass any solute quality issues. In other words, the groundwater metals data in Section 4.3.2 show that metals, whether solubilized from the formation or introduced as a trace component of molasses (or both) were not problematic in this demonstration outside the reactive zone. On the basis of this evidence, water quality impacts from the molasses injectate would typically not be expected. However, this is a potential issue that should be briefly considered in the design phase of IRZ projects.

4.3.5.2 Metals in Site Groundwater at End of Active Treatment Period

Total and dissolved metals data for groundwater were collected for the purpose of evaluating the possibility of secondary water quality impacts from IRZ implementation. The metals data are summarized in Table 4-8. Samples from this evaluation were collected in May 2003, approximately 27 months after the first molasses injection, and one month after the last injection.

Results for both dissolved and total metals analyses are compared to available drinking water standards (Federal MCLs or EPA Region IX Preliminary Remedial Goals [PRGs] for tap water). These standards are not necessarily ARARs at this facility, but were provided to put the results in perspective.

Two constituents, iron and arsenic, exceeded the listed standards in the reactive zone, at wells 35-MW-7, 35-MW-11, 35-MW-16 and 35-MW-20. No exceedances were present at further downgradient wells (35-MW-13, 35-MW-19A) or at wells on the fringes of the reactive zone (35-MW-18, 35-MW-12). This pattern confirms that secondary water quality impacts may occur within the reactive zone during implementation of IRZ, but that the effect appears to be limited to the extent of the strongly reducing zone. The results support the concept that the affected metals are reprecipitated/immobilized downgradient of the reactive zone when conditions return to their preexisting (less reducing) state. Similarly, it is expected that reprecipitation/ immobilization will occur within the IRZ area some time after system shutdown.

4.3.5.3 Arsenic – Field and Bench Scale Observations from Another DoD IRZ Site

Similar issues have been discussed during the implementation of pilot tests performed for DoD at a Massachusetts site. At the Devens Reserve Forces Training Area, ARCADIS conducted bench-scale and field-scale ERD pilot tests that, while the primary objective was degradation of PCE, were designed in part to test for arsenic mobilization. The following discussion is summarized from the Devens ERD Pilot Test Evaluation Report (ARCADIS, November 2002).

There appear to be three primary triggers that can cause the release/solubilization of geogenic arsenic, including development of high pH (greater than 8.5), the presence of high concentrations of competing anions (such as phosphate, bicarbonate, or silicate), and development of reducing conditions at circumneutral pH.

Within the anaerobic and reducing IRZ created by ERD technology, there is evidence that some control on arsenic solubility can be realized through the formation of low-solubility arsenic sulfide compounds. However, it is expected that the primary control on arsenic solubility will be provided by adsorption to and co-precipitation with hydrous ferric (iron) oxides under ambient oxidizing conditions.

Under the Devens site's normal aerobic groundwater conditions, both dissolved-phase arsenic and iron concentrations were below laboratory detection limits. In the field pilot, arsenic was solubilized in the pilot study area at levels greater than both the current and proposed MCLs for arsenic. However, field tests supported the expectation that the presence of soluble arsenic will be limited to the boundaries of reducing zones created by the ERD technology. Once the original aerobic and oxidizing poise of those reducing zones is restored, it is expected that dissolved arsenic will decrease to non-detectable levels. ERD application was therefore considered appropriate for treatment of CAHs provided the temporary presence of arsenic was appropriately monitored and managed.

In the bench-scale treatability study (flow-through column study), the initial aerobic poise of each of three soil columns was overcome by passing reduced groundwater containing dissolved concentrations of arsenic, iron, and manganese through the columns. Measurements of the three metals/metalloids and DO and ORP were recorded at intervals as the water was applied to the columns. After reducing conditions had been achieved, the aerobic poise of two columns was restored using two different oxidation techniques (air injection and hydrogen peroxide injection). Based on the treatability study results, the following observations were made:

- Even under reducing conditions, the aquifer materials provided a significant level of control on arsenic solubility
- The injection of air or hydrogen peroxide in the field can create an aerobic environment (most suitable for controlling arsenic solubility)

Thus, both empirical data from the Devens site and published research indicate that arsenic solubility as it relates to the use of ERD can be controlled, mitigating concerns associated with use of the technology.

4.3.5.4 Metabolic Byproduct VOCs

VOCs other than the target species for treatment (chlorinated ethenes and ethanes and trace CT) that were detected during three full monitoring events are summarized in Table 4-14 along with potentially applicable regulatory standards.

Among the VOCs of secondary interest is a petroleum constituent, ethylbenzene, that is probably attributable to the historical uses of the site. Other species detected were methylene chloride, which is a common laboratory contaminant, and chloroform. Chloroform is a known disinfection byproduct. Thus, it may have been introduced with the tap water used for injections (California Department of Health Services, Howard 1990). None of these constituents were detected above the listed regulatory standards.

However the ketones that were detected (acetone, 2-butanone) and carbon disulfide are probably byproducts of molasses biodegradation. All were present within the reactive zone, consistent with the idea that they are metabolic byproducts. Within the reactive zone the concentrations were below regulatory levels.

The occurrences of these byproducts are generally limited in extent and often sporadic in nature. Indeed, the data in Table 4-14 suggest that their concentrations had in many instances peaked and had declined by the final round of samples collected at all wells one month after treatment ceased. It is expected that the ketones are also utilized by bacteria in the IRZ. Almost all of these products are readily biodegradable as well and so are degraded on the downgradient edge of the ERD zone. Furthermore, the risks posed by these expected metabolic byproducts of the degradation of food grade carbon sources are very low in comparison to the risks posed by the chlorinated constituents that are targeted for remediation. (Note that metabolic byproduct VOCs never exceeded their regulatory levels, whereas the chlorinated compounds, especially TCE, were present at several hundred times their regulatory levels!)

4.3.5.5 BOD, COD, Sulfide and TDS

Data for the water quality parameters presented in this section are listed in Tables 4-4, 4-5 and 4-6. BOD and COD trends are illustrated in Figures 4-23 and 4-24. In general, the data confirm that, as expected, elevated BOD and COD occurred at monitoring wells nearest the injection points after injections began. (BOD and COD are measures of injected molasses and its metabolic products just as TOC is.) However, levels of both parameters were reduced to background levels within the demonstration area.

As would be expected in the development of a sulfate-reducing zone, elevated sulfide was detected in reactive zone wells. The pattern of sulfide production was in part the basis of the redox zonation maps in Figures 4-16 through 4-19. As pre-existing conditions are re-established in the demonstration area, the sulfide levels are expected to return to background levels.

TDS data for May 2003 are presented in Table 4-6. The data show that, shortly following the end of active treatment. TDS was elevated at 35-MW-20, the well nearest the injection points. TDS levels at other monitoring wells ranged from 690 to 1,300 mg/L and were comparable to the background range of 880 to 1,100 mg/L. Thus, like many of the other secondary water quality parameters, the extent of TDS impacts was limited to the strongly reactive zone.

4.3.6 Other Observations

4.3.6.1 Reactive Zone Size and Residence Time

The size of the reactive zone for one injection well was estimated from the zone of influence and redox zonation maps in Figures 4-11 through 4-19, and from the performance monitoring data in Table 4-17. At many ERD sites, the zone of effective dechlorination (reactive zone) is based on the delivery of measurable substrate, which is necessary for effective treatment. At Vandenberg, the extent of substrate delivery (measured as elevated TOC) eventually surpassed the monitoring network, measuring at least 120 feet downgradient by the end of the demonstration. Other geochemical changes followed, so that the sulfate-reducing and methanogenic zones also extended 120 feet or more from the injection wells. However, evidence of complete dechlorination was not seen at this distance, possibly because the methanogenic conditions had not existed long enough at the last sampling event to cause significant changes. Thus, for the purposes of this demonstration, the zone of effective dechlorination (reactive zone) cannot be equated with the zone of groundwater chemistry impact.

The length of the reactive zone is therefore at least 25 feet (or 4 months travel time, represented by 35-MW-16, the furthest point at which complete dechlorination was demonstrated) and up to 120 feet (35-MW-19A, where sampling frequency does not allow complete dechlorination to be ruled out). The length of the zone of groundwater chemistry impact is at least 120 feet, which should be taken into account during the design phase to protect any potential receptors.

The width of the reactive zone perpendicular to average groundwater flow direction was estimated from the most recent redox zonation map. The width of the sulfate-reducing zones for the two main lobes of the reactive zone grew to approximately 16 feet wide.

The depth of the reactive zone was by design limited to the ten-foot zone above the Sisquoc Formation, approximately 31-41 ft bgs. The impact of the reactive zone likely extended upward to shallower portions of the aquifer, but due to cost constraints, this effect was not evaluated.

To determine the residence time required to reduce CAHs in the demonstration area, it is necessary to separate out the travel time of the substrate between the injection well and the monitoring point, and the acclimation time required for microbial growth. The VAFB results were also complicated by low pH and the substrate delivery rate issues this caused. For this evaluation, the data for 35-MW-20 are considered most representative.

At this site, there was a lag time of 8 to 14 months between the time of the first injection and the beginning of enhanced TCE treatment at 35-MW-20. Travel time for the substrate to reach this well was influenced by its proximity to the injection point 35-I-2. Based on TOC and bromide arrival times (Figures 4-8 and 4-21), travel time to 35-MW-20 was 14 to 28 days (1/2 to 1 month). Therefore the majority of the 8 to 14 months of lag time is attributable to microbiological acclimation. However, during most of this time, the pH at 35-MW-20 was below the optimal range of 5-9 s.u.

Transformation of cis-DCE to VC took longer to occur, although there is evidence of early production of ethene. VC appeared at 27 months, approximately 16 months after clear cis-DCE production began. However, an increase in ethene levels was detected at the same time that cis-DCE and methane increases were seen, suggesting that a low rate of complete reductive dechlorination was immediately achieved upon establishment of methanogenic conditions.

In summary, enhanced TCE treatment at 35-MW-20 occurred 8 to 14 months after substrate delivery began. Subsequently, a low rate of cis-DCE treatment was immediately evident, although the appearance of VC did not occur for an additional 16 months. The time to achieve VC reductions was not determined in the demonstration, but ethene was generated as early as 14 months after the first injection. These lag times are thought to have been influenced by the low pH at the monitoring well. However, the strong performance of the system after the lag time passed under imperfect conditions suggests that a full-scale system with pH controls established at startup could achieve similar or better performance much more quickly.

4.3.6.2 Hydrogen Data Trends

Molasses is not directly consumed but rather goes to form a number of organic monomers, alcohols and organic acids, which in turn break down to form acetate and hydrogen, which serve as energy sources for methanogens involved in reductive dechlorination (Suthersan, 2002). It has been suggested that dissolved hydrogen can be a diagnostic parameter to monitor in groundwater from ERD monitoring wells, as it can suggest which microbially-mediated redox processes are predominating in the reactive zone. Though sampling and measurement of dissolved hydrogen from monitoring well groundwater is feasible, the results are subject to several potential problems. We believe that the cost of acquiring reliable hydrogen data is generally not justified at routine sites since the predominant redox processes in various zones can normally be delineated from other chemical measurements.

A detailed evaluation of methods of hydrogen measurement in the Hanscom demonstration (ARCADIS, 2003) led to the conclusion that hydrogen sampling during ERD projects may not be justified in most circumstances since:

- More reliable diagnostic information from which the predominant metabolic processes ongoing at the site can be inferred is available (measurements of alternate electron acceptors and the products of their use).
- Hydrogen sampling and analysis is relatively complex and costly, subject to numerous potential artifacts, and constrains pump selection substantially.

Hydrogen data from this demonstration are reported in Figures 4-53 and 4-54. Background hydrogen concentrations ranged from 0.8 to 6.5 nMolar (nM), a range which is generally interpreted as being steady-state for sulfate-reducing systems. However, there are numerous potential problems in hydrogen measurements (see Section 3.5.7.1.4 and Appendix C of Suthersan 2002), and none of the other indicators at this site (ORP, DO or H_2S) are consistent with an interpretation of sulfate-reducing conditions before treatment.

Substantially elevated hydrogen levels were exhibited at 35-MW-20, near the injection well, and at 35-MW-16, further downgradient, during the active demonstration and in the post-treatment phase. The more distant reactive zone well 35-MW-13 had below-baseline hydrogen levels through early post-treatment (May 2003) that rose more than an order of magnitude in the next 2.5 months (by July 2003). The levels observed at these three wells are within or above those generally associated with steady-state methanogenic conditions (5-30 nM). The appearance of methanogenesis as indicated by the hydrogen data is generally, but not completely consistent with the indications provided by the methane data.

Hydrogen levels in all other wells held steady between 0.8 and 3 nM throughout the demonstration.

4.3.6.3 Hydrogen Sulfide Trends

H_2S production in reactive zone wells occurred by the time it was first analyzed, 24 weeks after system startup in at least two monitoring wells (Figure 4-55). Relatively constant hydrogen sulfide levels were sustained throughout the demonstration. A spike in H_2S concentrations was seen after injections ceased, possibly indicating a relative increase in the activity of sulfate-reducing bacteria.

The size of the sulfate reducing zone was already substantial 8 months into the demonstration and it expanded only slightly between 8 and 20 months. However, by 27 months, it had expanded considerably (Figures 4-16 through 4-19).

4.3.6.4 Volatile Fatty Acids

VFAs, which are metabolic byproducts of the molasses degradation, were only determined on one occasion at this site (Table 4-15). Samples obtained in May 2003 showed acetic, propionic and butyric acids wells within the reactive zone. Pyruvic, lactic and formic acids were not detected in the reactive zone. At upgradient well 35-MW-14, no fatty acids were detected. Detection limits were 1 mg/l for all acids except pyruvic (4 mg/l).

Similar production of acetic, propionic and butyric acids in the reactive zone, and non-detection of pyruvic and lactic acids, has been observed at other ARCADIS ERD sites (Lutes, 2002). The acids detected fit with fermentation of a carbohydrate source such as molasses. Acetic acid is a common product of incomplete oxidizers and is also at the end of the fermentative pathway for many organisms. Propionic and butyric acids are both common end products of fermentation. More information on the breakdown of molasses and other carbohydrates is presented in Section 1.3 of the protocol (Suthersan, 2002).

4.3.6.5 Microbial Population Characterization

Evaluation of the microbial populations at the site included two rounds of testing by ARCADIS and one round by EPA-Ada:

- September 2000 (before treatment) – PLFA, DGGE
- May 2003 (at the end of active treatment) – PLFA, DGGE, DHE and VFAs at 35-MW-14, 35-MW-20 and 35-MW-7

- July 2003 (3½ months after the last injection) – DHE at 35-MW-20, 35-MW-13 and 35-MW-19A (by EPA-Ada)

The September 2000 and March 2003 microbial characterization reports are included in Appendix A-3. In the reactive zone (35-MW-20), the post-treatment bacterial population was an order of magnitude higher than pretreatment or upgradient background levels. Also post-treatment, fermenters dominated and VFAs were detected here. These results are expected based on our understanding of the sequential processing of molasses substrates in reactive zones (see Section 1.3 and Figure 1-2 in Suthersan 2002 and Figure 1 in Nelson 2004).

No DHE was found at 35-MW-20 in May 2003 (though VC was detected). However, DHE was detected at this well and at 35-MW-13 two months later, in July 2003 by EPA. The comparability of the DHE results from these two rounds is believed to be good, in spite of the use of different samplers and laboratories, since both were semi-quantitative enumerations performed by well-known laboratories.

Microbiology results were substantially different at 35-MW-7, which received lower TOC dosing. The post-treatment bacterial population there was somewhat lower than at 35-MW-20, though above background. The major sequences detected by DGGE were closely related to *Sulfuricurvum,* a sulfide oxidizing bacteria. This is consistent with sulfate reduction being important in the overall consortium. DHE was not detected at this well in May 2003.

The upgradient, post-treatment control (35-MW-14) was reported as “typical for shallow subsurface microbial communities” with low biomass and a community dominated by proteobacteria. This is consistent with the biogeochemical conditions at this well. DHE was not detected at this well in May 2003.

4.3.7 Comparison of Results with Objectives

Objectives for this demonstration were discussed in Section 4.1 and were grouped into primary and secondary objectives. A brief comparison of results with objectives is given in Table 4-2; longer discussions are provided in this section. Criteria were based primarily on performance objectives agreed upon by ESTCP/AFCEE and ARCADIS in the planning stages of the project (see demonstration plan, ARCADIS, April 2000). Other criteria are included in an effort to conform with new reporting guidance issued during the implementation of the demonstration (ESTCP, October 2002).

4.3.7.1 Primary Objectives

During the 26-month period of active treatment, and for as much as three months after the last injection, the treatment system demonstrated slow but effective TCE removal by biodegradation in a dissolved phase plume that showed very limited TCE degradation before treatment. Multiple lines of evidence of complete treatment – production of ethene, reduction in *cis*-DCE and no accumulation of VC, were seen in the most effectively treated downgradient wells. Effective treatment was seen only where substantial substrate (molasses and its breakdown products) and anaerobic conditions were observed in downgradient monitoring wells. The rate of treatment was significantly affected by the low buffering capacity of the aquifer, which initially limited the carbon dosing rate, thereby slowing the performance of the treatment system. Addition of a buffer to the injectate starting in October 2002 allowed a nearly four-fold increase in the dosing rate and resulted in improved CAH biodegradation. Treatment was also somewhat uneven within the targeted zone due to non-homogeneous groundwater flow patterns; however, a substantial zone was established with a limited number of injection wells.

Primary Qualitative Criteria. Primary qualitative performance criteria (Table 4-2) included technology evaluation and prevention of "stalling." Performance of the technology evaluation criterion at Vandenberg was clearly fulfilled by the collection of extensive system performance data from an array of 11 monitoring wells downgradient from the three injection wells. The data collection plan, designed to provide a breadth of data not commonly available in a typical pilot test, was met with few exceptions.

Before treatment, the dissolved phase TCE plume showed very limited TCE degradation in an aquifer that was not sufficiently reducing to carry the reductive dechlorination process to completion at an acceptable rate. After unbuffered injections of the carbon substrate were initiated, evidence of improved rates of biodegradation were seen at some wells (e.g., improved cis-DCE production at 35-MW-20), but the process was still slower than at many other ERD applications due to the low buffering characteristics of the aquifer. Addition of a buffer to the reagent 20 months into the demonstration allowed the system to overcome any apparent "stalling" of ERD during active treatment.

Active process monitoring and application of controls (water pushes and buffer addition) were key factors in overcoming or avoiding "stalling" of this sensitive system. In part due to the aerobic and low buffering characteristics of the aquifer, the system required a relatively long acclimation period to achieve complete dechlorination, but production of vinyl chloride and ethene were seen in the final full monitoring round at some monitoring locations. Ultimately, the treated system has required lag times of 20 months or more to reach this level of complete dechlorination.

Lag times to DCE and VC production were almost certainly prolonged by difficulties in managing pH levels during the unbuffered phase. The low pHs may have themselves reduced microbial diversity, and required reductions in the rate of carbon substrate addition. High substrate loadings have been associated with optimum performance in these systems (Suthersan, 2003). Recent practice within ARCADIS has shifted to a more presumptive use of buffering at sites similar to Vandenberg.

Primary Quantitative Criteria. Primary quantitative performance criteria (Table 4-2) included reduction of remediation time and percent reduction of contaminants. The performance goal for remediation time was 1 to 5 years in a typical full-scale application. Although the demonstration was not full-scale, the 26-month pilot system achieved significant contaminant reductions and ethene production. As discussed in the previous section, the pilot period expended an initial 20 months under sub-optimal operating conditions (without a reagent buffer), which would not be the case in a scaled-up system at this site or others in similar biogeochemical settings. Thus it is expected that a full-scale system under the same site conditions would reach ethene production sooner. Under the improved operating conditions defined by the field pilot, a remediation time of

5 years or less may be attainable at Vandenberg, although the demonstration did not proceed far enough to make this determination quantitatively.

CAH reductions achieved during the demonstration are summarized in Tables 4-17a through 4-17d. The 80% target contaminant reduction for total CAHs was not met within the target time of one year, though TCE reductions of ≥80% were reached at specific wells by the post-treatment period. Results in terms of total CAHs and TCE reductions were as follows:

- Reductions of total CAHs were determined on a molar basis, based on the data given in Table 4-17d. Molar concentrations for the four most highly treated reactive zone wells (35-MW-7, 35-MW-11, 35-MW-16 and 35-MW-20) fell by 12 to 66% during active treatment. This range includes desorption peaks and continued production of daughter products late in the treatment period. Greater reductions would be expected with continued operation of the system.

- Reductions of TCE were determined based on the data given in Table 4-17a. TCE concentrations for the same four reactive zone wells fell by 42 to 74% during active treatment.

- 85% TCE reductions were achieved within the post-treatment period at 35-MW-16 (29 months after the first injection; three months after the last injection), and 80% TCE reduction was achieved at 35-MW-7, also within the post-treatment period (36 months after the first injection; 10 months after the last injection; based on an average pre-treatment concentration of 997.5 ug/L calculated from September through December 2000).

These reductions include possible natural attenuation effects as suggested by a loss of molar concentration in most monitoring wells during the treatment period. CAHs also decreased in background and cross-gradient wells during the demonstration, apparently due to changes in groundwater flow direction. Due to the early buffering problem and long lag times for TCE degradation, cis-DCE and VC concentrations had not yet peaked at most reactive zone wells by the end of the post-demonstration monitoring period.

4.3.7.2 Secondary Objectives

Secondary Qualitative Criteria.

System Performance Optimization. Despite the numerical guidelines listed in Table 4-2 for this objective, it is listed as a qualitative criterion because an optimized system seldom fits neatly within these parameter limits. At the Vandenberg demonstration site, an anaerobic environment was successfully created in response to continuous "tuning" of the system. The low buffering capacity of the aquifer initially caused some variability in the performance parameters that was mitigated with the buffer addition. Frequent performance monitoring, conducted immediately before injection events, allowed for timely adjustment of reagent delivery rates. Ultimately, the performance monitoring approach was successful in allowing system operators to establish and apply an effective substrate dose. Injection rates ranged from 120 to 240 pounds of molasses per month (per injection well) during the most effective treatment period at the end of the demonstration (Section 4.3.3.1). However, no single optimal strength and frequency can be defined. Rather, the optimal injection rate for full-scale system operation is better defined as that rate necessary to maintain the optimal substrate loading (shown by TOC and specific conductance) and microbial community (methanogenic) at the monitoring wells.

Reliability. The reliability of ERD technology has been demonstrated through its repeated use. No reliability issues were anticipated for this demonstration. Only minor corrective actions were required to keep the Vandenberg system running reliably; these included equipment maintenance (replacement of hose connection parts, etc.) and re-development of two injection wells in an effort to optimize their performance (Section 3.5.1).

Ease of Use. Field implementation of a properly designed ERD system is relatively straightforward, requiring an environmental technician with appropriate safety training, with office support from degreed scientists or engineers. However, system design and operation oversight should only be conducted by experts experienced in ERD technology, typically degreed scientists or engineers. A geologist is required for well installations.

Versatility. IRZ technology was originally developed for application to metals, and has been shown to be effective for many other contaminants in addition to CAHs (Sections 1.1, 2.1.1). IRZ technology has also been used at a wide variety of geological and hydrogeologic conditions and configurations (Suthersan, 2002).

Maintenance. The demonstration met this criterion, needing only minor maintenance by the field technician, and well development for performance optimization. Maintenance issues are discussed in Section 3.5.1.

Scale-up Constraints. Although scale-up has not occurred at this site, the expectations of the performance metric have not changed ("scale-up issues anticipated to be efficacy of manual batch injection mode and area of influence determination"). Batch injection was proven successful at Vandenberg, and area-of-influence was evaluated as discussed in Section 4.3.6.1. Scale-up issues and cost implications are discussed in Section 6.3 and in Section 5.7 of the protocol document (Suthersan, 2002).

Secondary Quantitative Criteria.
Geochemistry Manipulation. The quantitative goals of DO less than 1 mg/L and ORP less than 50 mV were generally met within the reactive zone at Vandenberg. A sufficient anaerobic environment was created to enhance reductive dechlorination at the most effectively treated wells (Section 4.3.4.3). However, as discussed in that section, a high level of TOC was achieved briefly, but not sustained in some other wells (i.e. MW-11, MW-16).

It is noted however, that the even distribution of substrate is a significant factor in creating a geochemically effective reactive zone. As has been noted elsewhere in this document, treatment was somewhat uneven within the targeted zone due to non-homogeneous groundwater flow patterns; thus the observed treatment was variable at monitoring wells located at similar distances downgradient from injection points. The volume of substrate delivered to the reactive zone was also temporally variable due to buffering issues. However, a substantial zone of geochemically favorable conditions was established with a limited number of injection wells.

Contaminant Mobility. At the Vandenberg site, there was little organic matter in the soil and thus a limited amount of sorbed contaminant. The Vandenberg plume was thus primarily a dissolved phase plume, and not much would be expected in the way of contaminant "spikes" upon desorption. However, in some wells (e.g., 35-MW-11), modest spikes were observed in TCE concentrations after active treatment began (Section 4.3.4.3).

Contaminant Reduction (Rate). Biodegradation rate constants were determined as discussed in Section 4.3.4.5, for four wells in the reactive zone. Degradation rates for TCE at Vandenberg were slow compared to other ERD applications, partly due to the long acclimation period when unbuffered reagent was used, but compared well with typical natural attenuation rates previously observed in the field at other sites.

Hazardous Materials. This criterion met the expected performance metric, wherein potentially hazardous materials were limited to soil cuttings from well borings and purge water. Both were characterized and disposed of at licensed treatment or disposal facilities.

4.3.8 Technology Comparison

Based on the results of the demonstration as outlined in this document, the use of ERD to treat CAH impacts in groundwater via transformation to innocuous end-products has been demonstrated to be successful, albeit slow at this site. In addition, as outlined in the work performed during the demonstration, the technology has provided many advantages over other conventional and emerging remediation techniques including the following:

- Ease of deployment – including very limited 'hard' design,
- Limited permitting & approvals,
- Ease of operations & maintenance,
- Flexibility,
- Limited health and safety risk directly related to the technology and reagent handling,
- Implementation with little impact to ongoing facility operations and/or future development activities.

These advantages as well as the competitive cost of application of the technology provide a convincing case for the applicability/desirability of the technology in a variety of application scenarios. However, the results of the demonstration illustrate some limitations of ERD application in comparison to other technologies. These limitations include the following:

- Speed at which desired reactions/treatment results can be expected to occur,
- Possible incomplete treatment of parent CAHs, and
- Possible solubilization of inorganics as a result of the reducing conditions.

Overall, these limitations are likely to be limited to a small percentage of sites and/or applications if the technology is implemented properly. However, they need to be carefully considered during both the technology selection and remedial design phases of the project to ensure success.

Table 4-16 contains a general comparison of ERD to several other common remediation technologies used for the treatment of CAHs, specifically, groundwater extraction & treatment, aquifer sparging, and chemical oxidation. This general comparison considers the relative effectiveness, reliability, speed and ease of use of each technique for comparison purposes.

4.3.8.1 Groundwater Extraction and Treatment (Pump & Treat)

Pump & treat technology is an effective approach for plume containment and concentration reduction, but is no longer considered a viable remedy for site closure in most instances because of mass transfer and thus mass removal limitations. Restoration of the site using pump and treat would require a very long time to achieve, if it could be achieved at all. It is likely that a more cost-effective approach would be to utilize an in-situ remedy such as ERD on source areas, and perhaps additional IRZs between source areas and potential receptors (although at this site there is no evidence that the contamination is currently reaching receptors important from a human health perspective).

4.3.8.2 Aquifer Sparging

The use of sparging is often an effective means to remediate CAH impacts. At Vandenberg, this technology is technically feasible and would be expected to effectively treat dissolved phase and any residual adsorbed phase CAHs. Compared to ERD technology, capital costs would likely be higher because of the need for an array of fixed, engineered sparging and vapor collection equipment, and the likelihood that the density of sparging points would be significantly higher than required for ERD injection wells. The rate of TCE removal may be relatively slow, and low cleanup goals may be difficult to reach. Any TCE daughter products present would likely respond well to sparging.

4.3.8.3 Chemical Oxidation

Given the in-situ nature of the technology, chemical oxidation would be expected to be a successful means of treating residual dissolved and adsorbed phase CAH impacts at the site. However, given the relatively low concentration of COCs at this site, and the expected consumption of oxidant by non-target compounds, chemical oxidation may well be cost-prohibitive at this site, if used for a full-scale plume treatment approach. More likely, chemical oxidation would be selected to play a limited or ‘surgical’ role in the overall restoration strategy using it in a program where it would be reserved for treatment of higher concentration areas or areas where rapid clean-up time periods outweighed cost concerns.

4.3.8.4 ERD

The results of the ERD demonstration at the site indicate that the technology can be successfully applied and, if properly operated, can result in complete degradation of the CAHs present in the dissolved phase, as well as modest enhancement of desorption of adsorbed phase CAHs. (Concentrations of adsorbed-phase VOCs in the treatment area were almost certainly low.) Given the scope and limitation of the demonstration, treatment to current MCLs was not demonstrated, although substantial degradation was. However, ERD technology has achieved MCLs at other sites (see Appendix sections A-2.4 and A-2.8 of the protocol document [Suthersan, 2002]; Panhorst et al. [2002]; Payne et al. [2001], Lutes 2004, Lutes 2004B).

In comparing the use of ERD to other technologies, the chief advantage of ERD is likely cost. The limited infrastructure required to deploy the technology as well as the low reagent costs will likely make ERD the least expensive means to address the residual impacts when implemented at full-scale.

4.3.9 Lessons Learned

ERD in an IRZ application has been applied at a broad range of sites since 1995. These sites have included a variety of constituents to be treated - including PCE, TCE, 1,1,1-TCA, carbon tetrachloride, pentachlorophenol, and chlorinated pesticides; various groundwater concentration ranges; and numerous hydrogeologic settings (including shale and karstic limestone bedrock, low permeability glacial tills and saprolite, and high permeability alluvium and glacial outwash environments).

As with all groundwater remediation activities both in-situ and ex-situ, the successful application of ERD relies mainly on sufficient and accurate hydrogeological information for the given site. The application of ERD to treat CAHs in groundwater at many sites located in varied in-situ hydrogeologic settings under different concentrations has provided a valuable knowledge base that has taught many lessons for future applications of the technology both at the pilot-and full-scale. These lessons learned are also applicable to applying other in-situ remedial techniques. Some specific lessons learned from the Vandenberg demonstration are included below.

4.3.9.1 Substrate Dosing Required for Successful Treatment

The second phase of active treatment at Vandenberg, when pH levels were stabilized to acceptable levels, demonstrated effective levels of substrate dosing for successful treatment. Figures 4-31 and 4-34 suggest that successful treatment at Vandenberg was associated with a wide range of TOC values above 10 and as high as 3,000 mg/L. In comparison to the guidance in the protocol document (Suthersan, 2002, Section 4.5) based on observations at many sites, that 50-200 mg/L TOC in monitoring wells is sufficient for complete degradation, the demonstration illustrates the wide variability of site responses to dosing rate. Methane data was too infrequent to provide a strong correlation, but levels of methane above 1,000 ug/L were generally present when CAH trends indicated effective treatment, further suggesting that methanogenic conditions as indicated by methane concentrations in excess of 1,000 µg/L are associated with rapid, complete treatment.

At VAFB, pH changes in the monitoring wells as well as in the injection wells limited the substrate injection rate. The use of a clean water push to disperse the injected TOC further beyond the injection well after injection is beneficial at some sites However, clean water pushes and reduced carbon doses failed to allow recovery of pH levels at VAFB. Eventually, the addition of the sodium bicarbonate buffer allowed the molasses injection rate to be substantially increased without further pH drops at the injection wells.

4.3.9.2 Optimization Time Required

Most ERD pilot systems are operated for a period of 6 to 18 months to gather the information needed to determine whether and how to scale up the system. However, in some cases, more time is required to optimize the pilot system, leading to added O&M costs. At Vandenberg, a 26-month program, optimization time was prolonged primarily by buffering issues. The Vandenberg experience, as well as other applications, has led to the recommendation for presumptive use of a buffer for any aquifer with low buffering capacity. The effort of optimization should primarily be expended during the pilot phase to minimize any costs associated with delays or system modifications at larger scale.

4.3.9.3 Microbial Acclimation / The Role of Bioaugmentation

"Stalling" of an ERD system at cis-DCE production is a concern at some sites. The production of VC and ethene at Vandenberg indicates that the system is not stalled, although a period of 20 months or more was needed to achieve this result and the entire reactive zone has not exhibited these daughter products to date.

Following the addition of an electron donor, the microbiological community present at the site is required to acclimate to the changing aquifer conditions. During this interval, some originally prominent members of the community may decline in numbers or cease to exist entirely within the community at large. Other microorganisms that were previously present in relatively insignificant concentrations may find the changing conditions more suitable to their metabolic needs and expand in number. Once substrate has been delivered to an area within the aquifer, a period of several additional months is often required for the successive consumption of various electron acceptors, which in turn requires successive changes in the microbial community. It is ARCADIS' experience that the implementation of the ERD technology typically results in a bacterial succession as described above where bacteria that are important for the biodegradation of CAHs become a functional part of the new bacterial community that is given rise by ERD implementation. The bacterial community present in the aquifer prior to carbohydrate injection is shifted towards species better adapted to a more reduced environment.

In rare instances, ARCADIS has implemented bioaugmentation at ERD sites. Bioaugmentation is the introduction of a specific bacteria or mixture of bacteria to a site where it is felt that the community already in existence is lacking the capability to biodegrade a given contaminant. However the practicality of bioaugmentation for the cost-effective treatment of large areas has not yet been widely shown (Suthersan and Payne, 2003).

Although there was at some wells a lag of 20 or more months between the time of first injection and the beginning of enhanced cis-DCE treatment, the lag appeared to be due largely to difficulties controlling the biogeochemistry of the system, which likely affected biological acclimation times. We believe that further applications of this technology at this and other similar sites can largely overcome these difficulties with a more presumptive approach to the use of pH buffers.

An alternate approach that has been suggested to reduce microbial acclimation time is bioaugmentation. We also note that the Vandenberg demonstration was not designed as a comparison of bioaugmentation vs. biostimulation, and therefore to analyze the potential applicability of bioaugmentation at this site reference to the broader literature is necessary. A critical review of the published bioaugmentation work can be found in section 2.3.1.5 of a book that will be published before this report (Suthersan and Payne, 2004). For an overall assessment by a leading proponent of bioaugmentation see Major (2003).

The core of our economic analysis is that the choice for this site is not merely “bioaugment or not” but “natural advective flow or induced recirculation”. As discussed in more detail in Suthersan and Payne, the published bioaugmentation studies have relied on recirculation. Recirculation involves groundwater withdrawal, amendment and re-injection to distribute the introduced microorganisms and support precise microbial habitat control in the groundwater. Thus, any consideration of the incremental cost/benefit of bioaugmentation must include not only the relatively modest cost of the culture, but also the very high cost of dense recirculation well networks and operations of the pumping system.

While we agree that bioaugmentation may in some cases reduce lag times, bioaugmentation systems also require substrate addition (biostimulation) to establish proper environmental conditions. Thus, even a hypothetical biostimulation system at Vandenberg would have required time for the effects of substrate addition to take hold and for adjustments such as changes in the dosing level and buffer addition to be made. In future applications at this site, either biostimulation or bioaugmentation systems could reduce this lag time, by designing dosing strategies based on the results of this demonstration.

Lag time comparisons should include all of the time required from remedy selection to achievement of the remedial goal. In this light, it is important to take into account the relative permitting times required for the two technologies. Of interest for Vandenberg specifically, recent California precedent suggests that the permitting process for bioaugmentation is still lengthy and that costly permit conditions were imposed (Molnaa, 2004). More broadly bioaugmentation has only been accepted so far in 14 states, and has been resisted in some (Hood and Cox, 2004). In contrast carbohydrate based biostimulation has been applied 32 states and 8 countries (Lutes 2004), and biostimulation with HRC has been practiced in all 50 states.

In our view small differences in lag time are most likely to be critical at urgent sites driven by:

- An imminent exposure of human or ecological receptors; or
- The need to complete remediation rapidly to allow a property transfer or future land use.

Neither circumstance appears applicable at Vandenberg Site 35. Therefore, our preliminary conclusion would be that the added costs of recirculation for bioaugmentation are likely to outweigh the benefit in acclimation time reduction.

4.3.9.4 Long Lag Times to Complete Dechlorination

As discussed in the previous section, the lag time to complete dechlorination can be significant. In ARCADIS’ experience with many ERD sites, Vandenberg represents a relatively long lag time, both because it was initially aerobic and because of buffering issues. Remedies for both conditions are well documented within this report. During the pilot testing phase, it is important to define and address any conditions that may delay the onset of complete dechlorination. At Vandenberg, a scale-up design for ERD would certainly incorporate a buffer in the reagent from start-up, which we believe would cut the acclimation time significantly.

Bioaugmentation has been recommended by some as a potential remedy for long lag times. In the view of the authors, it may be useful in limited situations where remediation is urgent and a period of effective biostimulation has not enhanced degradation sufficiently. However as discussed in sections 4.3.4.4 and 4.3.9.3 the potential benefits of bioaugmentation in reducing microbial acclimation time must be balanced against the increased costs of recirculation systems required to distribute the organisms and the greater regulatory approval time likely with bioaugmentation."

4.3.9.5 Vinyl Chloride Production

The formation of VC has been an issue raised generally about reductive dechlorination systems but during the demonstration it has not been sufficiently extensive to be of concern at this site. Furthermore, reductive dechlorination of VC to ethene should occur with the ERD process (and has occurred in this demonstration); VC is also quickly biodegraded by aerobic microorganisms. For these reasons, the production of VC or other intermediate products is considered a temporary situation and does not represent a major impediment to the technology but should be monitored during application of the technology.

4.3.9.6 Fermentation and Byproduct Formation

During the application of ERD, a highly reducing biogeochemical environment is generally created throughout the treatment zone. In addition, this zone will contain a large excess of organic carbon. During the application of ERD, most commonly when the contaminated aquifer possesses lower hydraulic conductivity (10^{-5} cm/sec [2.8×10^{-2} ft/day] or less), these conditions can result in the formation of organic acids in the groundwater as part of the degradation process. As a result of the formation of these acids, the ambient pH in the treatment zone can be lowered, and in turn, conditions conducive to fermentation-based reactions are then created. This environment can create low pH conditions that are detrimental to methanogenic bacteria.

The formation of undesirable byproducts including acetone and 2-butanone has been observed at sites where reagent dosing has commenced without careful monitoring of groundwater conditions near the injection wells. The occurrences of these byproducts are generally limited in extent and often sporadic in nature. It is expected that these ketones are also utilized by microbes in the IRZ. Almost all of these products are readily aerobically degradable as well and so are degraded on the downgradient edge of the ERD zone. Furthermore, almost all have higher risk-based limits (i.e., MCLs) than the target compounds of the ERD system. However, the possibility of production of these byproducts needs to be accounted for in the project planning stage. Therefore, the lessons learned regarding these potential occurrences are as follows:

- Careful and regular monitoring of groundwater within the treatment zone should be provided in order to ensure that pH levels are not depressed ($pH < 5$ at monitoring wells, $pH < 4$ in injection wells) and TOC levels are not excessive (site specific, but generally above 5,000 to 10,000 mg/L in injection wells).
- The remedial plan for application of ERD should be flexible enough to allow for modification of both the delivery frequency and mass of organic carbon delivered, and in the case of poorly buffering (low alkalinity) aquifers, addition of a buffer. Modifications in reagent delivery should be tied to regular pH and TOC monitoring in the treatment zone.

At Vandenberg, as discussed in Section 4.3, pH decreases in the injection wells limited the substrate injection rate. The use of a clean water push was beneficial in dispersing the injected TOC further beyond the injection well immediately after injection, and the use of a sodium bicarbonate buffer in the injectate was essential in preventing further drops in pH. These modifications allowed the molasses injection rates to be substantially increased. As discussed in Section 4.3.5, although ketones were generated as metabolic byproducts of molasses degradation, they did not pose an appreciable risk.

4.3.9.7 Secondary Water Quality Impacts

The formation of secondary byproducts including acetone and 2-butanone has been observed at sites where reagent dosing has commenced without careful monitoring of groundwater conditions near the injection wells. The occurrences of these byproducts are generally limited in space and time, and are often sporadic in nature. It is expected that these ketones are also utilized by microbes in the IRZ. Almost all of these products are readily aerobically degradable as well and so are degraded on the downgradient edge of the ERD zone. Furthermore, almost all have higher risk-based limits (i.e., MCLs) than the target compounds of the ERD system. However, the possibility of production of these byproducts needs to be accounted for in the project planning stage.

As discussed in Section 4.3.5, secondary water quality impacts (including metals mobilization and high COD/BOD) were observed, but as expected were limited to the area of the reactive zone and did not appear to be significant downgradient. Although ketones were generated as metabolic byproducts of molasses biodegradation, they did not appear to pose an appreciable risk.

4.3.9.8 Groundwater Chemistry Impacts

As seen at Vandenberg, the geochemical impacts of the ERD may extend farther downgradient than the zone of effective treatment. Effective treatment at this site to date has been limited to the first line of monitoring wells, but the zones of redox, TOC and bromide impacts (Figures 4-15 and 4-19) extended to approximately 120 feet. One of the goals of pilot testing is to determine the extent of such impacts so the design for the full-scale system spaces injection wells at an appropriate distance from potential downgradient receptors such as surface water bodies.

5. Cost Assessment

5.1 Cost Reporting

An evaluation of costs specific to the demonstration and an estimate of unit costs will be provided in the Cost and Performance Report at the completion of the project, when final project financial information is available. At that time, we will also discuss costs associated with the demonstration that would be expected to differ at full-scale. A cost breakdown for a hypothetical case is provided in Section 5.2.4 and Table 5-1, using the Level 2 and 3 work breakdown structure given in U.S. Army Corps of Engineers, 2001 and elements of the cost tracking guidance provided in ESTCP, October 2002. Information is also presented in this section regarding cost comparisons between ERD and other technologies, based on our experience and that of others as presented in the literature.

5.2 Cost Analysis

In general, CAH plumes in groundwater may take one of three forms:

- Pure dissolved phase contamination
- Sorbed or emulsified source material with a dissolved phase plume
- Free phase (pumpable) DNAPL source with a dissolved phase plume.

The second case is by far the most common and is the condition assumed to exist at Site 35. Cost analyses presented in this section are therefore geared toward this type of plume.

Additionally, ERD can be applied in at least three configurations – as a barrier, as a plume-wide treatment, and as a spot treatment of a source area. The choice of configuration for a given site depends on a variety of technical, economic, regulatory and risk factors. However, a common ERD approach is to treat the whole plume (above specified concentrations, leaving low-concentration fringes to attenuate naturally). This approach is assumed. Analyses presented in this section are based on a dissolved phase plume with a sorbed, emulsified source area.

5.2.1 Cost Comparison

5.2.1.1 Cost Comparisons with Alternate Electron Donors

A number of electron donors in common use were listed in Section 2.4.1 of this report. The economic application of soluble carbon substrates requires the ability to match the biogeochemical and hydrodynamic character of the aquifer to the biogeochemical character of one or more sources of soluble carbon. The selection of a carbon substrate(s) will be primarily driven by overall reaction rates, which are, in turn, controlled by the site conditions. A goal should be to minimize overall project cost by minimizing the number of required injection points, the number of injection events, and reagent cost (Harkness, 2000). Substrate dosing should be sufficient to achieve and maintain methanogenic conditions in order to maximize the rate of dechlorination (see the protocol document, Suthersan, 2002, especially Appendix B also see Suthersan and Payne 2004, especially section 2.3.1). The physical characteristics of the substrate (i.e., phase and solubility) may also make certain substrates more suitable than others in particular applications.

A cost comparison for a variety of different substrates is presented in Table 5-2 (Suthersan 2002; see also Harkness, 2000). This makes clear that there are dramatic price differences on a cost per pound basis for various substrates. However, as discussed previously, cost per pound should not be the sole criteria for substrate selection.

Additional details are provided in Table 5-2. The cost ranges presented in the table represent a range of costs observed throughout the U.S., and also represent both low volume (e.g., tens of gallons) and bulk (200+ gallon) purchases. Based on experience, loading rates for differing scenarios are expected to be on the order of 0.001 – 0.01 pounds of TOC per gallon of groundwater flux per day.

As a rule of thumb, the cost of a molasses reagent typically represents less than 10% of the total project cost. The percentage of the total project costs associated with the reagent injections is typically greater than 50%.

5.2.1.2 Cost Comparisons at Commercial Sites vs. Pump & Treat

The best way to estimate the potential benefit of an innovative remediation technology is to evaluate its cost at sites where it has been demonstrated alongside more conventional technologies. ARCADIS has extensive experience in replacement of pump and treat systems with IRZ technology. Some examples of actual and projected savings associated with these sites are listed in Table 5-3. The geometries of the listed CAH sites are inter-comparable, being generally plume-wide or multiple-transect applications (as opposed to single linear containment barriers) and not solely source area hot spot treatments. The CAH sites also generally fall into the category of dissolved phase plumes with sorbed source material. The same type of application would likely apply at the Vandenberg Site 35 plume.

5.2.1.3 Cost Comparisons at Commercial Sites vs. Other Innovative Technologies

Cost comparisons with other, more innovative technologies are available as well. For a South Carolina site, ARCADIS performed a cost comparison of several potentially applicable technologies (Table 5-4). The site contained a dissolved PCE/TCE plume in low-permeability, saprolitic soils. The comparison favorably portrays the application of an IRZ as a cost-competitive way of treating the contamination in the shortest predicted remedial interval.

DuPont has developed and published a computerized, controlled methodology to compare the costs of remediation for a standardized hypothetical site contaminated with PCE (Quinton et. al., 1997). The site was hypothetically established as being 1,000 ft long and 400 ft wide with free product. The DuPont study considered remediation duration, estimated engineering and flow/transport modeling costs, equipment costs, operation and maintenance, and monitoring costs when designing the controlled methodology. Following development of the comparison methodology, DuPont considered these treatment options: natural attenuation, substrate-enhanced anaerobic bioremediation (recirculating contaminated groundwater through the source area of the plume while injecting sodium benzoate as a carbon source), a biological substrate-enhanced anaerobic barrier (comparable to ARCADIS' IRZ technology), an *in-situ* permeable reactive barrier incorporating zero valent iron, and a pump and treat system with air stripping and carbon adsorption.

Natural attenuation, biological substrate-enhanced anaerobic barrier, *in-situ* permeable zero-valence iron reactive barrier, and pump and treat were evaluated as plume containment to be implemented 1,000 ft from the hypothetical spill zone. The scenario assumed that no free product removal technology would be implemented at the source area for containment technologies. Substrate-enhanced anaerobic bioremediation was evaluated as a technology that directly attacked the contamination in the spill zone.

To accurately determine and compare the costs of the listed technologies, DuPont included unit cost measure, cost elements making up the overall cost and period of time over which the cost is incurred in the actual remediation of the evaluation. The results of the evaluation from Quinton et al. are summarized in Table 5-5.

With the assumptions made during the DuPont evaluation, substrate-enhanced biobarrier (comparable to ARCADIS' IRZ technology) ranks third on cost. However, ARCADIS does not typically implement this technology as a containment technology in remedial situations where there is known to be free product in the source zone. In combination with a free product removal technology and a good knowledge of the subsurface hydrogeology, our company has found that it can more cost-effectively remove the free product and remediate the dissolved plume with our IRZ technology. It is our belief that, if DuPont's approach took this change in assumption into account, the substrate enhanced biobarrier evaluation would exchange places in the table with the recirculating source zone remedial approach to become the most cost-effective technology except natural attenuation.

Cost will certainly depend on scale, and generally the cost of the IRZ technology expressed per unit of CAH mass or gallon of water treated, decreases with increasing scale. This decrease occurs since transportation, mobilization, design and reporting costs are nearly fixed and can thus be spread over more units. This effect is generally similar for most remediation technologies, conventional or innovative.

5.2.2 Cost Basis

Two cost comparisons were made in the preceding section. In the first, ARCADIS compared projected costs for remediation of several sites based on estimated capital and O&M costs and the number of years required for each technology option to reach remedial goals, adjusted to present worth. The second (DuPont) cost comparison was constructed on a similar basis, but since it was based on a hypothetical site, was also extended to unit costs per volume of water and mass of contaminant treated. For a real site, the mass or volume of water treated in-situ is difficult to estimate with acceptable accuracy.

5.2.3 Cost Drivers

Section 2.3 provides a general discussion of cost factors associated with ERD. An even more extensive discussion of ERD cost drivers has recently been published as Sections 4 through 6 of the protocol document (Suthersan, 2002). Although a project-specific cost analysis has yet to be conducted (but will be provided in the cost and performance report), anticipated cost drivers are briefly summarized as follows:

- The majority of the costs related to reagent injection are related to labor (including preparation and support), temporary and permanent equipment, type of application (source reduction vs. plume-wide treatment), etc. The cost of the reagent material is relatively insignificant. The typical cost per pound of TOC delivered is as outlined on Table 2-2.
- Based on our experience and analysis, the two largest cost factors for ERD implementation are the injection well installation and the O&M associated with reagent injections. Three other factors that need to be given special consideration during design in order to develop the most cost effective approach for site remediation are:
    - Plume size
    - Depth of target zone
    - Magnitude of groundwater flux

5.2.4 Life-Cycle Costs

Extensive information about cost experience in actual practice with this technology has been provided in Appendix A of the protocol document (Suthersan, 2002). These costs are broken down into capital and O&M only.

A more detailed breakdown of life-cycle costs for a hypothetical, typical site is provided in Table 5-1, using the Level 2 and 3 work breakdown structure given in U.S. Army Corps of Engineers, 2001. The hypothetical example assumes the following conditions:

> *The hypothetical site is a commercial property with a TCE plume. The TCE exists largely in the dissolved phase, but residual source material remains in a sorbed, emulsified state; no pooled DNAPL remains. A combination of ERD and monitored natural attenuation (MNA) will be used to achieve cleanup standards. The ERD is targeted for the portion of the plume where TCE concentrations range from 1 to 5 mg/L. This area is approximately 400 feet in length, 100 feet in width, 20 feet in thickness, and extends to a depth of 50 feet. Groundwater velocity is 0.5 feet/day. The portion of the plume targeted for ERD is to be treated with a 10% molasses solution, injected through 25 injection wells. Injections are performed monthly for the first two years of treatment, using mobile, trailer-mounted injection equipment. The rate of injection is then reduced to bi-monthly for three additional years. The project duration is five years from the initiation of the ERD program, including three years of MNA. MNA costs are not presented here.*

Table 5-1 includes capital, operating and regulatory (permitting and reporting) costs. Since costs are based on complete destruction of CAHs, no future liability costs are included.

The hypothetical site represents a whole-plume application where no DNAPL is present in the source area. This approach is potentially appropriate for the Vandenberg plume, where no separate-phase CAH is thought to exist. Similar applications at real sites are represented in Table 5-6.

The duration of ERD injections and MNA are of course different for each site and dependent on site conditions. The example of five years of injections, followed by three years of MNA, is typical, based on ARCADIS' experience. Treatment at many sites is much faster. At least six ARCADIS ERD sites have succeeded in reaching MCLs for target CAHs or even obtaining closure certifications within 18 months to 2.5 years after the initiation of ERD (see Appendix sections A-2.4 and A-2.8 of the protocol document [Suthersan, 2002]; Panhorst et al. [2002]; Payne et al. [2001], Lutes 2004, Lutes 2004B).

Unit costs for remediation of the hypothetical plume using ERD were estimated on a basis of gallons of water treated. Two estimation methods were used: first, assuming that the initial volume of contaminated water is the total volume to be treated, and second, considering the flux of water through the plume area for the five-year duration of treatment. This approach provides a conservative range of costs.

- For an aquifer with total porosity of 0.3, the initial volume of groundwater in the hypothetical plume is 240,000 cubic feet, or 1,795,200 gallons. With a total project cost of $680,298 (from Table 5-1), the cost per initial gallon of water treated is $0.39. This cost is overestimated, since desorption and other effects require treatment of several pore volumes of water, thereby substantially increasing the volume of water that must be treated.

- The cross-section of the plume perpendicular to groundwater flow is 100 feet wide and 20 feet thick, for a cross-sectional area of 2,000 square feet. At a velocity of 0.5 ft/day, the flux through the cross-section is 300 cubic ft/day. Over the 5 years (1,825 days) of treatment, 547,500 cubic feet, or 4,095,300 gallons of water will flow through the cross sectional area. With a total project cost of $680,298 (from Table 5-1), the cost per gallon of water treated is $0.17. This estimate provides a lower bound on the potential range of unit costs.

- If the duration of the MNA period following ERD was longer than 3 years, the added annual cost (not accounting for inflation), can be estimated using the figures in Table 5-1 for sampling (assumed to be reduced to 4 wells annually), laboratory analysis, and progress reporting (assumed to be annual). At an estimated sampling cost of $3,500, with analytical costs of $1,440 and annual reporting costs of $5,000, the total annual cost of MNA would be approximately $9,940. Thus, an additional 5 years of MNA would increase the total project cost by $49,700 (around 7.4% of the original project estimate); an additional 10 years of MNA would cost an additional $99,400; and 30 years of additional MNA would cost $298,200. However, as stated above, extended post-treatment MNA is unlikely if sufficient active treatment is applied.

Conditions at the Vandenberg site differed from the hypothetical cost example in having no appreciable residual source material in the tested area, (although a source appears to exist upgradient at Site 35), but also in having a somewhat non-homogeneous flow pattern, thereby affecting the distribution of substrate. Under these circumstances, which have off-setting cost implications, the relative cost is likely only slightly higher than costs for the average ERD site, because of a requirement for a higher density of injection points. In a full-scale application at Vandenberg, it is expected that pH could be controlled relatively inexpensively with the use of a buffer applied from the start of the treatment program, thereby reducing the lag time experienced in the demonstration. Thus, the injection parameters used in the hypothetical example are considered typical based on ARCADIS' experience, and are not solely based on the Vandenberg example.

Based on ARCADIS' experience, actual project costs have ranged from approximately $75,000 for a small-scale application and/or pilot study or demonstration-scale project to $2,000,000 for a large plume treatment with a fully automated reagent injection system. Table 5-6 presents a selection of cost examples with concentration and size information. The full-scale system for the automated site included installation of over 100 reagent injection wells to provide aggressive plume-wide treatment.

Operating costs (including reagent injection, monitoring and reporting) are generally on the order of $50,000 to $100,000 per year. The percentage of the total costs associated with the reagent injections is typically greater than 50%. On the other hand, the actual cost of the reagent itself typically represents less than 10% of the total project cost.

The cost data presented in Table 5-6 clearly illustrate the effective nature of the ERD technology in addressing CAH contamination in groundwater. For example, two sites have been completed with "no further action" notifications from the regulatory agencies, for less than $500,000 each. In conclusion, we would like to remind the reader that the practice of remediation engineering with each of the technologies discussed is rapidly evolving. Thus, we recommend conducting a realistic, site-specific relative cost analysis for any significant site. Competitive bid, and ideally competitive bids for guaranteed cost to regulatory closure, is the preferred way of making such a comparison.

6. Implementation Issues

6.1 Environmental Checklist

Potential regulations that affect the ERD demonstration are limited to those addressing *in-situ* remediation technologies. These regulations include underground injection control (UIC) permit issues and the products of the ERD treatment process. There are no unusual issues involving the transport, storage or disposal of wastes and treatment residuals. The standard issues of drill cuttings produced during injection well installation and purge water produced during well sampling may apply.

The amount of interaction with regulatory agencies required to execute the ERD projects is sometimes substantially greater than with traditional technologies, until a particular regulatory agency becomes familiar and comfortable with these technologies. However, the technology has been permitted in numerous jurisdictions and the regulatory community's experience base is growing. ARCADIS currently has more than 130 IRZ projects in 32 states that are complete or underway. Of these, at least 47 are full-scale implementations. Reagents approved for use at various ERD sites include molasses, corn syrup and whey (Lutes 2003, 2004).

Many states regulate the injection of materials into the subsurface and may require a Safe Drinking Water Act-mandated UIC permit prior to implementing the technology. The UIC permit includes information regarding the chemical nature of the substrate solution, and addresses potential concerns with water quality resulting from the injection process. Typically, the carbohydrate reagents recommended are food-grade, contributing to the rapid acceptance of the technology. UIC permitting for injection of carbohydrates is generally waived or is implemented with minimal paperwork (for example, permitting by rule). This issue is not considered to be a major impediment to ERD implementation.

Previous experience with state regulatory agencies where ERD technology has been performed indicates that an initial meeting to establish the proposed course of action for the project is the most effective process. The concerns of the UIC permit staff at state regulatory agencies must be addressed at the onset of the project to avoid delays. Usually, the information required to satisfy the requirements of the UIC permits is readily available, and should not represent a major regulatory hurdle. Continued close communications with the regulatory agencies during the planning and execution of ERD greatly increase the potential for a successful demonstration. A teaming relationship with the local environmental regulatory agencies is important to technology success.

Public participation during the technology process should be addressed on a site-specific basis. Inquiries on behalf of public entities should be addressed in a timely manner by the project management. The ERD technology is a relatively straightforward and non-threatening process, and thus it is anticipated that any public communications will be favorably received.

6.2 Other Regulatory Issues

Ongoing work at IRP Sites 32/35 is overseen jointly by DTSC and RWQCB under a 1991 Federal Facilities Site Remediation Agreement (FFSRA), which addresses cleanup of IRP sites at VAFB. The FFSRA is a cooperative agreement that recognizes that provided cleanup of IRP sites continues under DTSC and RWQCB oversight, enforcement actions will not be taken against VAFB.

In accordance with the FFSRA initiated in 1991 at the site, the cooperative nature of the agreement specifies agency oversight and involvement, without an extensive permitting process (some permits are exempt). Interactions with DTSC and RWQCB are handled primarily by Vandenberg AFB personnel, though ARCADIS did provide written and in-person information to the agencies at several points throughout this project. Approval was obtained from both agencies before initiating the demonstration and then again prior to initiating buffered injections. At the request of the base a preliminary version of this report was submitted to the base (10/03) and then to the regulators (3/04).

Since this demonstration was entirely within the Vandenberg AFB boundaries and not in a residential area there was no formal public participation requirement. The demonstration is briefly described on the bases public environmental website http://www.vandenberg.af.mil/30sw/organizations/30msg/CES/IRP/pdf/irpclnup.pdf . Vandenberg AFB has an active community advisory board for cleanup matters.

6.3 End-User Issues

The IRZ/ERD technology is being implemented at over 130 sites and, within the limits recommended in Table 3-2, may potentially be applied to any groundwater CAH plume. CAH contamination is a common remediation concern at DoD installations. EPA has estimated that more than 3,000 DoD sites in the US alone are contaminated with chlorinated hydrocarbons. The information in the FY 2001 DERP Annual Report to Congress, which is organized by site type, was used to estimate that DoD has 6,800 total solvent sites of which 2,300 are sites “in progress”. ARCADIS’ applications of ERD to Federal sites are detailed in Section 6.3.3. A recent report states that the Air Force has 253 TCE sites and the Navy has 450 PCE, TCE and DCE sites (Harre, 2003).

6.3.1 Secondary Water Quality and Gas Production Issues

Secondary water quality and gas production issues as they relate to stakeholders and end-users are discussed in detail in Section 1.4. Briefly, the following issues were identified:

- The production of intermediate products of CAHs as the ERD process converts more highly chlorinated CAHs to less chlorinated and eventually non-chlorinated end products. The cascading reactions can result in the production of vinyl chloride. The production of vinyl chloride or other intermediate products is considered a temporary situation and does not represent a major impediment to the technology but should be monitored during application of the technology.

- Gases such as methane, hydrogen sulfide, and carbon dioxide may be produced and may potentially migrate and/or accumulate in the vadose zone. Since engineering solutions are fairly easily implemented, this issue is not considered to be a major impediment to technology implementation.

- The by-products of substrate consumption may include metals mobilized from the solid phase, COD, BOD, TDS, taste, odor, and sulfides. However, these impacts are typically limited to the reactive zone itself. Furthermore, it is generally believed that metals will be reprecipitated or immobilized downgradient of the reactive zone when the conditions return to their preexisting state and within the IRZ area some time after system shutdown.

- Molasses itself is a potential source of metals. The molasses-water mixture did not produce secondary water quality issues in this demonstration (see Section 4.3.5). However, this is a potential issue that should be briefly considered in the design phase for IRZ projects. The paucity of available data suggests that further work should be done to explore the metallic content of different sources of molasses.

Thus the potential for secondary water quality impacts needs to be fully identified and addressed during design and in consultation with all applicable regulatory agencies and the public.

6.3.2 Procurement and Implementation Issues

Equipment required for technology implementation as applied at Vandenberg, described in Sections 2.3 and 3.5.1, is non-specialized and readily available. System design must be customized for each application to account for regulatory and site conditions, hydrogeological and geochemical characteristics, but the elements of a batch-fed IRZ/ERD are available commercially-off-the-shelf (COTS) and through subcontract with laboratories, drilling contractors, etc. As summarized in Table 4-2, ERD technology is relatively easy to implement and beyond the design phase and should generally only require environmental technicians for field implementation and maintenance. Automated systems and those involving extraction/ re-injection systems require custom design, and the ease of implementation of such systems is design-dependent.

The primary scale-up issue is the addition of injection wells to expand the IRZ, based on the geometry of the IRZ as determined during the field pilot test. If the number of injection wells required is excessive, or if drilling costs are prohibitive due to depth or difficult geological conditions, scaling up could pose significant hurdles. However, such barriers are usually foreseen before a pilot test is implemented.

Licensing is required to apply the technology. ARCADIS is the owner of Contractor Patented Technology for the in-situ addition of carbohydrate substrate material to create reactive zones for the removal of chlorinated hydrocarbons from groundwater as set forth in U.S. Patent Nos. 6,143,177 and 6,322,700. ARCADIS and the U.S. Government have agreed for ARCADIS to grant to the Government a paid up, non-exclusive limited license for government owned facilities only (this agreement is related to the demonstration effort "In situ Substrate Addition to Create Reactive Zones for Treatment of Chlorinated Aliphatic Hydrocarbons" under Contract No. F41624-99-C-8032). No rights to assign, sublicense or other ownership interests are to be conveyed therein, nor shall the License apply to any other patented technology that is owned or licensed by ARCADIS. To discuss application of this technology at government sites please contact “Government contact name and #” and Chris Lutes of ARCADIS in Durham, NC at 919-544-4535 or clutes@arcadis-us.com. For commercial application please contact ARCADIS only.

The technology was customized for the demonstration only in the sense that all sites require a customized system design and adjustment of operations as monitoring data is gathered. As implied by the widespread existing use of the technology (see Section 2.2), it has already been successfully commercialized and transferred.

6.3.3 Transition

The IRZ bioremediation technology discussed herein was developed primarily in the private sector and has been applied (at more than 130 sites) to treat metals and CAHs. These sites involved regulators and a variety of site conditions in several different geographic areas of the country. The technology is mature as a plume remediation strategy or barrier strategy and ready to transition to commercial application in the DoD. It has been used successfully for concentrations up to 150 mg/L initial TCE (see Section A.2.13 of the protocol document [Suthersan, 2002]). It is applicable to a wide range of contaminants and geological conditions (see Sections 1 and 2 of Suthersan, 2002). It is not, however, a “silver bullet” applicable to all sites and all contaminants and/or mixtures of contaminants. Additional demonstrations are not necessary for treatment of groundwater plumes but would provide useful data to further elucidate applicability to varying conditions and/or contaminants. Additional demonstrations are desirable to evaluate potential to various source zone architectures (for example, sites with DNAPL entrapped in soil pores or present in fractured bedrock) and to evaluate different delivery mechanisms, such as recirculation wells, for deeper/thicker plumes). Additional demonstrations are also desirable, and some are ongoing, to extend the technique to additional contaminants such as explosives and perchlorates (see for example May, 2003; Morie, 2002; Owsianiak, 2003). ARCADIS has demonstrated that the technique is applicable to a wide variety of subsurface conditions. However, experienced personnel familiar with IRZ must carefully evaluate each site in order to identify conditions, including adverse geochemistry, that could impact remedial design.

Finalization of the protocol “Technical Protocol for Using Soluble Carbohydrates to Enhance Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons” occurred in December 2002 and will be a major technology transfer step. While not a demonstration need, collection of case histories will provide a useful guidance tool. This process has begun as Appendix A of the protocol (Suthersan, 2002) and is expected to continue during DoD’s effort to prepare the “Principles and Practices of Enhanced Anaerobic Bioremediation” document, now ongoing with ARCADIS participation.

As inventor of the technique (and current patent holder), ARCADIS is the most experienced firm to apply soluble carbohydrates for the enhancement of anaerobic biodegradation. ARCADIS is already aggressively and successfully seeking to roll out the IRZ technique at other DoD and DOE facilities. ARCADIS has the following IRZ projects underway at Federal facilities:

- A successful pilot scale application completed at Fort Devens, Massachusetts (see Section 4.3.5.3) under a guaranteed fixed price contract with scale-up to full-scale pending

- A completed pilot study for the Navy at Naval Weapons Industrial Reserve Plant, Dallas, Texas, (see Enhanced In-Situ Biotransformation Pilot Study Report, to NFESC March 29, 2002)
- Two sites at Lompoc Federal Penitentiary where IRZ pilot studies have begun in late 2002 at a guaranteed performance contracting site (this is a DoD/FORSCOM project; it was a disciplinary barracks and was transferred to Bureau Of Prisons during BRAC)
- A successful bench scale study of IRZ for uranium completed under a contract with DOE NETL using samples from Fernald
- Under a guaranteed fixed price contract at Fort Leavenworth, Kansas, we are implementing pilot IRZ systems (started September 2003) at two sites
- An application has been ongoing since May 2003 under a guaranteed fixed price AFCEE task order for Charleston AFB in South Carolina
- An ongoing demonstration for energetics that was contracted through AEC/Plexus for Milan Army Ammunition Plant in Tennessee (begun July 2003; successful results for TNT reported in May 2004)
- An application under a contract with Army COE to AHTNA (a native American firm) for a pilot study at Fort Ord beginning in January 2001
- Two additional ongoing applications at confidential Federal facilities
- Applications to 10 sites, at five Federal facilities are under contract but not yet started

Perhaps one of the most likely sources of funding will be redirection of funding as IRZ approaches are substituted, with regulatory approval, for marginal or ineffective pump and treat systems. The Army's Groundwater Effectiveness Technical Evaluation Review (GWETER) program managed by the Army Environmental Center (AEC) and supported by ARCADIS demonstrates how this process works. Under this contract, ARCADIS has performed life-cycle analyses and expert technology reviews of existing groundwater pump and treat systems at ten active and inactive (Army Base Realignment and Closure [BRAC]) sites to evaluate whether or not existing remediation systems are appropriate, efficient and cost effective in achieving site-specific goals. Success include Former Fort Ord (Monterey, California) where plans are under way for remediating a large chlorinated plume using in-situ technologies, and an in-situ pilot test at Milan Army Depot (Milan, Tennessee) on explosives (RDX, TNT, HMX) in groundwater. The Milan project will demonstrate an extension of IRZ to destroy explosives. As noted previously, there are many potential opportunities under Army, Navy and Air Force jurisdiction to substitute IRZ for existing pump and treat systems and realize substantial savings and a shorter path to closure. The action remains for DoD contracting groups and installation restoration program managers to seek more effective solutions.

As noted previously, IRZ is a bioremediation technique utilizing an electron donor to create the conditions needed to achieve treatment objectives in situ. While IRZ is applicable to a wide variety of sites and contaminants, expert knowledge is necessary to choose those situations with greatest potential for performance success and treatment cost reduction. In the last few years, the DoD has extended performance based contracts (PBCs) to include remediation projects. PBCs are nearly ideal approaches for transfer of IRZ and other similar technologies to the user. A well-written PBC scope of work describes treatment objectives but leaves the choice of remedy to potential remediation service providers. This paradigm shift away from “cost plus” approaches leaves DoD officials in control as performance is monitored against various milestones set by the firm providing remediation services, while allowing the private sector firm flexibility to work with regulators to choose remedies that best meet site specific requirements and optimize profitability of the job. The Army, Navy and Air Force are all working PBC remediation strategies. Additional procurement guidance will be needed as lessons learned are applied. The potential for cost savings is substantial. The need to transition to PBC approaches and realize maximum benefit from PBC approaches is urgent.

This demonstration project was performed by ARCADIS. ARCADIS is a private sector firm providing remediation services to a wide variety of industrial and government clients. The work was funded in part by ESTCP and AFCEE and managed by AFCEE. ARCADIS is already aggressively marketing IRZ to industry and government sectors and seeking other private sector organizations interesting in adding this technology to their tool kit. To date, ARCADIS has implemented IRZ solutions at more than 130 sites in the U. S. and abroad and is working with other private sector partners to facilitate broader application of the technique.

ARCADIS will continue ongoing IRZ marketing efforts to both private sector and government clients. The firm’s objective has never been to be the low cost provider, but to provide best and most cost effective solutions. IRZ is an integral part of ARCADIS’ GRiP® fixed price remediation contracting approach. Ongoing efforts at AFCEE, US Army Corps of Engineers (USACE) Omaha District, Army FORSCOM and elsewhere all support IRZ technology transfer efforts by emphasizing performance and price vs. low unit cost plus fee. Contracts are already in place with these agencies that encourage adoption of innovative technologies like IRZ. Increased utilization of these contracts should be encouraged. In addition ARCADIS is very willing to cooperate with other firms in implementing this technology under other government contracts at sites where they are the lead consultant.

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8. Points of Contact

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Project Lead Signature:

Christopher C. Lutes, ARCADIS G&M, Inc. Date

LIST OF FIGURES

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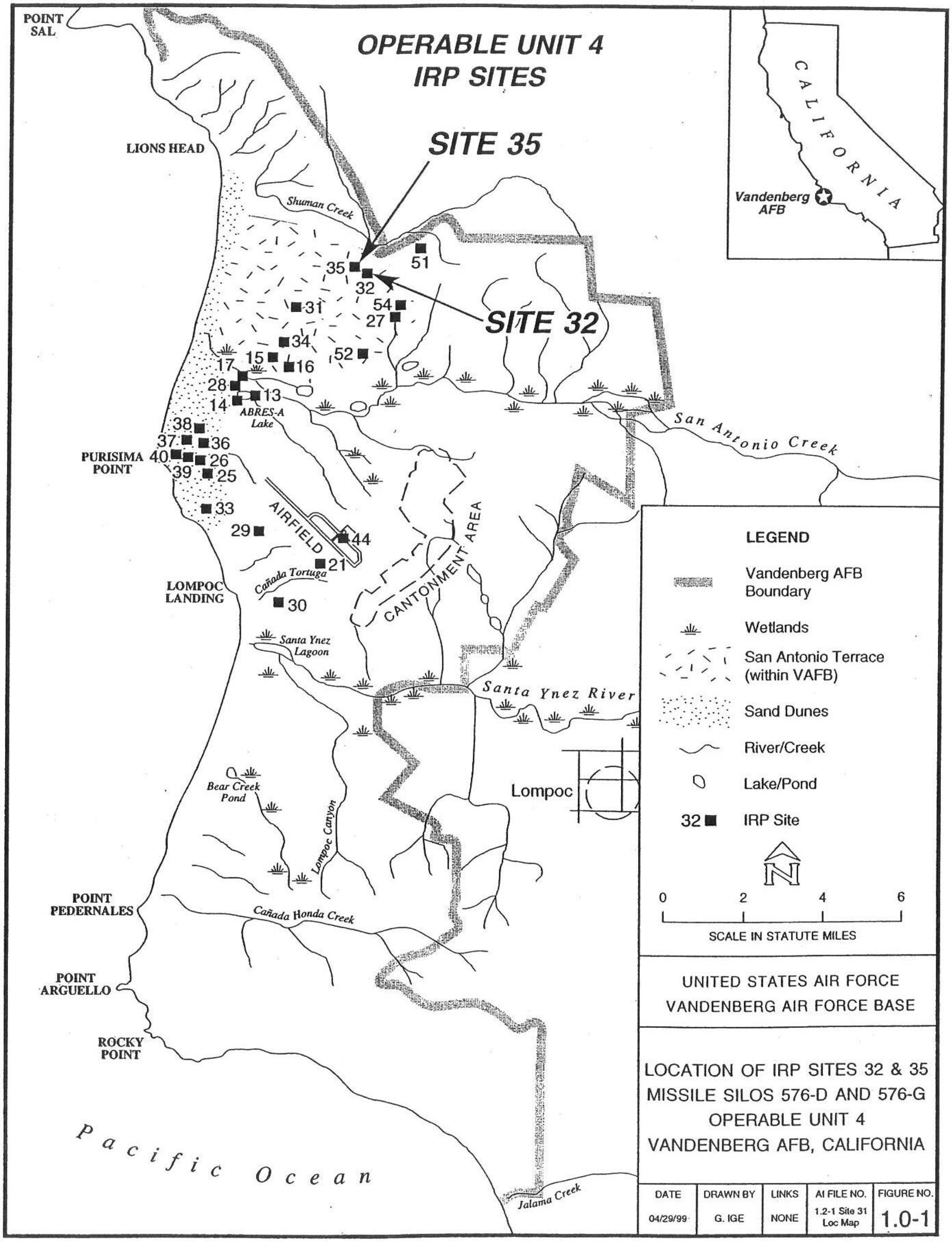


Figure 1-1 VAFB Site Map

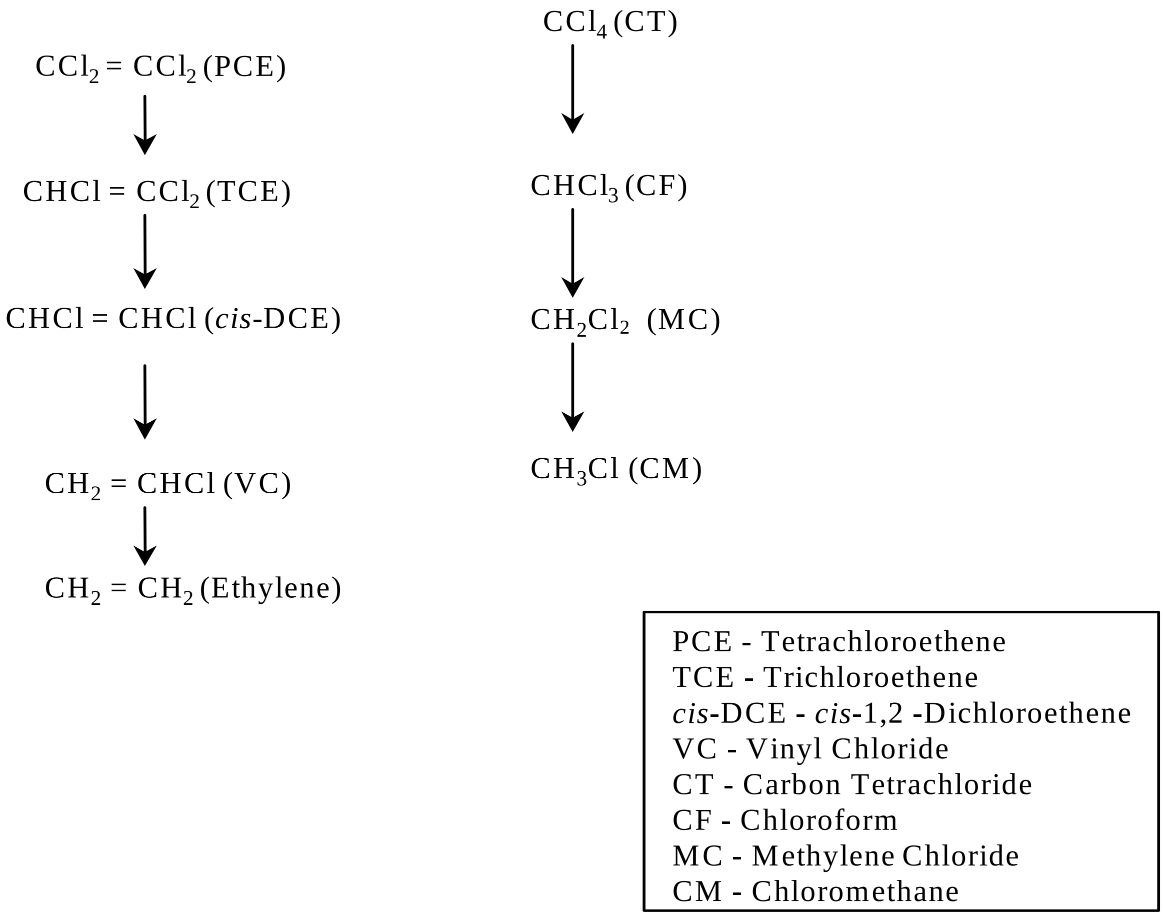


Figure 2-1 Anaerobic Transformations of Selected CAHs and their Daughter Products (after Vogel et al., 1987 and McCarty et al. 1c993)

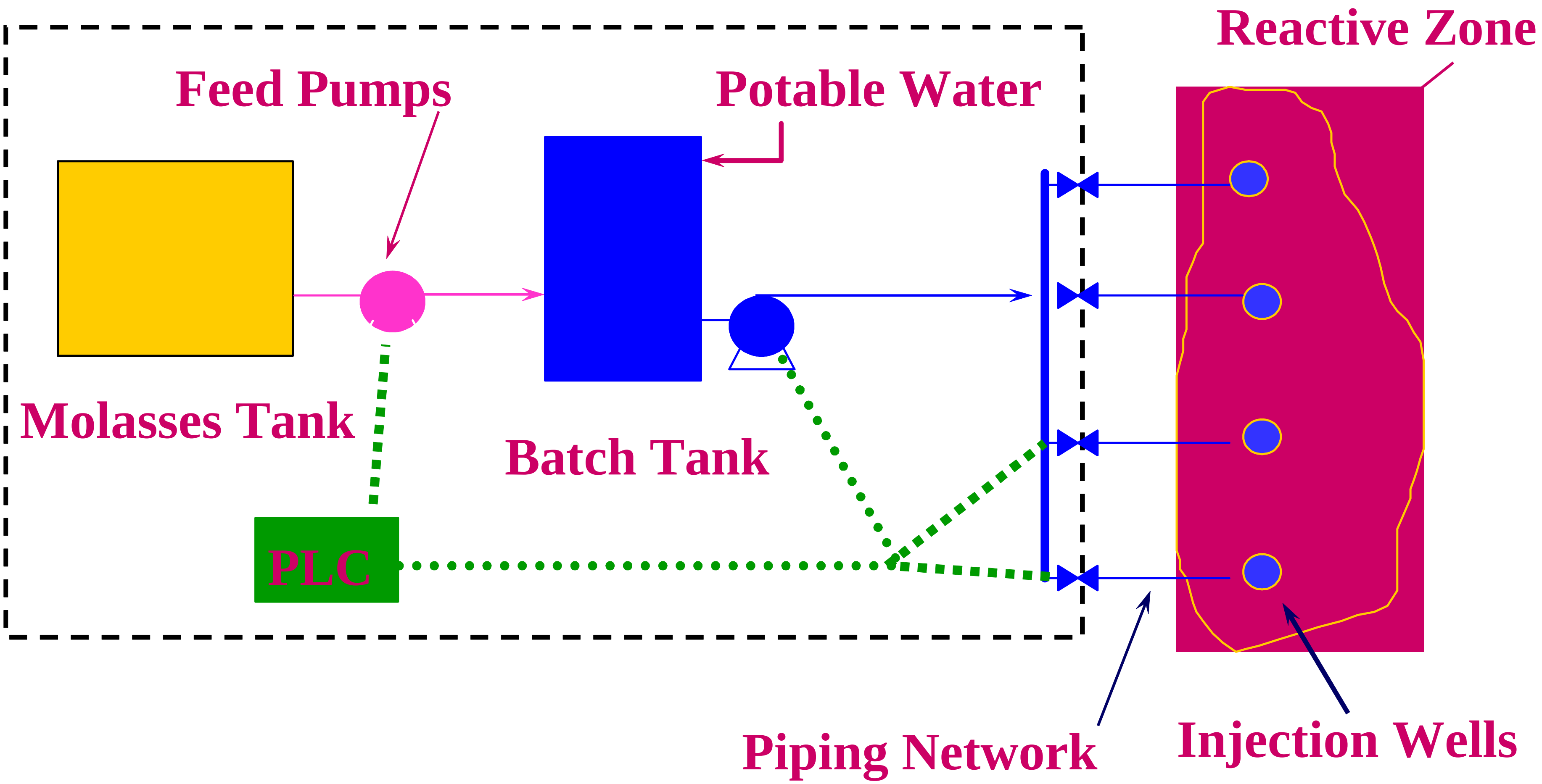
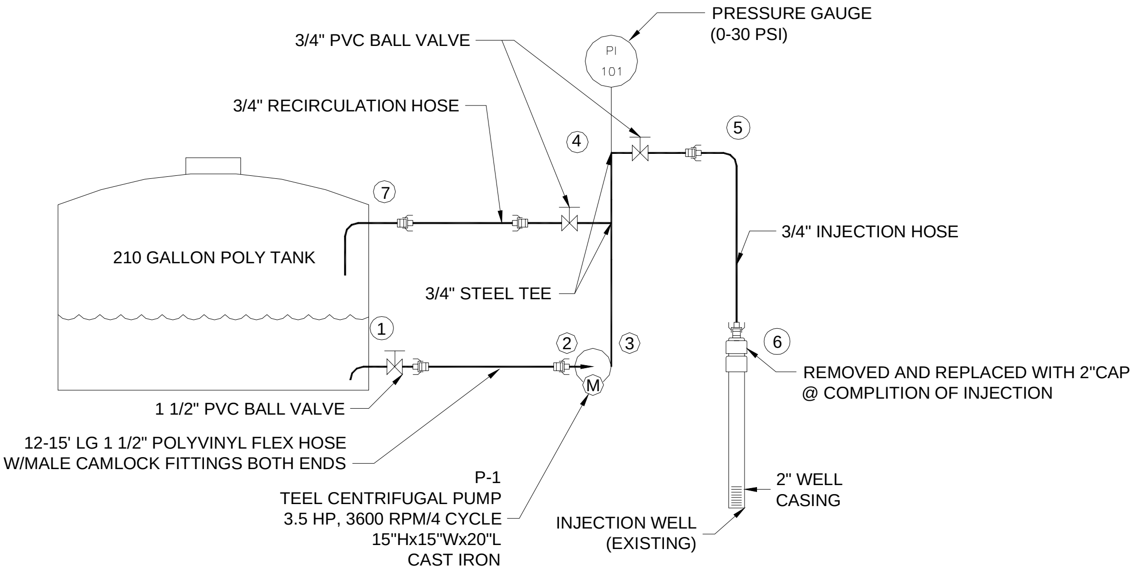


Figure 2-2 Conceptual Design for an ERD System Layout



ZONE	COMPONENT DETAILS
①	90 DEG PVC ELBOW (INSIDE TANK) 2" PVC TANK ADAPTER PVC REDUCER 2" - 1 1/2" (OUTSIDE TANK) 1 1/2" PVC BALL VALVE 1 1/2" FEMALE CAMLOCK FITTING
②	1 1/2" FEMALE CAMLOCK 1 1/2" STEEL NIPPLE/ UNION (INLET CONNECTION TO PUMP)
③	1 1/2" STEEL NIPPLE / UNION (OUTLET CONNECTION TO PUMP) 1 1/2 - 3/4" STEEL REDUCER 3/4" STEEL NIPPLE
④	3/4" STEEL TEE LIQUID FILLED PRESSURE GAUGE
⑤	3/4" MALE CAMLOCK FITTING 3/4" (150 PSI) SWAN CONTRACTOR WATER HOSE (~25' LONG) WITH 3/4" FEMALE CAMLOCK FITTINGS @ BOTH ENDS
⑥	2" PVC COUPLING SLIP TO MP 2" PVC COUPLING 3/4 X 2" REDUCER 3/4" MALE CAMLOCK
⑦	3/4" PVC TANK ADAPTER 3/4" MALE CAMLOCK FITTING 3/4" (150 PSI) SWAN CONTRACTOR WATER HOSE (~25' LONG) WITH 3/4" FEMALE CAMLOCK FITTINGS @ BOTH ENDS

Figure 2-3 Reagent Mixing and Injection System Schematic

Figure 2-4 Reagent Mixing and Injection System

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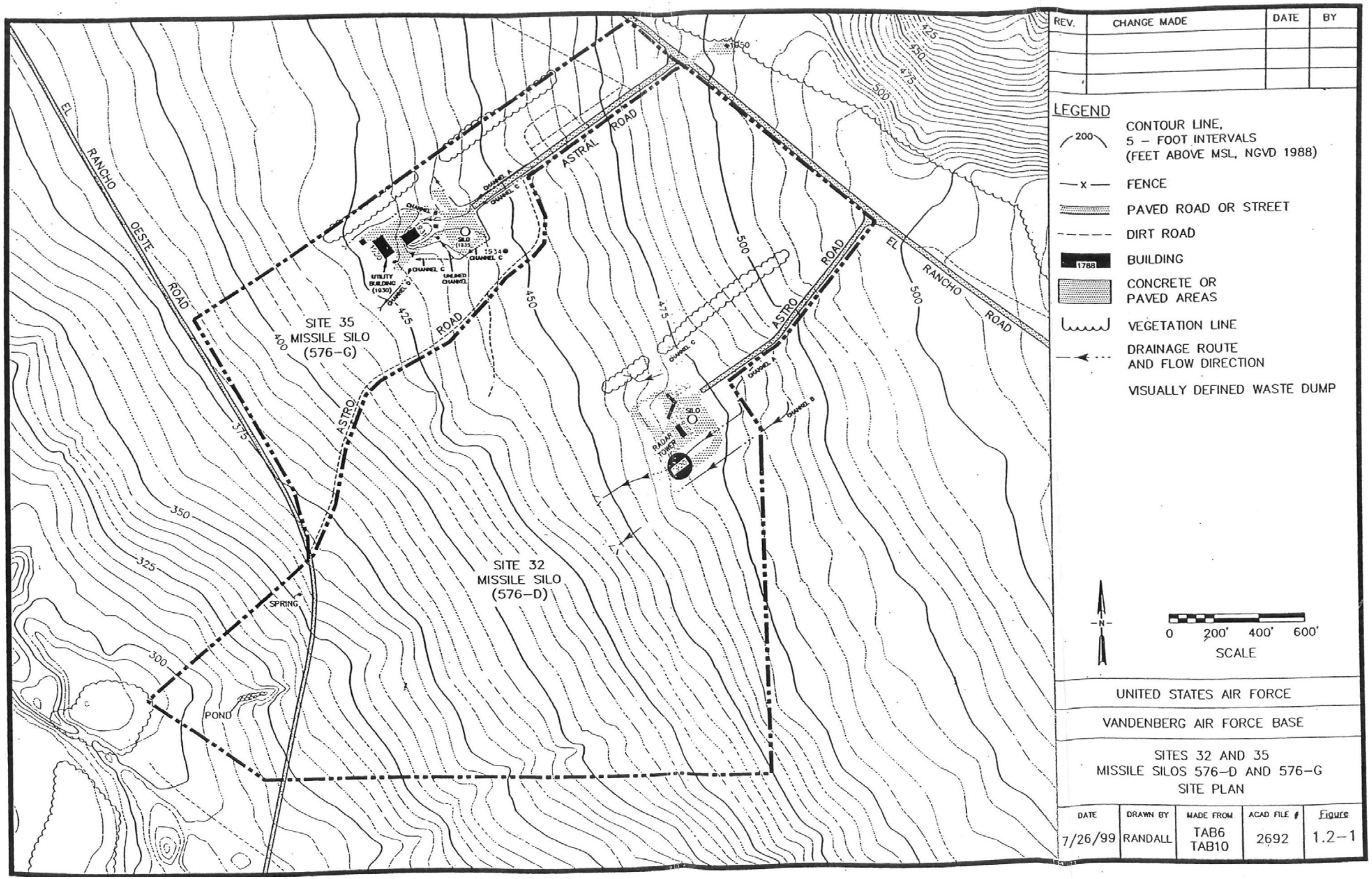


Figure 3-1 Sites 32 and 35 Site Plan

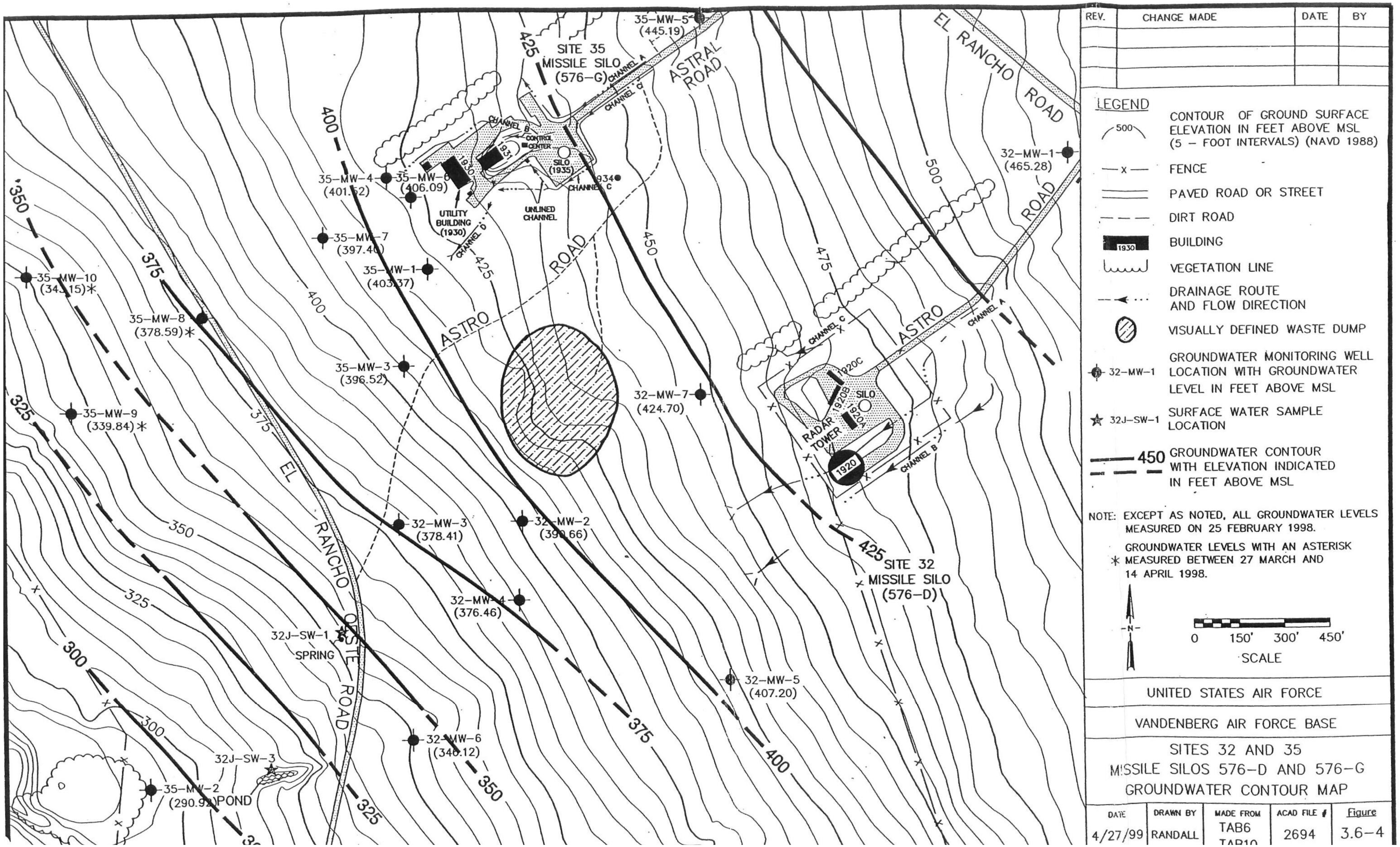


Figure 3-2 Sites 32 and 35 Potentiometric Surface Map

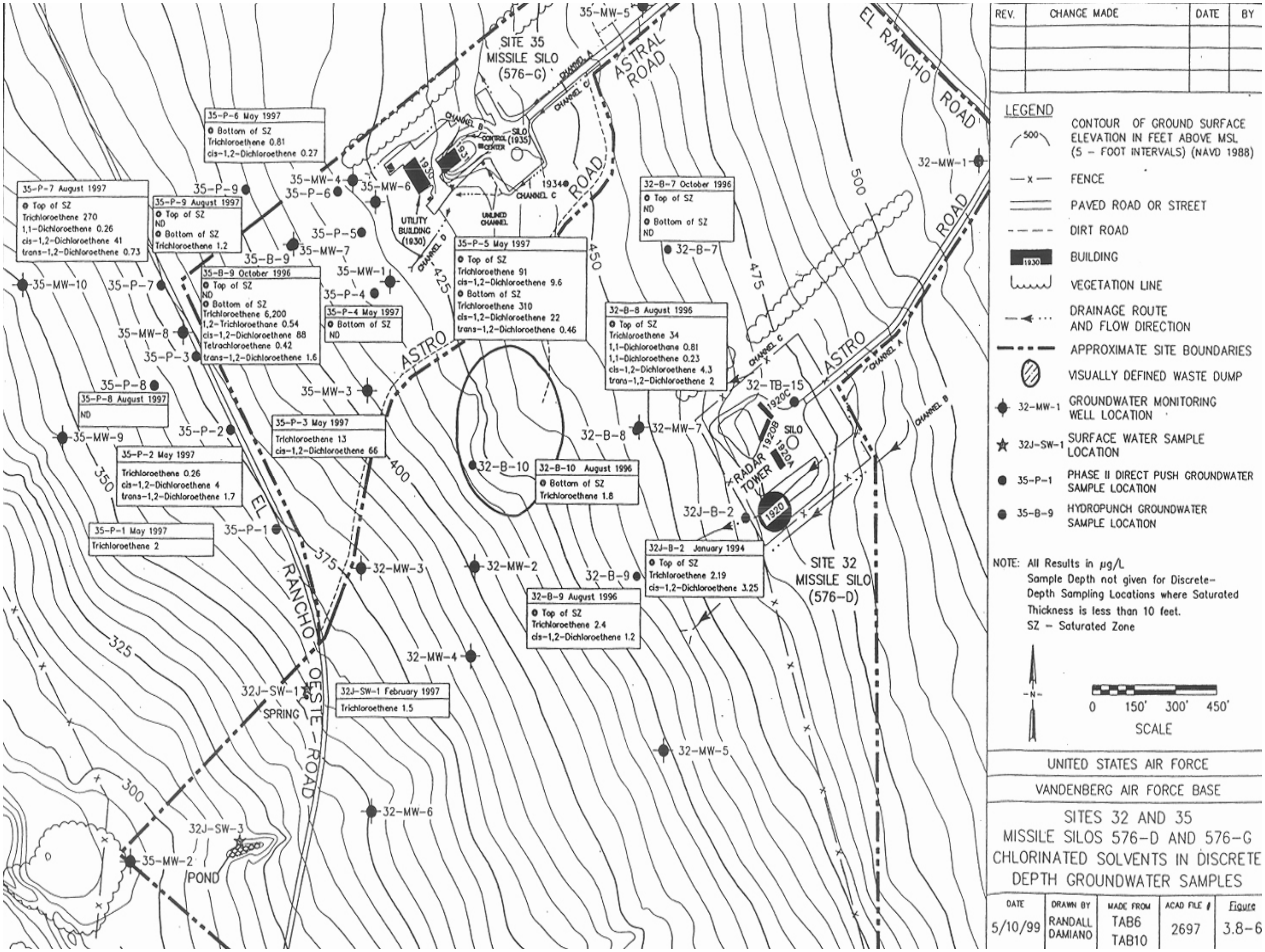


Figure 3-3 Sites 32 and 35 CAH Distribution Map (Pre-Demonstration)

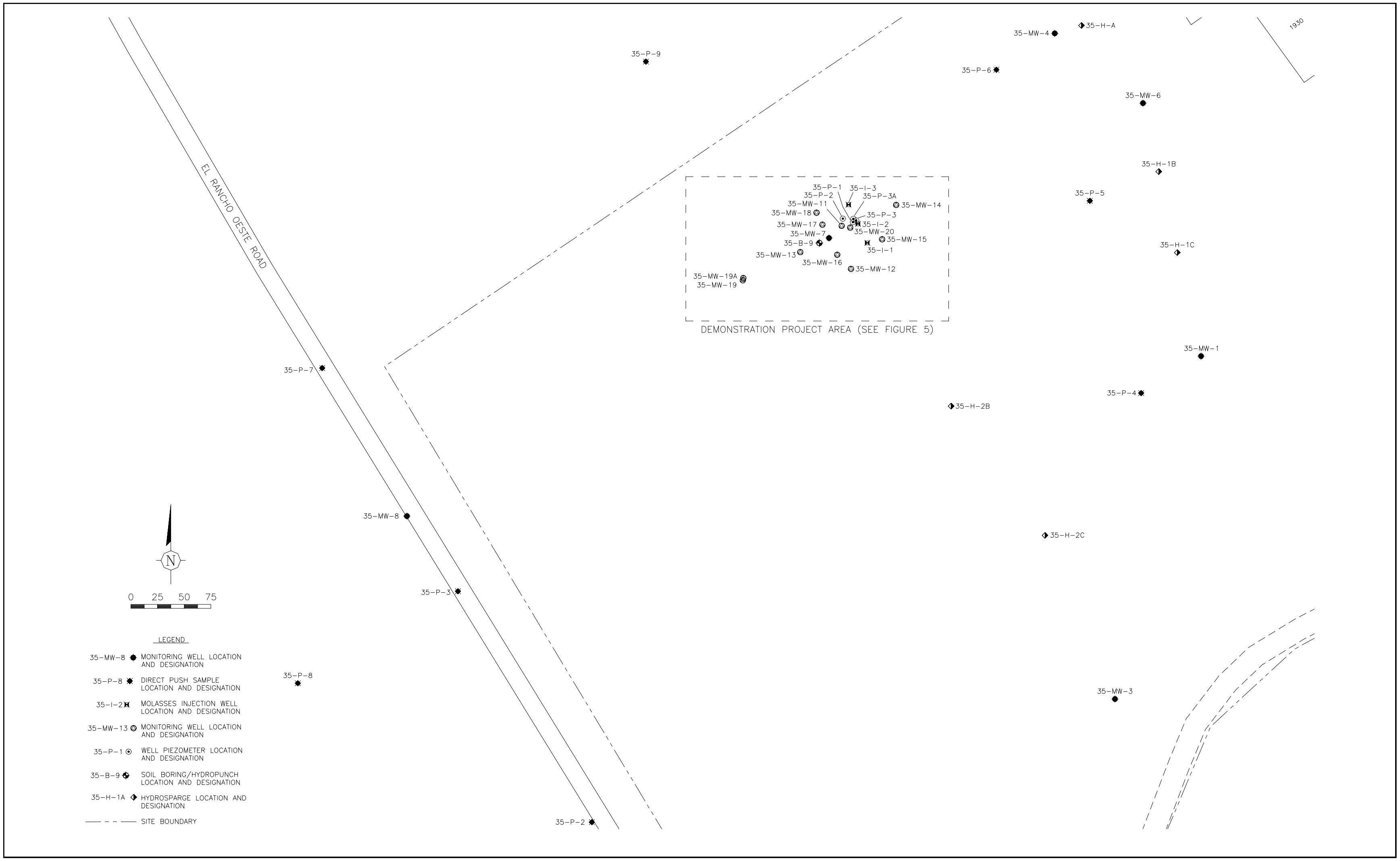


Figure 3-4 Sites 32 and 35 Subsurface Sample Locations

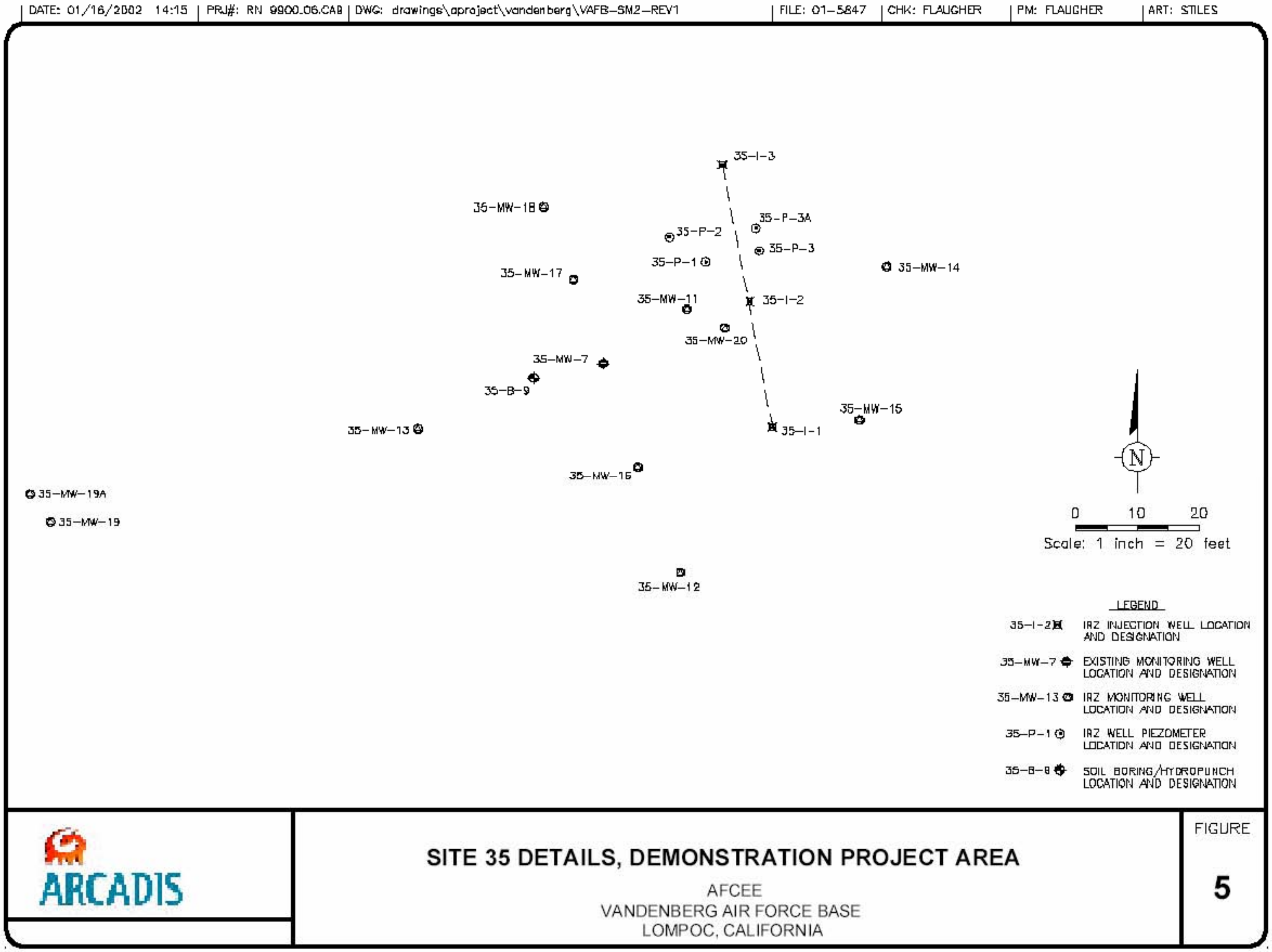
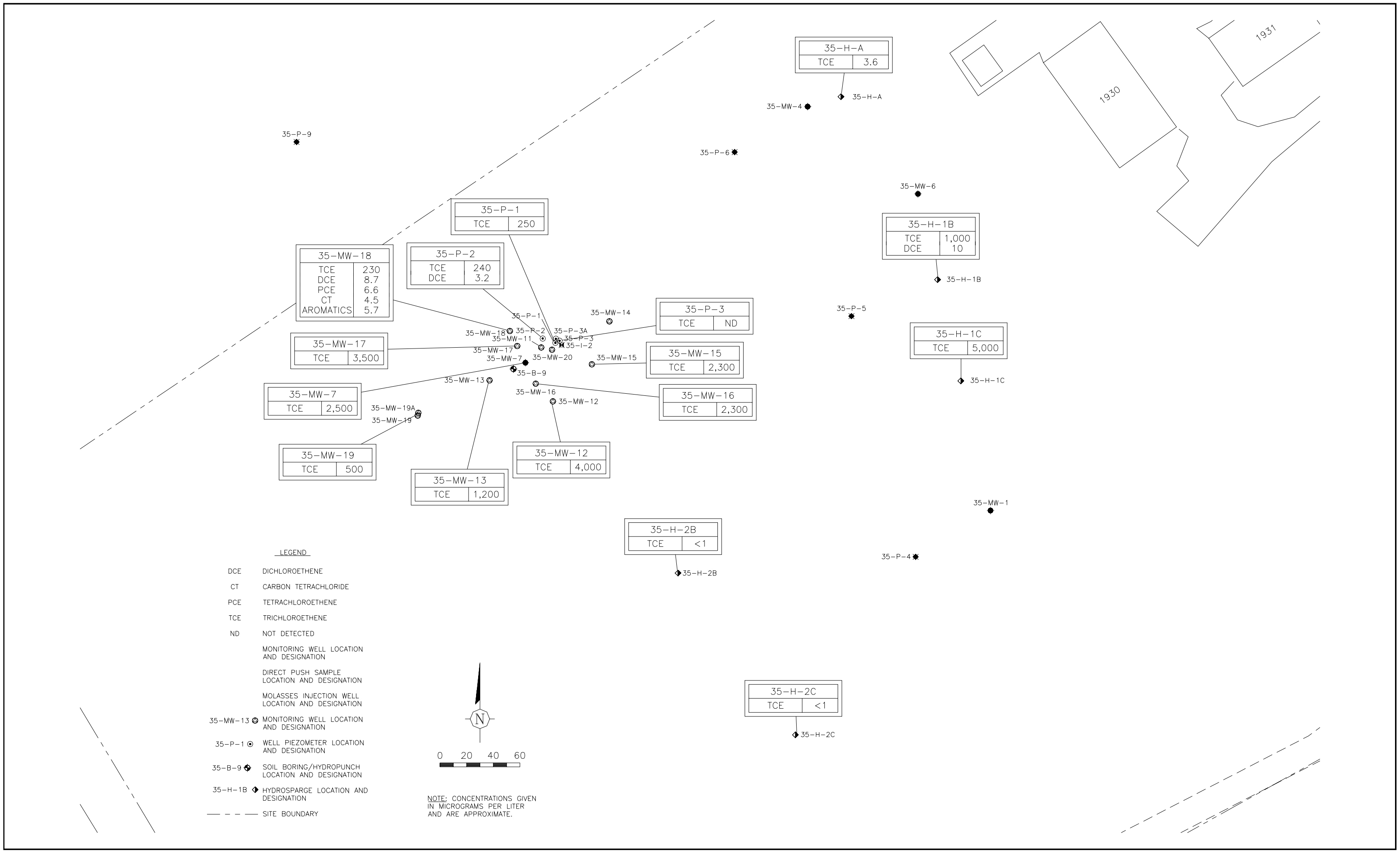


Figure 3-5 Site 35 Details, Demonstration Project Area



NOTE: CONCENTRATIONS GIVEN IN MICROGRAMS PER LITER AND ARE APPROXIMATE.

Figure 3-6 Groundwater Hydrosparge Results, Before Treatment, September 2000

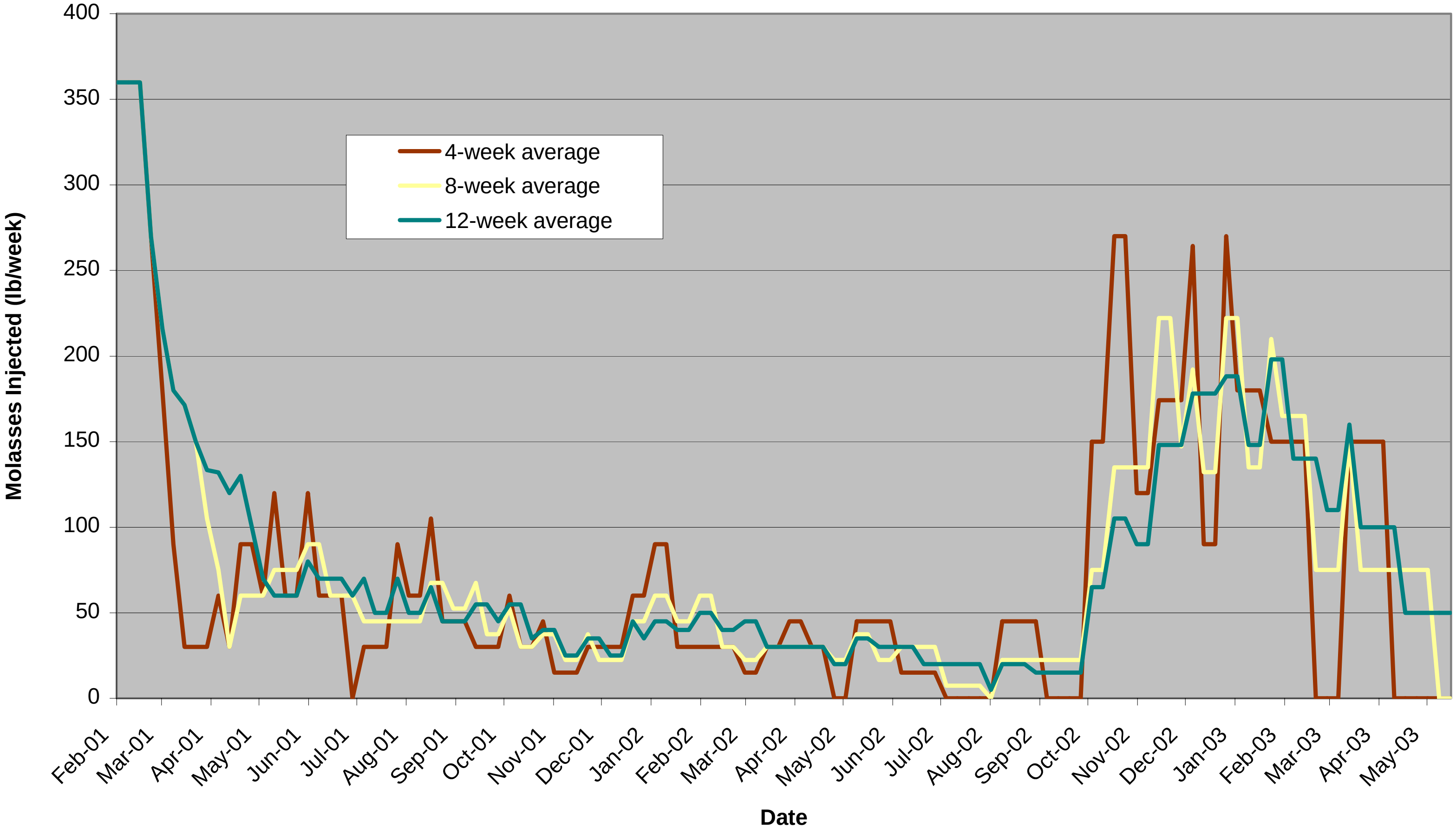


Figure 3-7 Rolling Average Weekly Molasses Loading

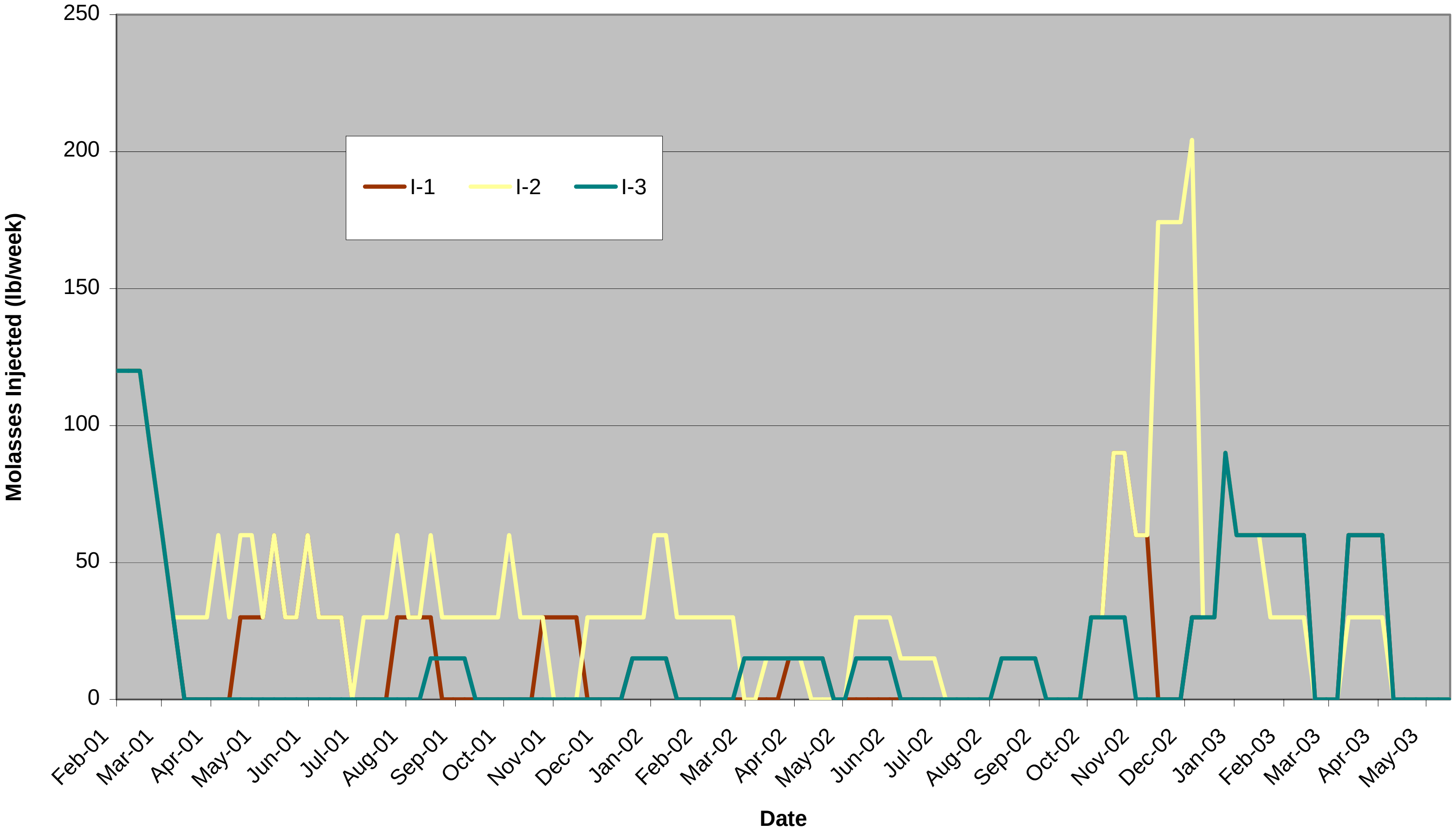


Figure 3-8 Rolling Average (4-Week) Molasses Loading per Injection Well

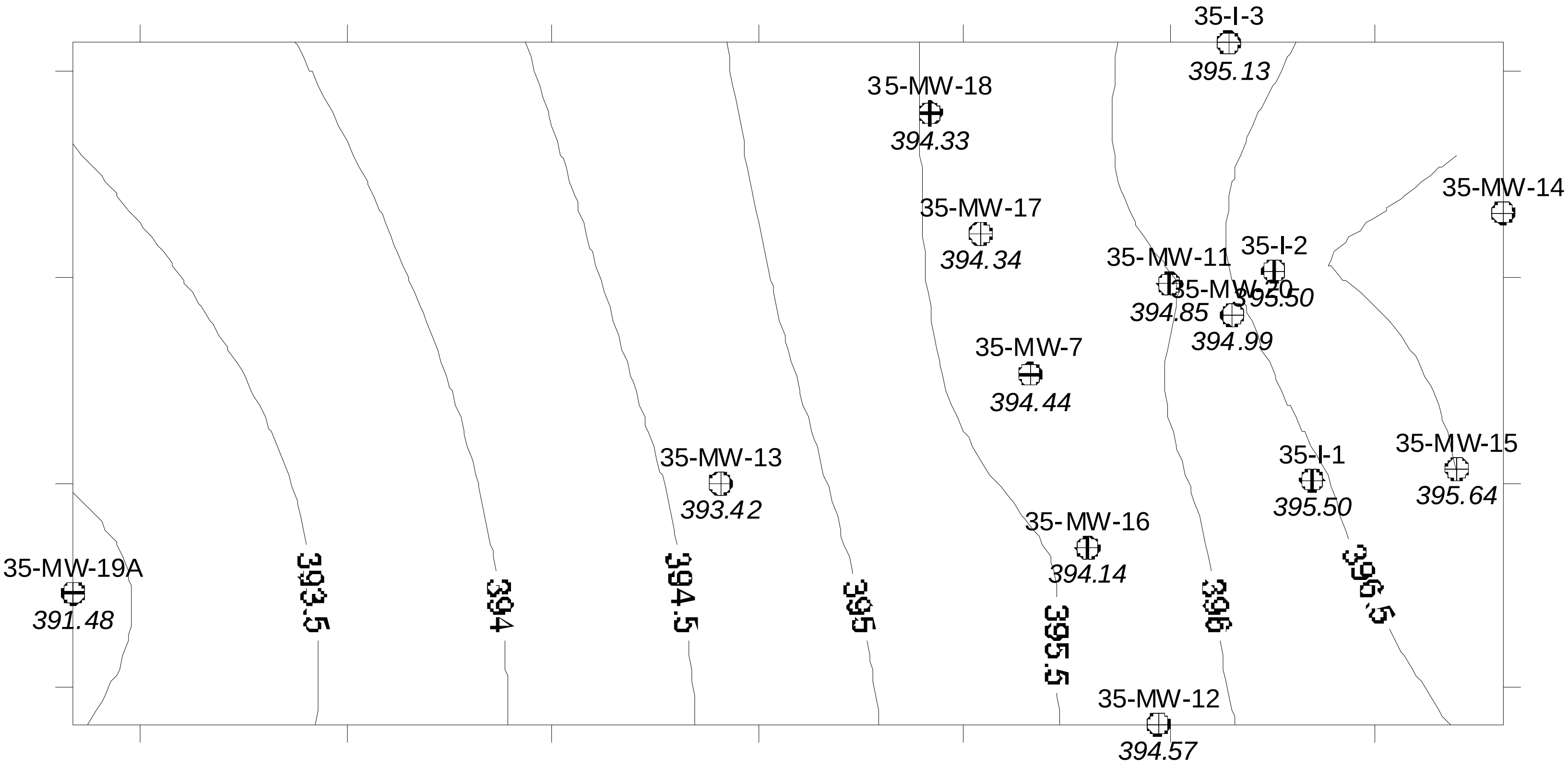


Figure 4-1 Potentiometric Surface Map for January 23, 2002

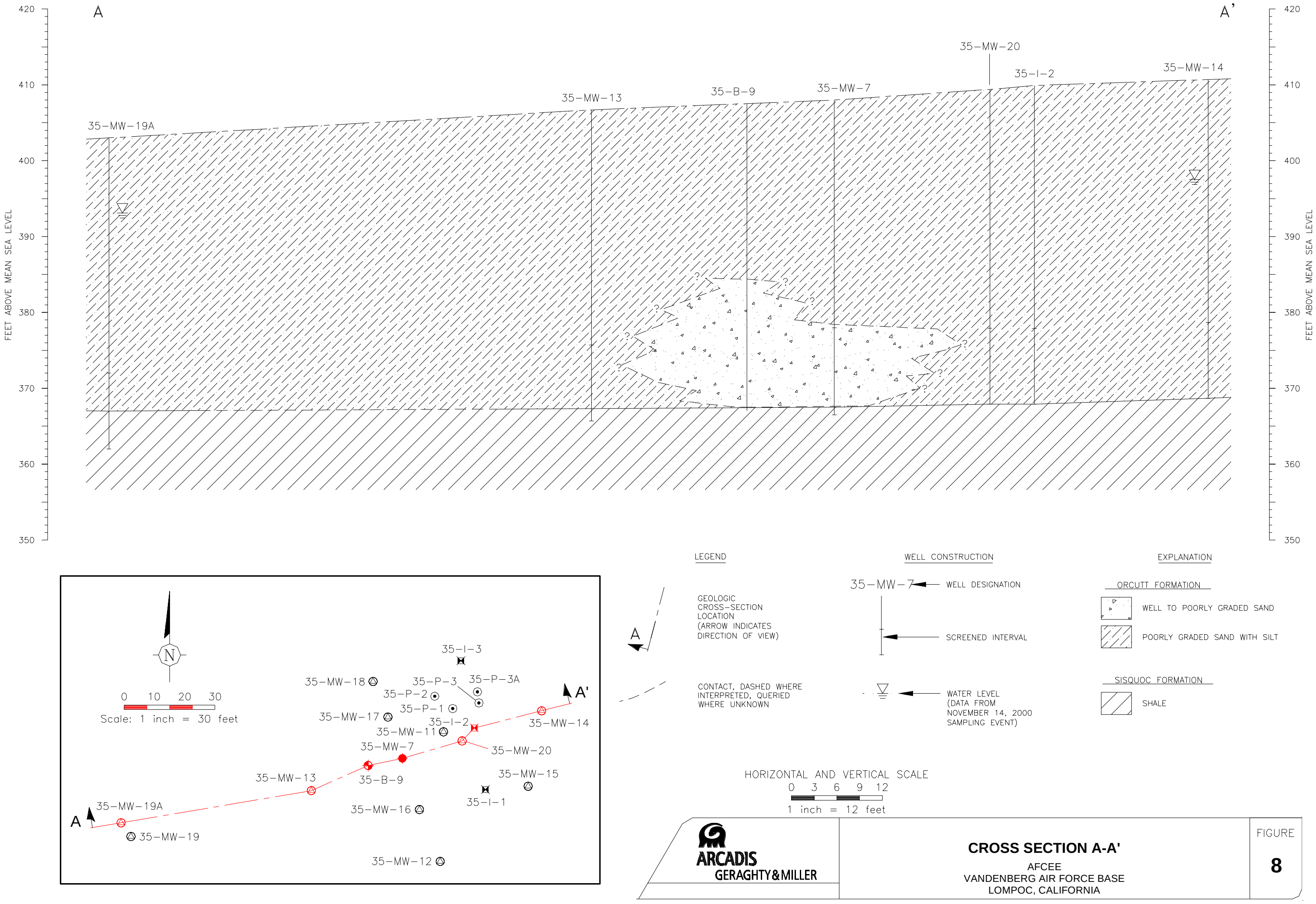


Figure 4-2a Cross Section A – A'

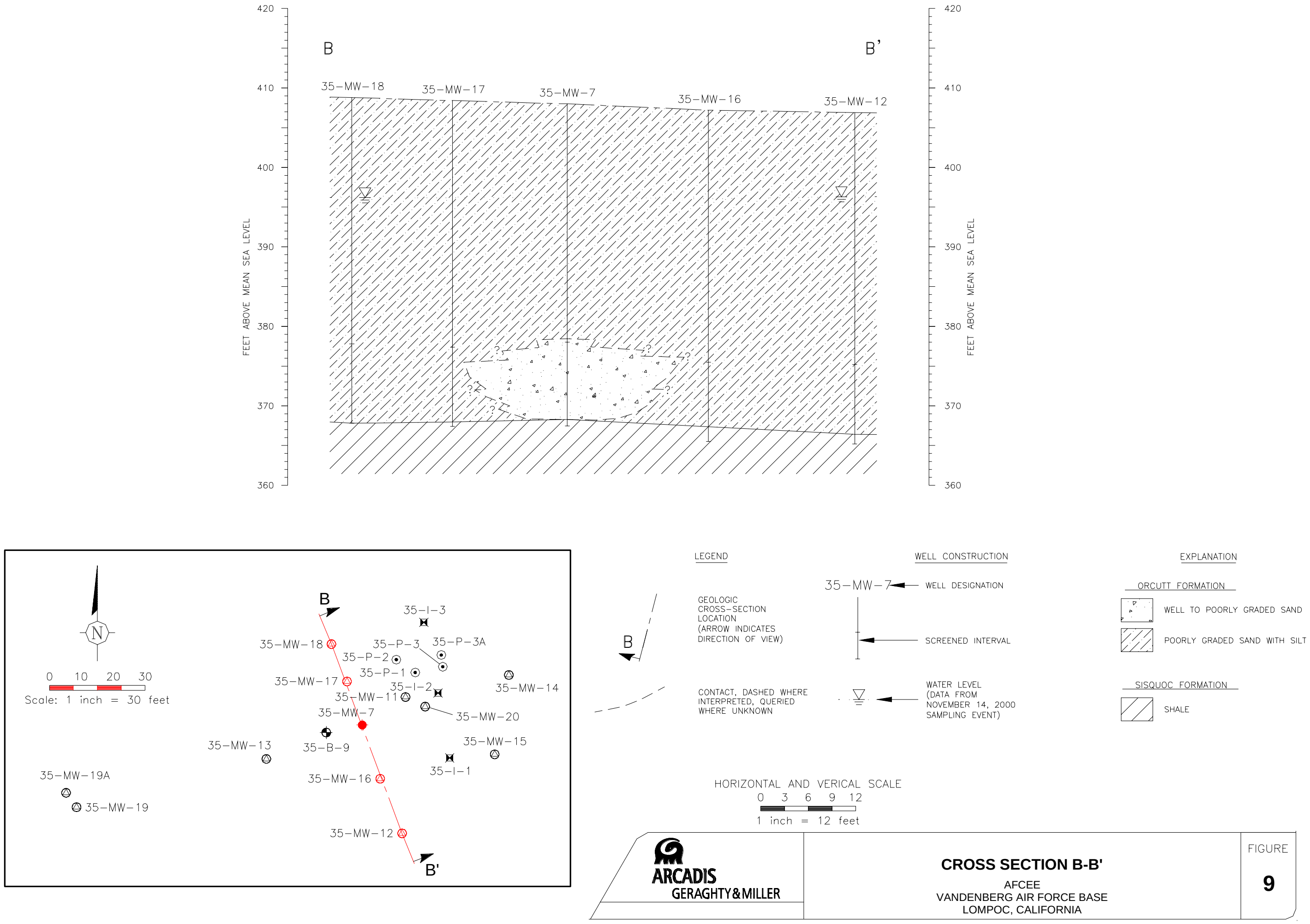


Figure 4-2b Cross Section B – B'

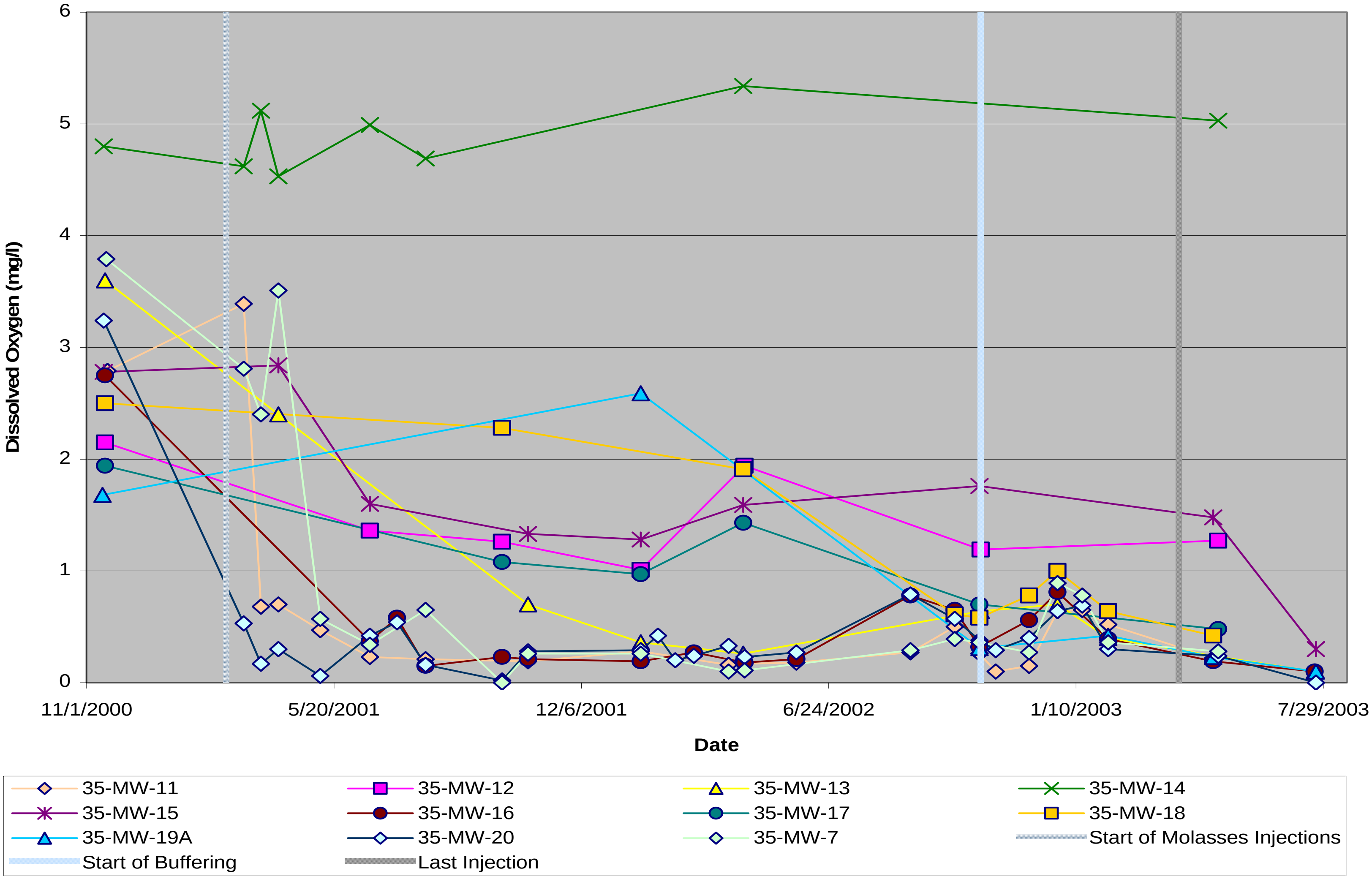


Figure 4-3 Dissolved Oxygen Trends for Vandenberg AFB

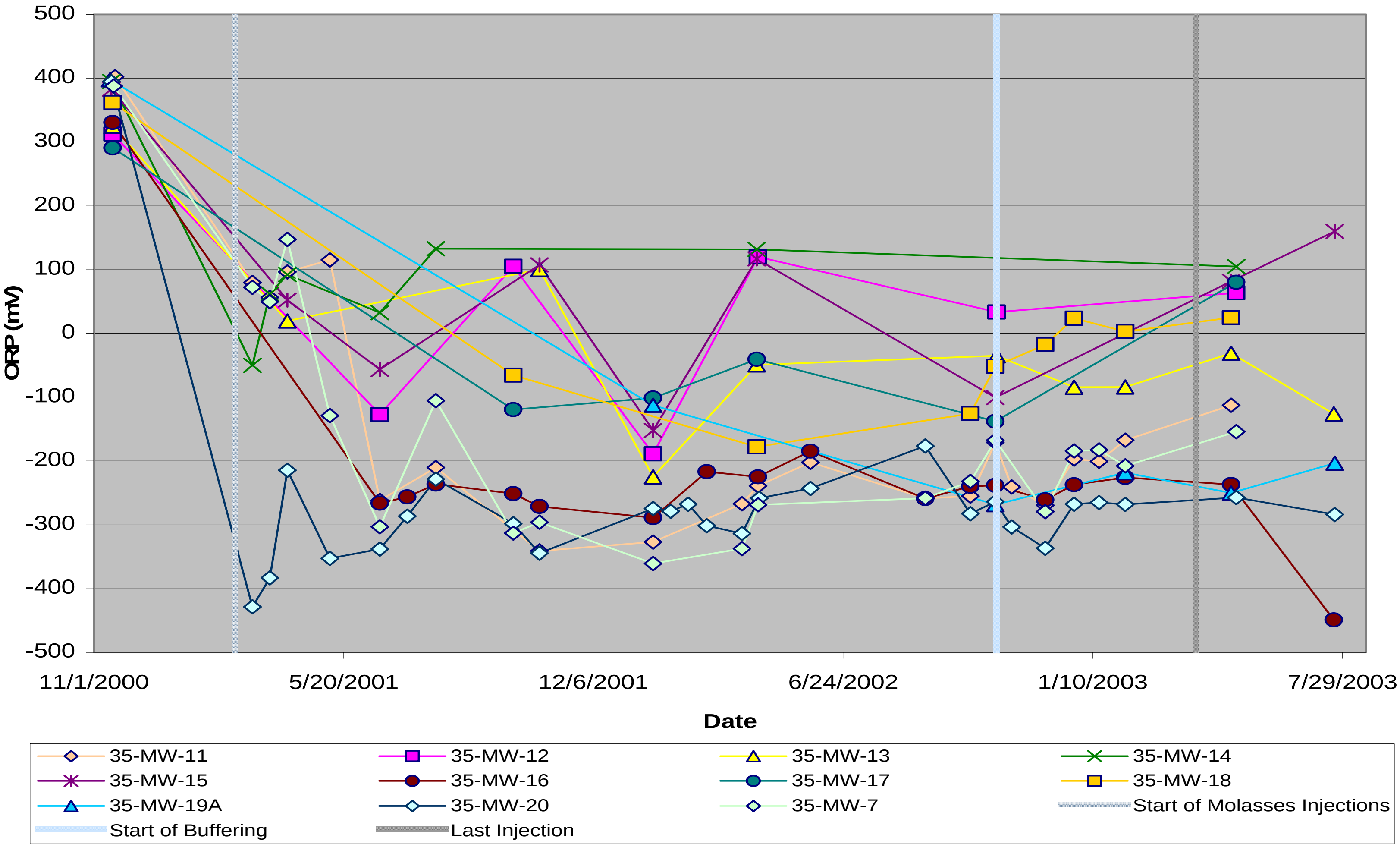


Figure 4-4 Redox Trends (pH Corrected)

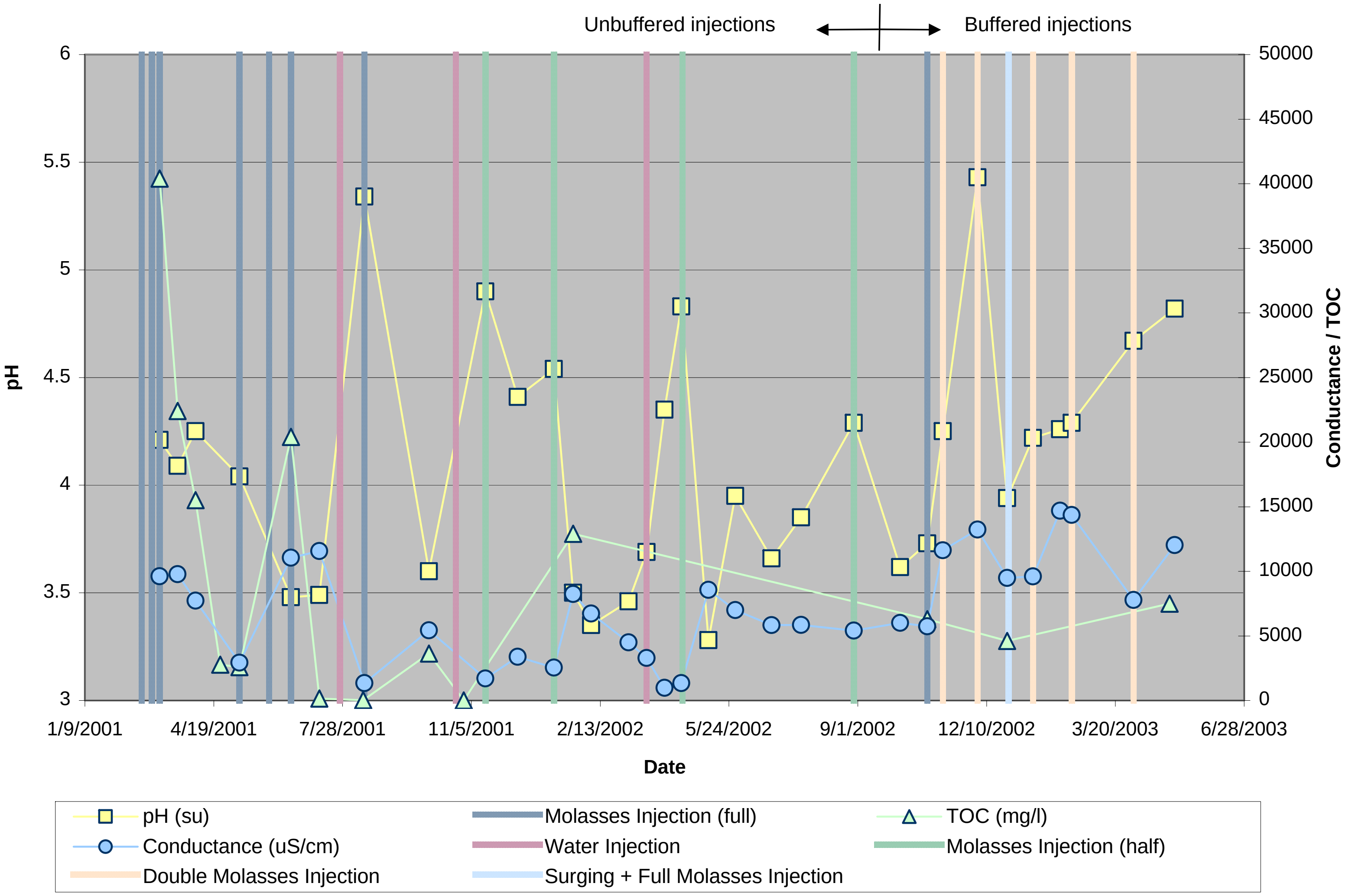


Figure 4-5 35-I-1 Performance

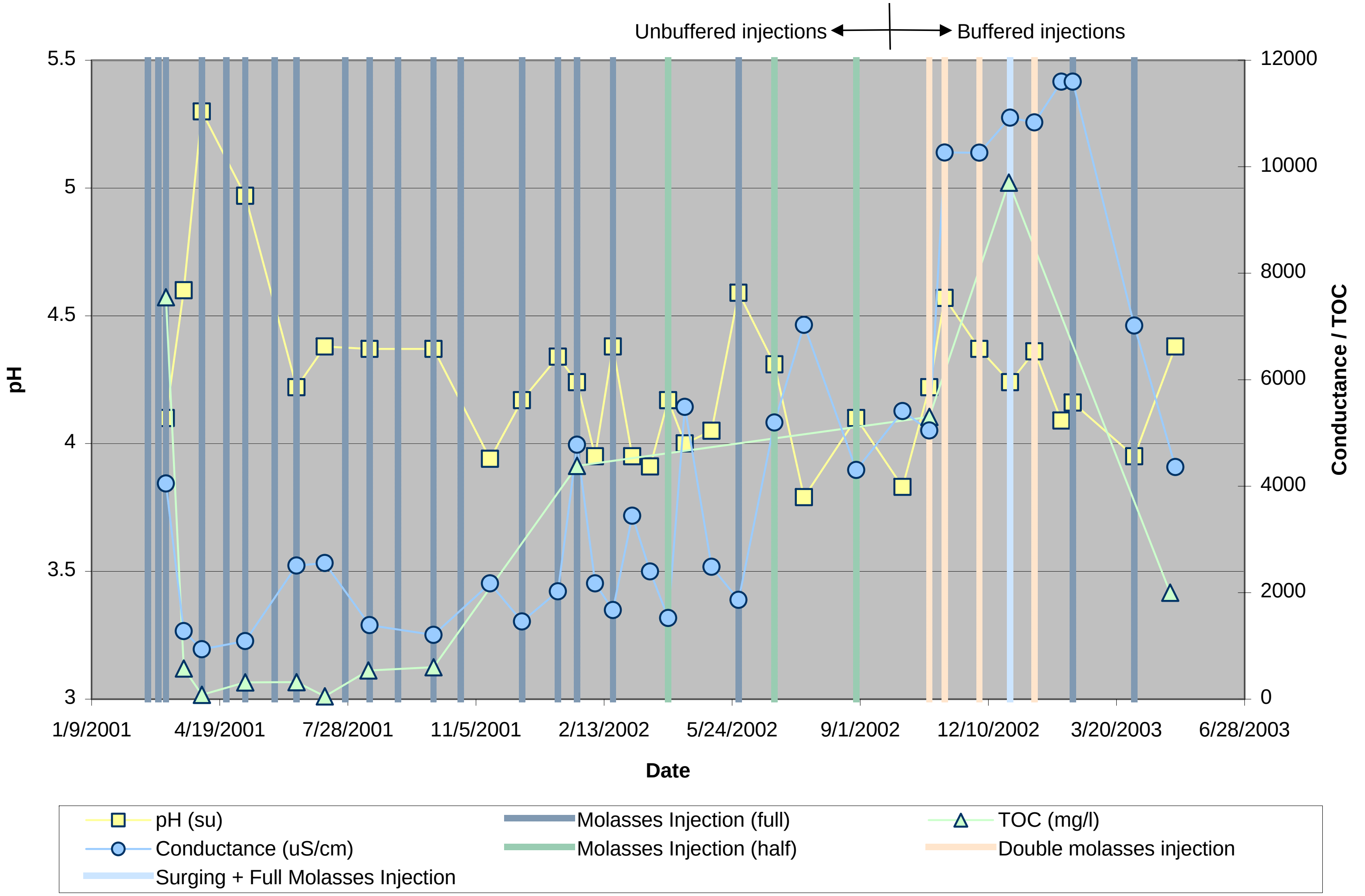


Figure 4-6 35-I-2 Performance

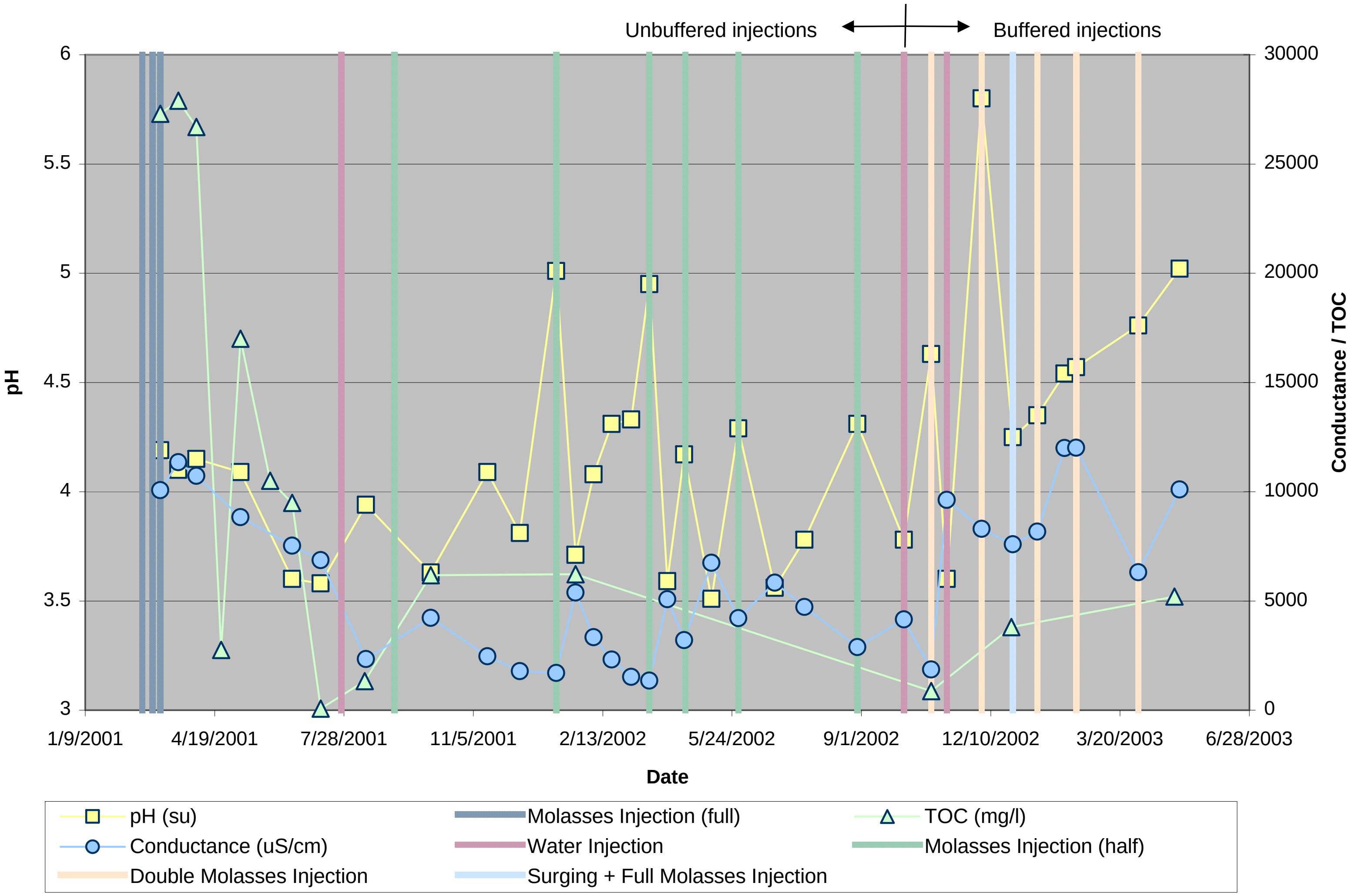


Figure 4-7 35-I-3 Performance

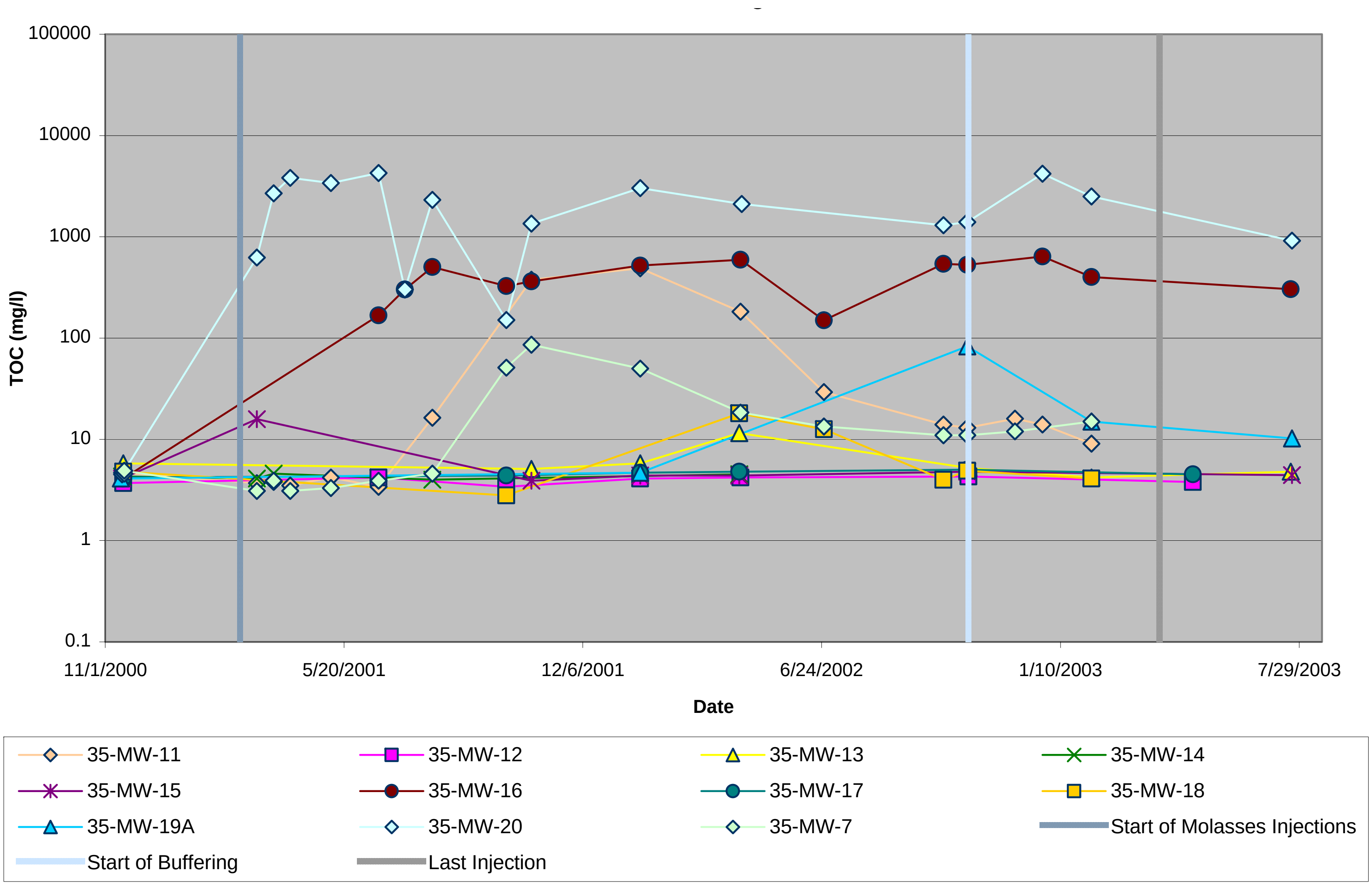


Figure 4-8 TOC Trends

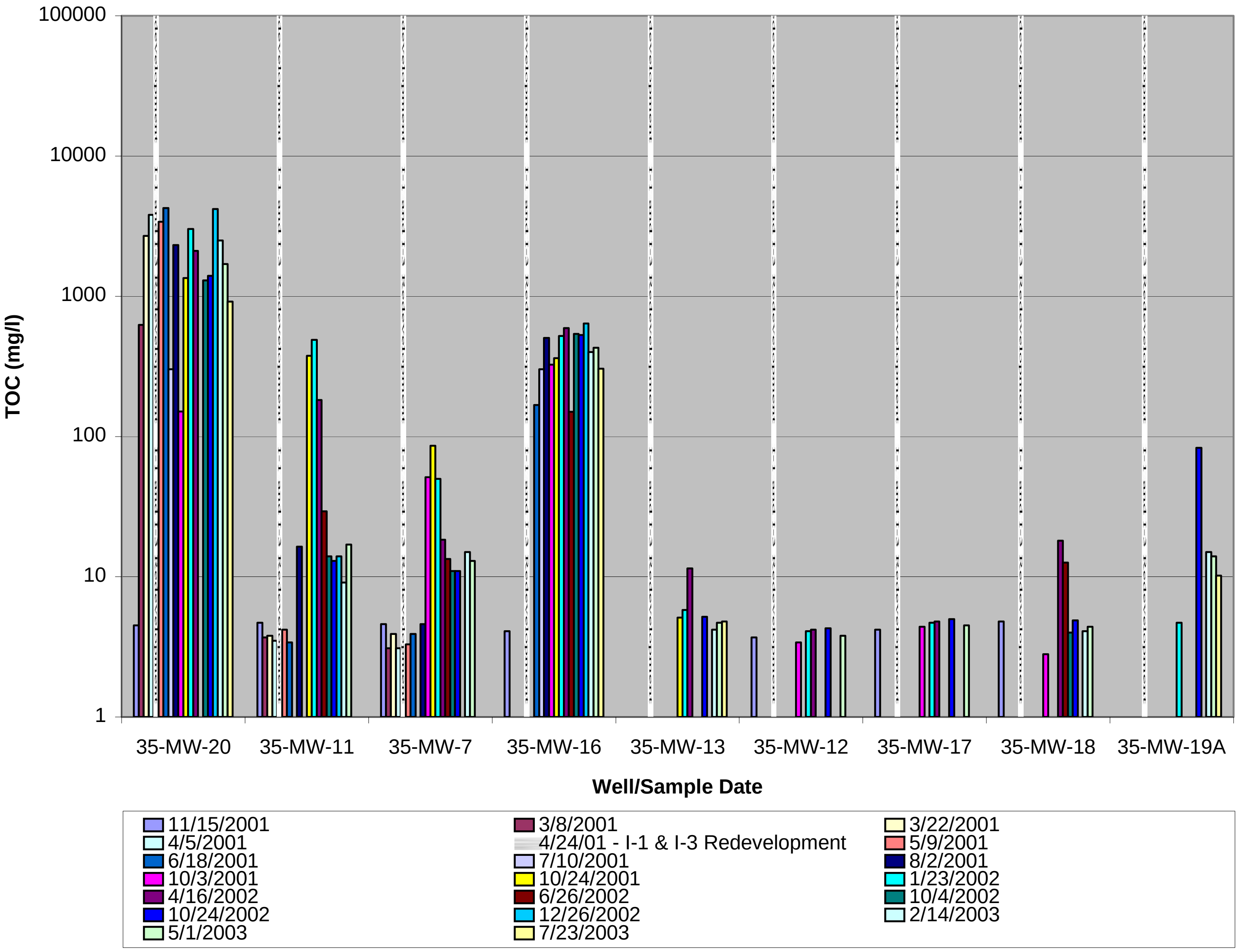


Figure 4-9 TOC Trends – Bar Chart

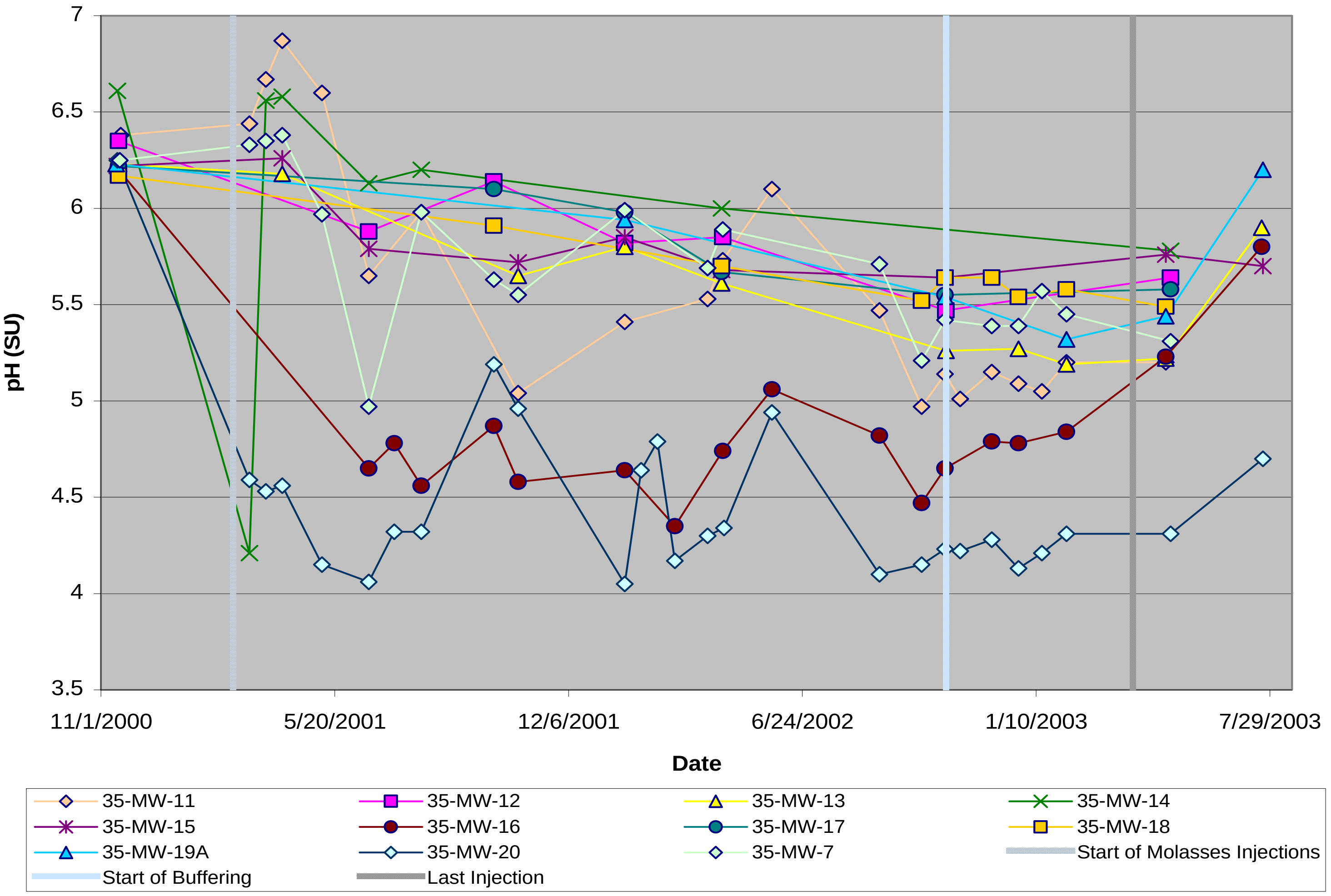


Figure 4-10 pH Trends

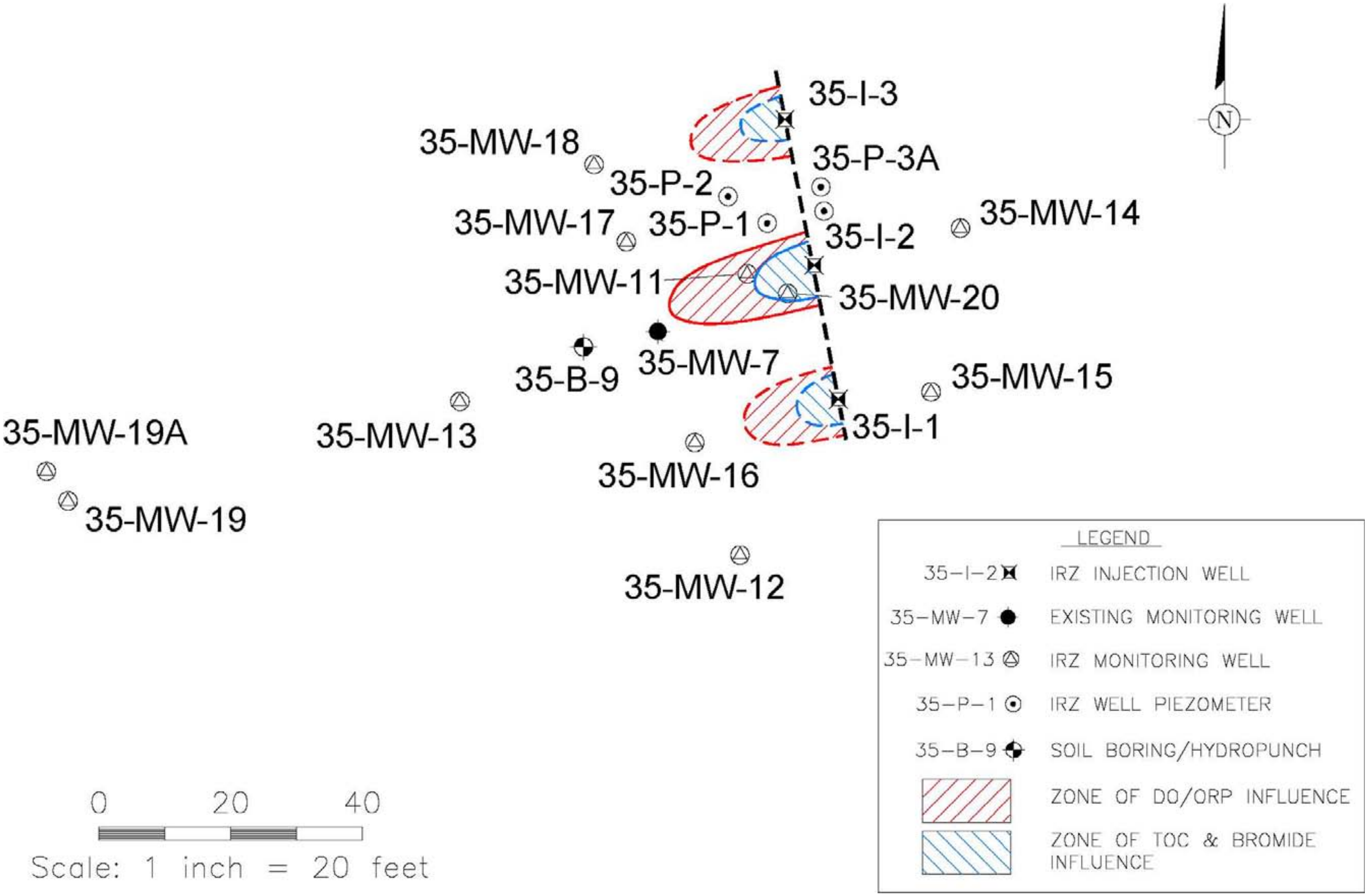


Figure 4-11 Zone of Influence Map for April 5, 2001 (After 2 Months of Active Treatment)

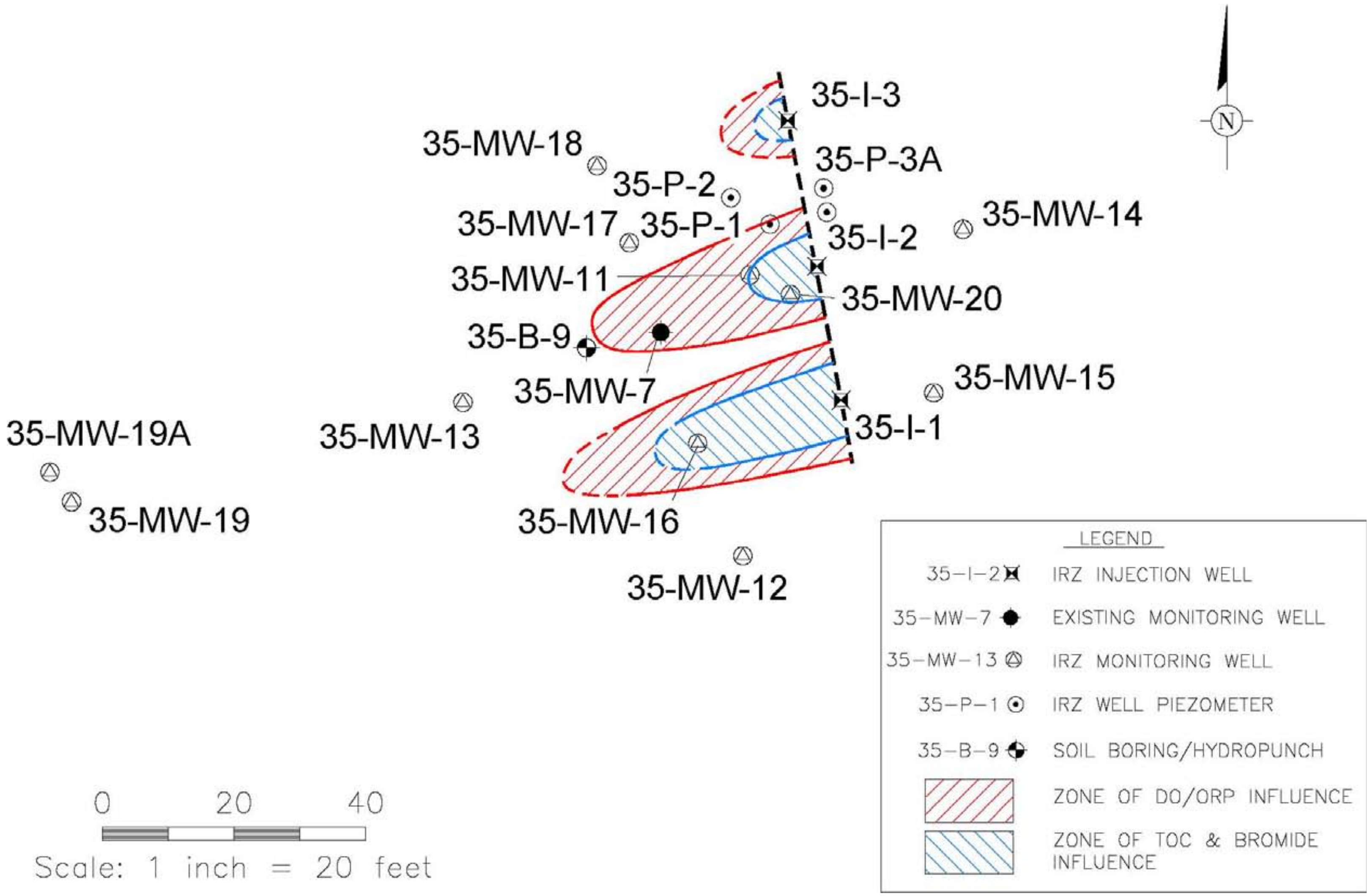


Figure 4-12 Zone of Influence Map for August 2, 2001 (After 6 Months of Active Treatment)

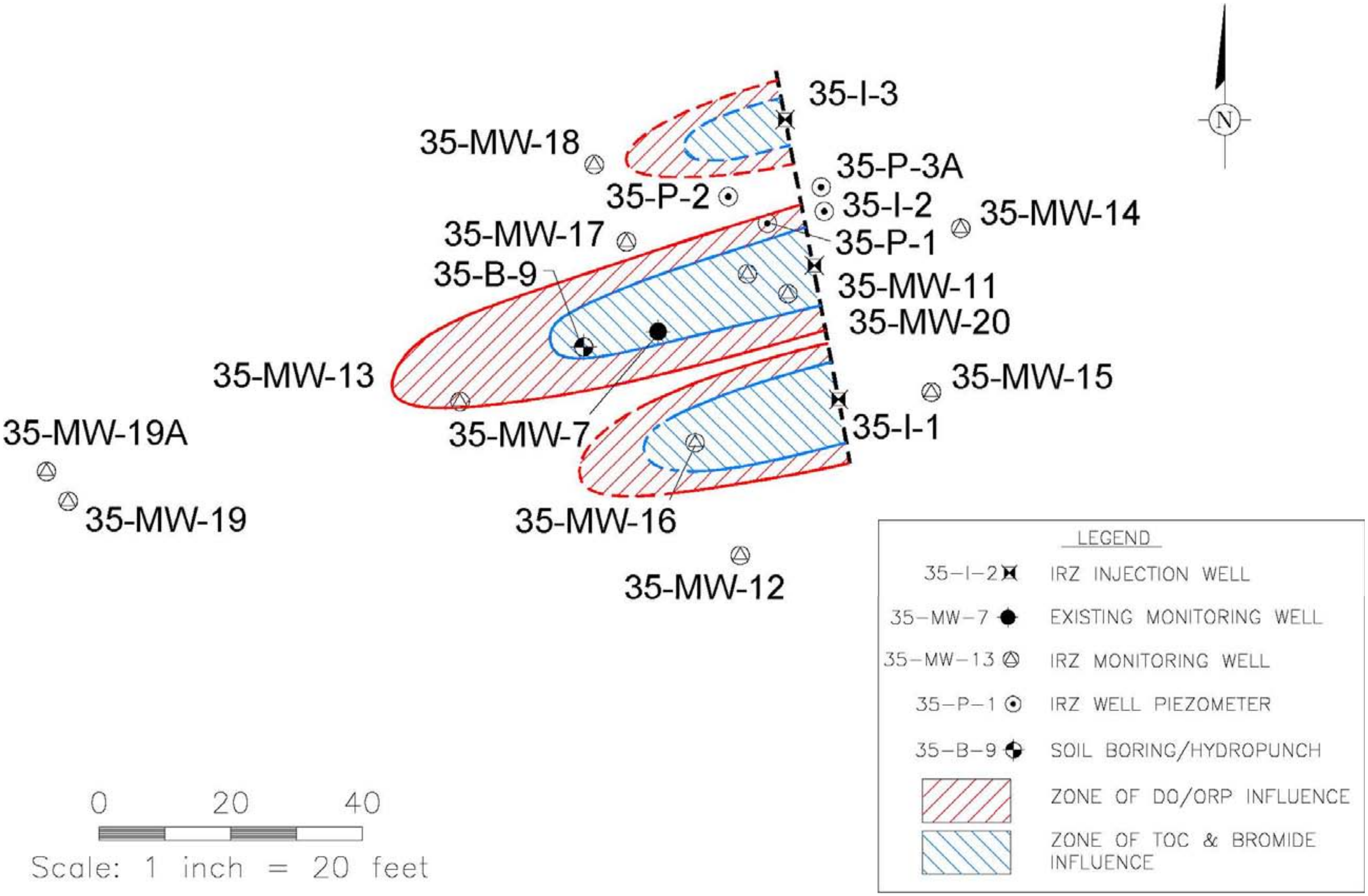


Figure 4-13 Zone of Influence Map for January 23, 2002 (After 11 Months of Active Treatment)

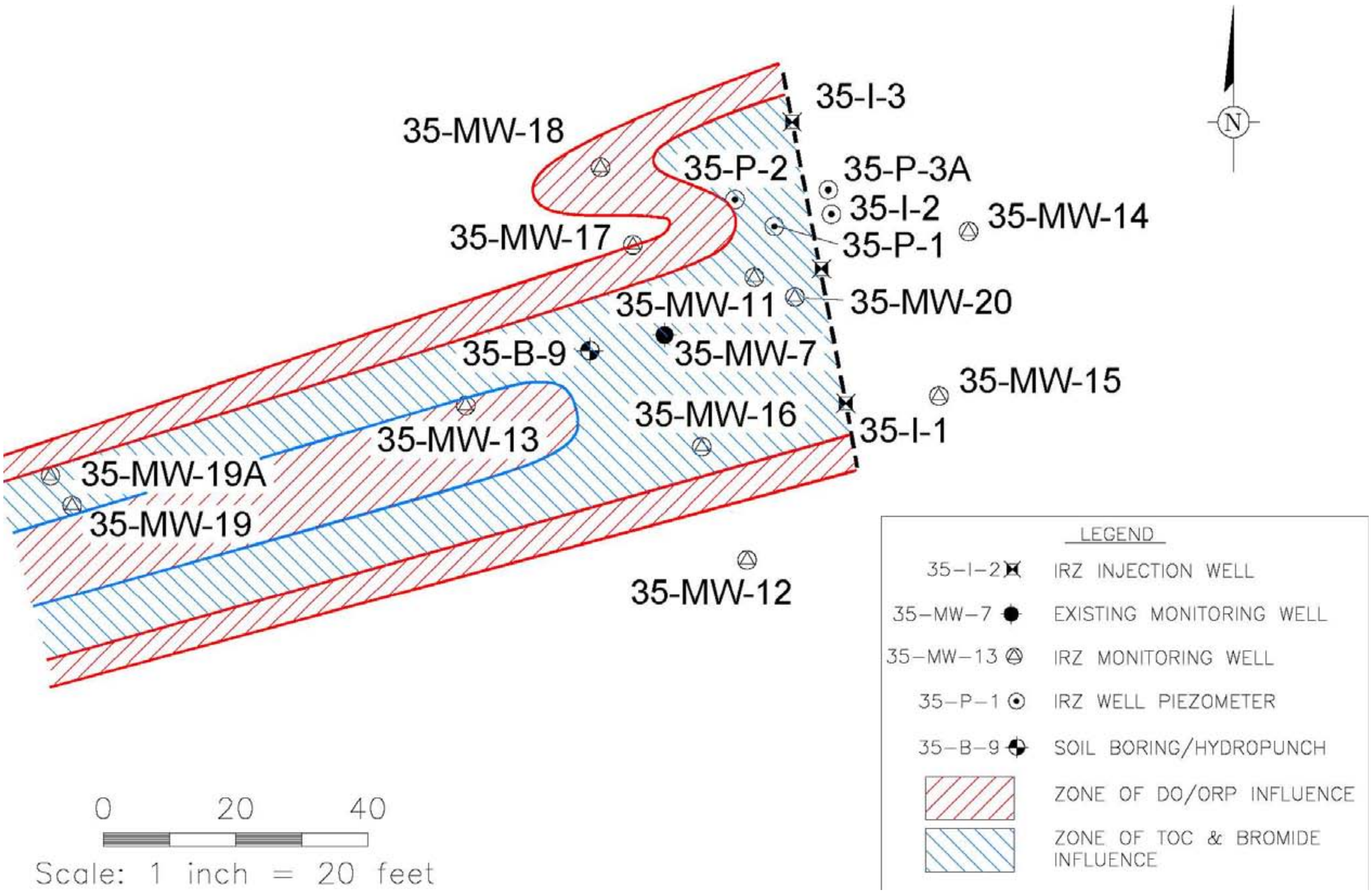


Figure 4-14 Zone of Influence Map for October 24, 2002 (After 20 Months of Active Treatment)

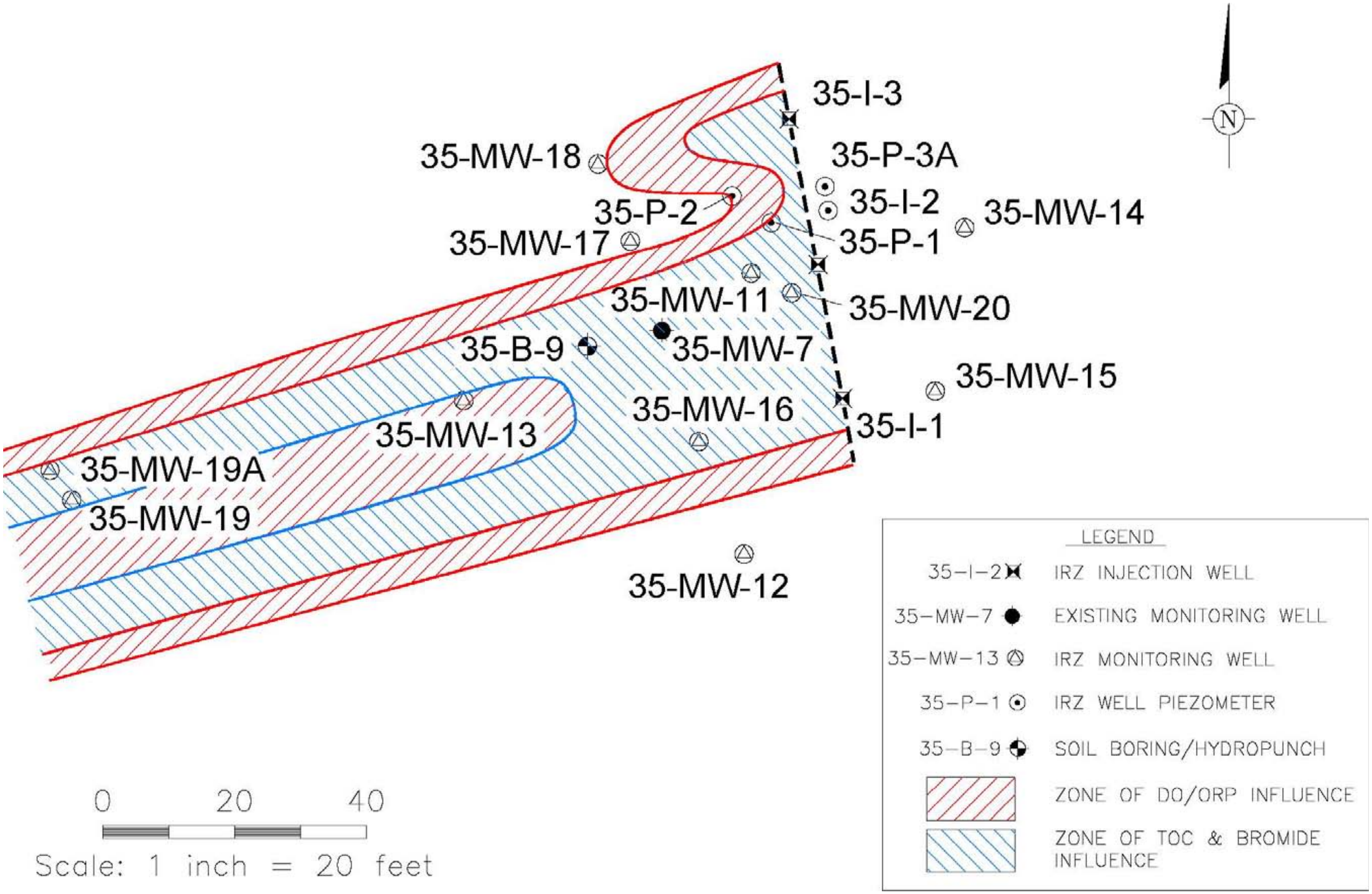


Figure 4-15 Zone of Influence Map for May 1, 2003 (27 Months After First Injection, 1 Month After End of Active Treatment)

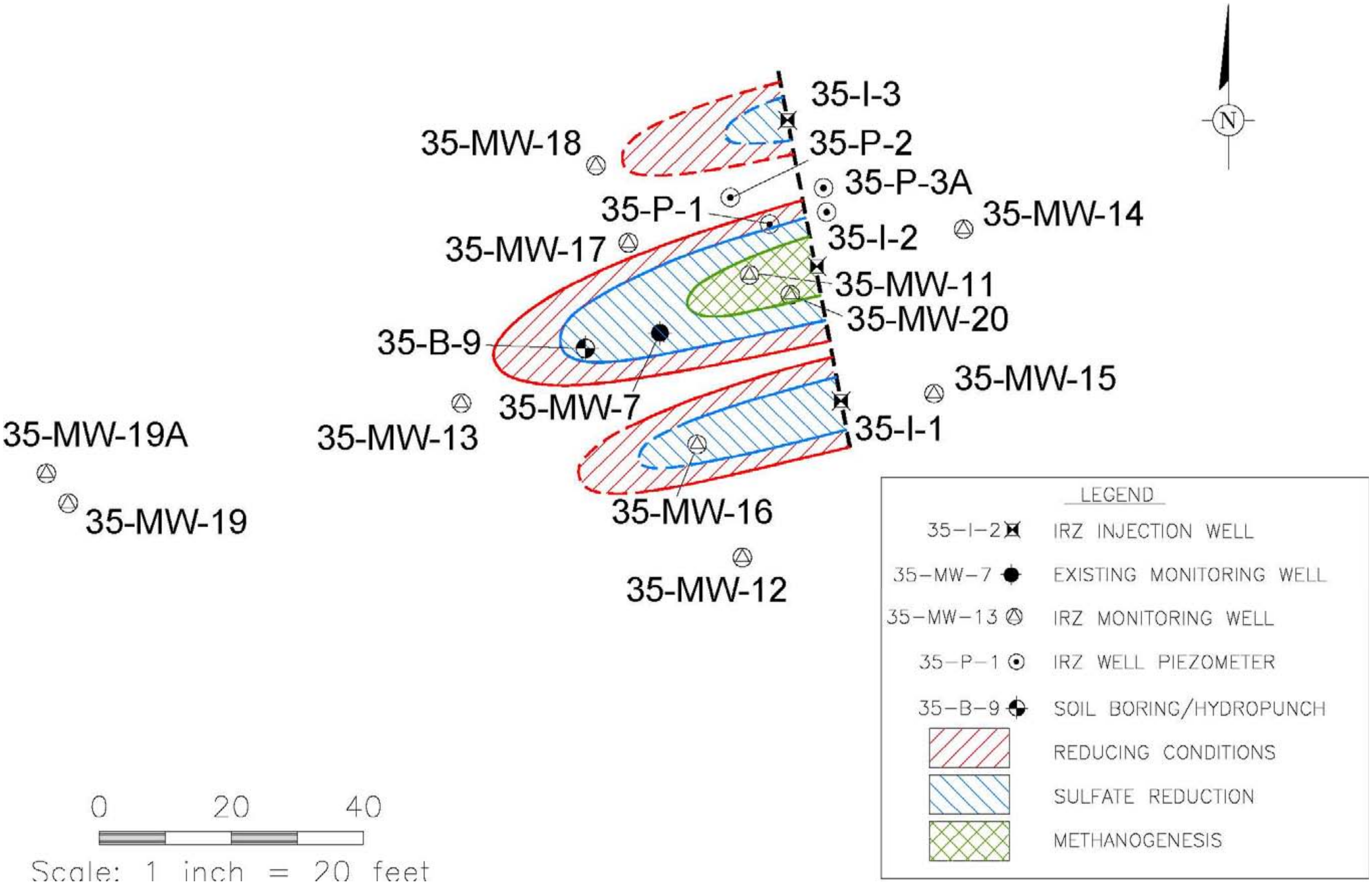


Figure 4-16 Redox Zone Map for October 24, 2001 (After 8 months of Active Treatment)

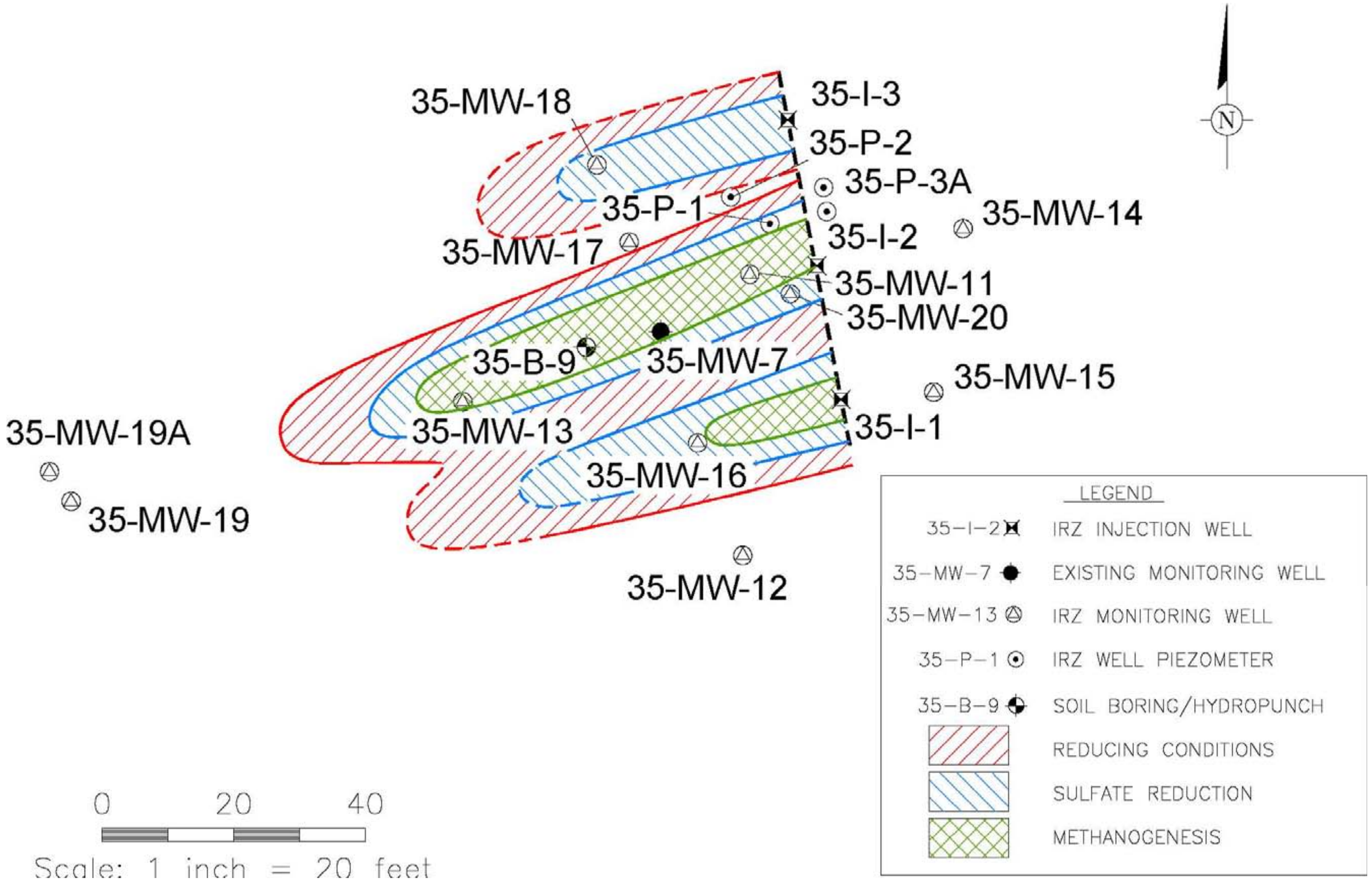


Figure 4-17 Redox Zone Map for April 18, 2002 (After 14 Months of Active Treatment)

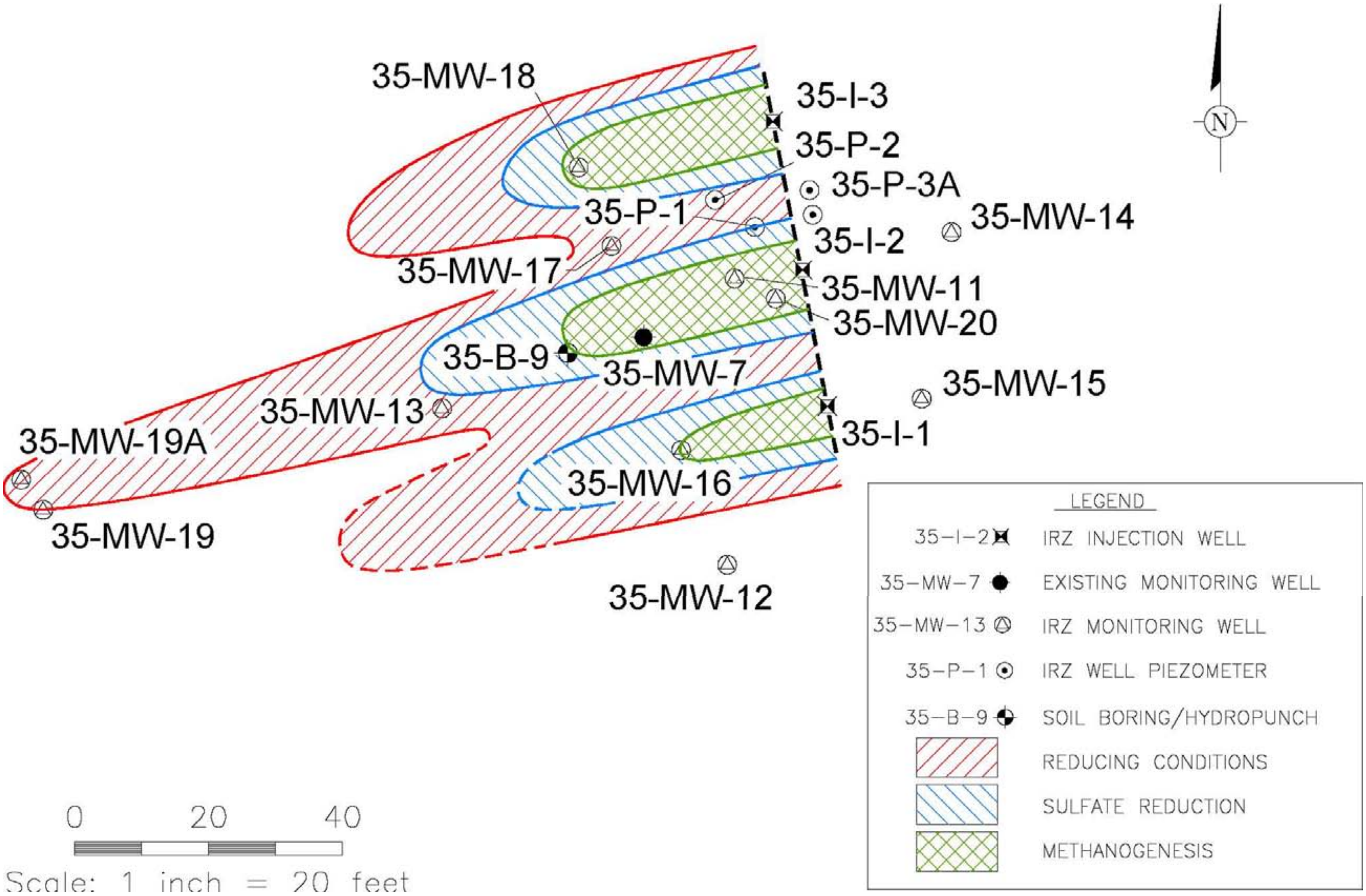


Figure 4-18 Redox Zone Map for October 24, 2002 (After 20 Months of Active Treatment)

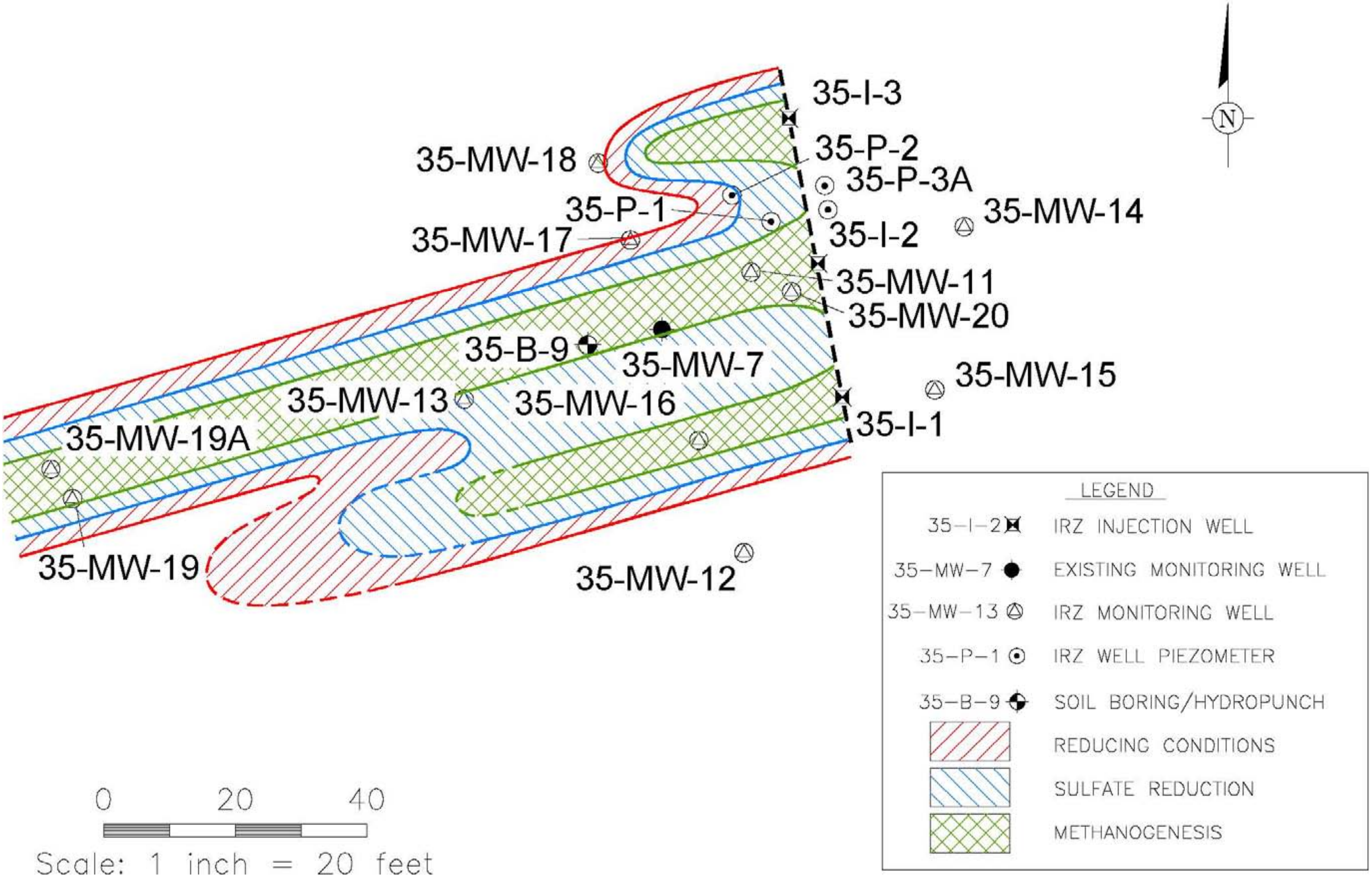


Figure 4-19 Redox Zone Map for May 1, 2003 (27 Months After First Injection, 1 Month After End of Active Treatment)

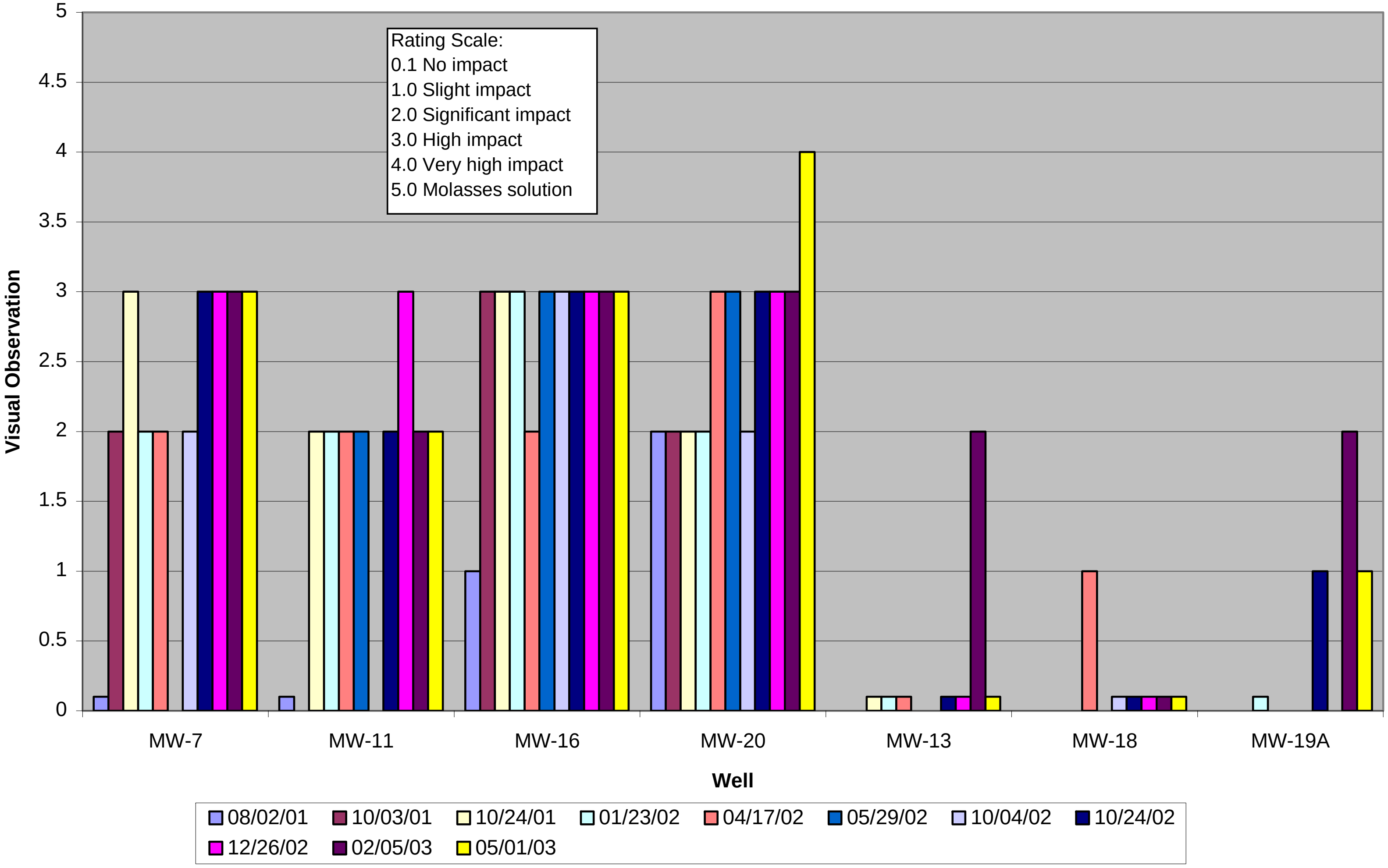


Figure 4-20 Visual Well Observations by Well

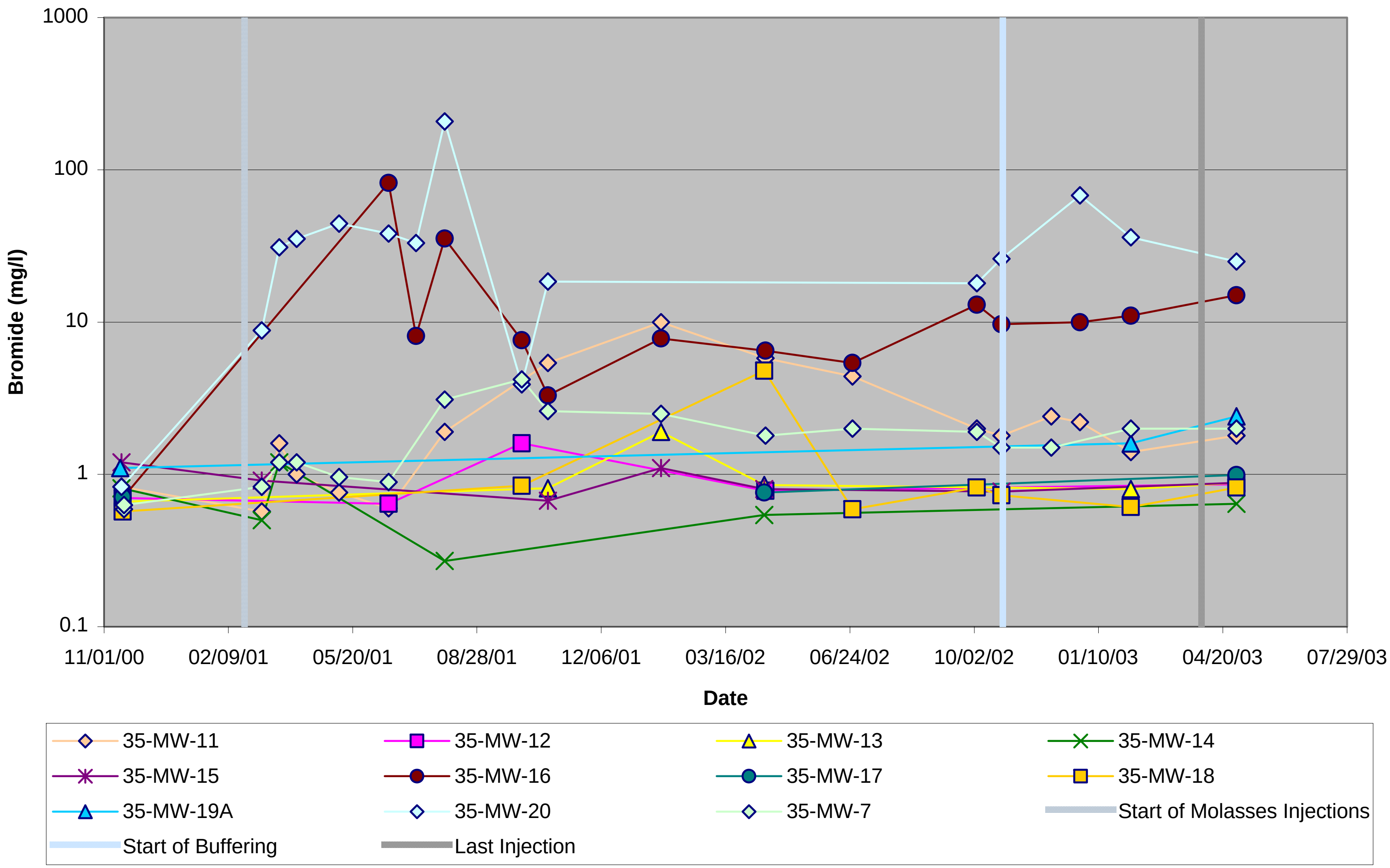


Figure 4-21 Bromide Trends

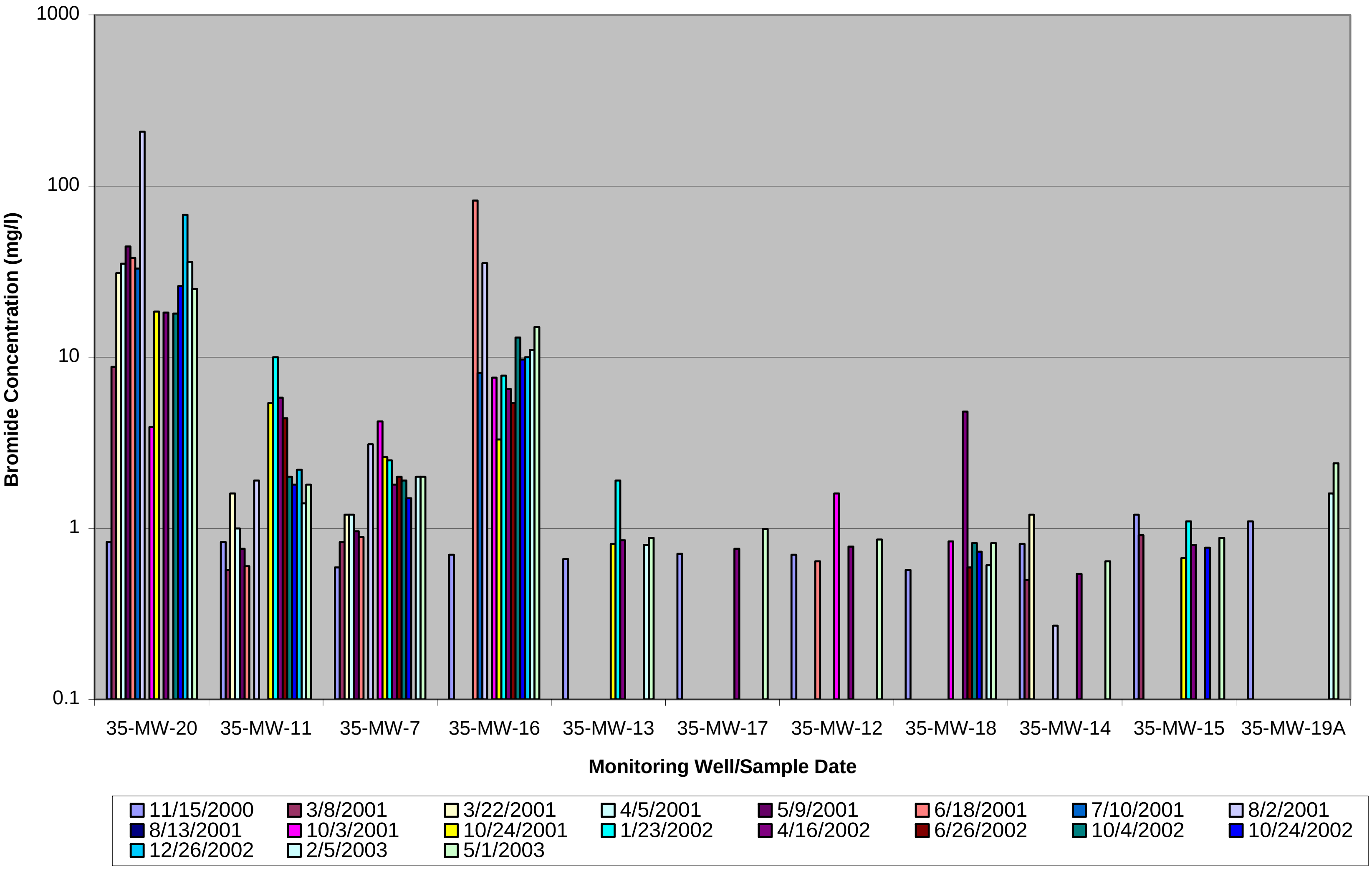


Figure 4-22 Bromide Trends – Bar Chart

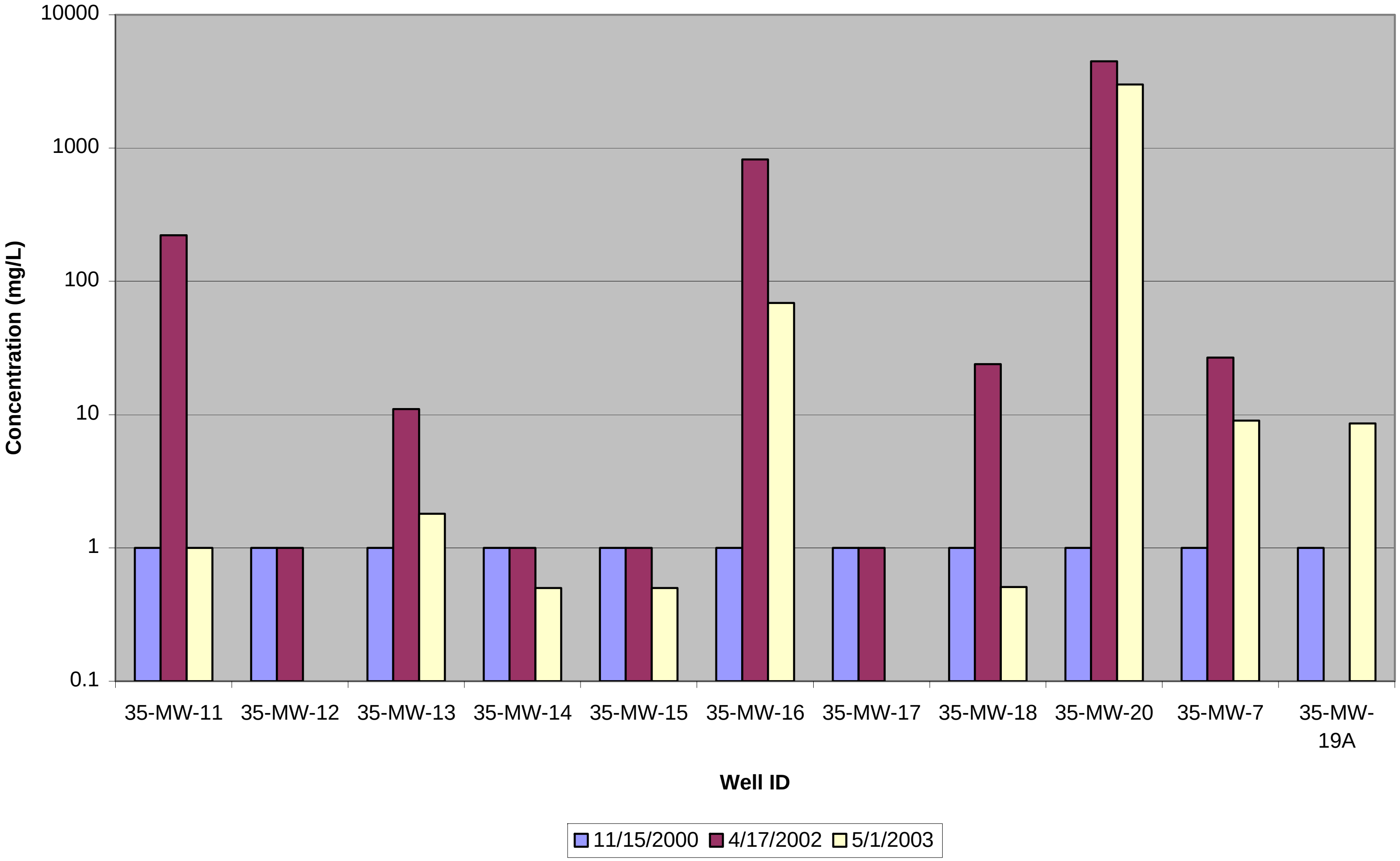


Figure 4-23 BOD Trends

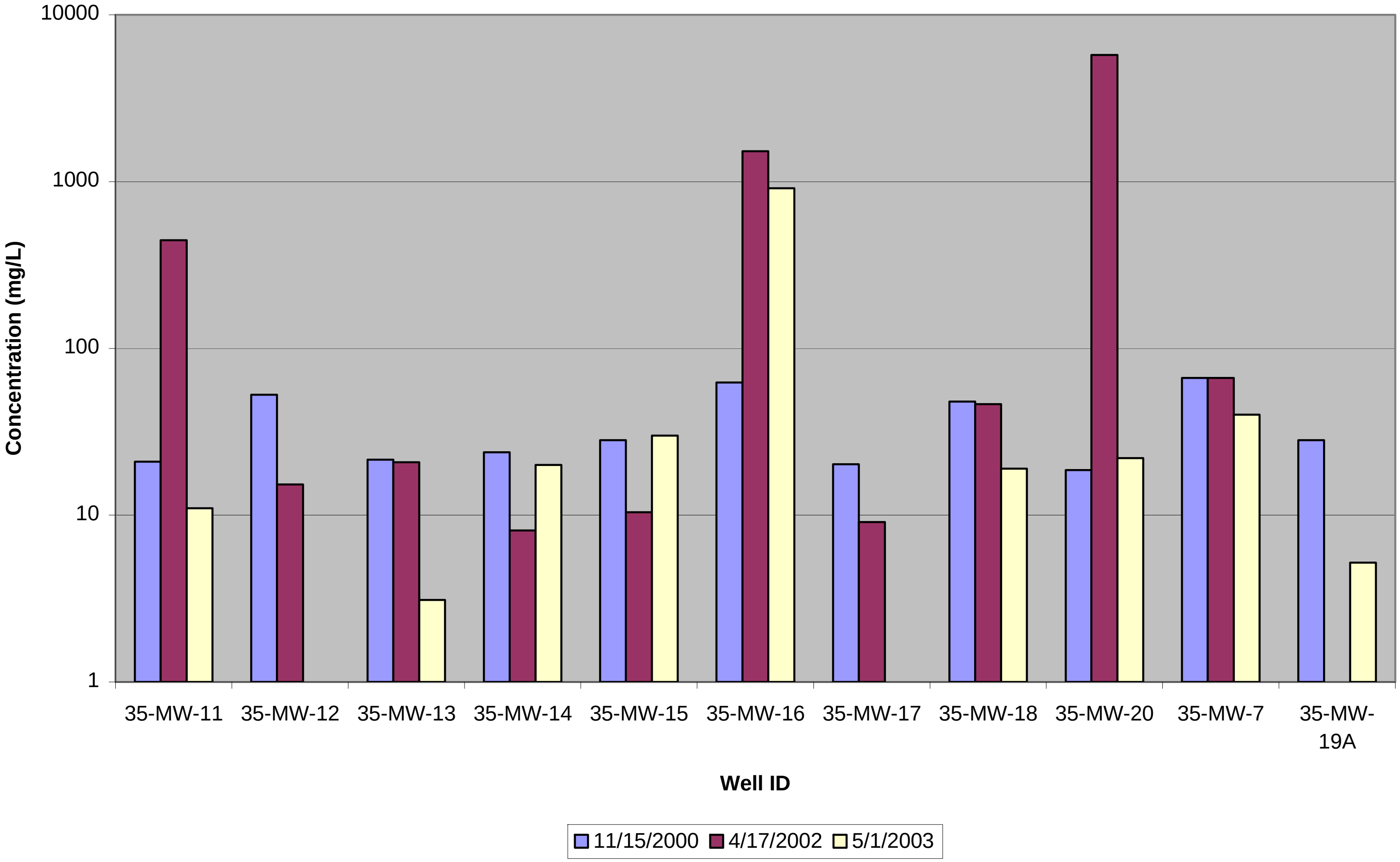


Figure 4-24 COD Trends

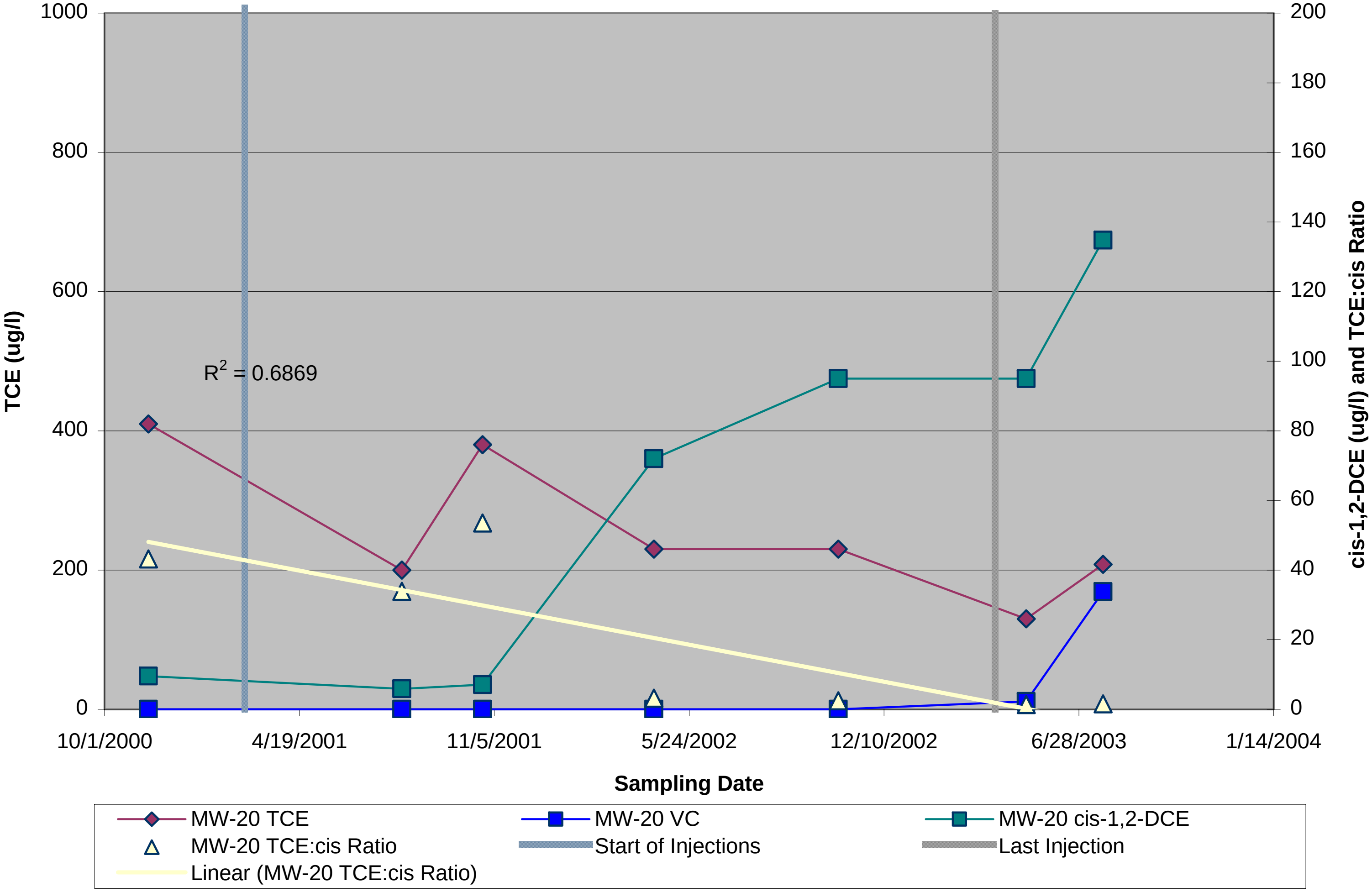


Figure 4-25 35-MW-20 CAH Trends

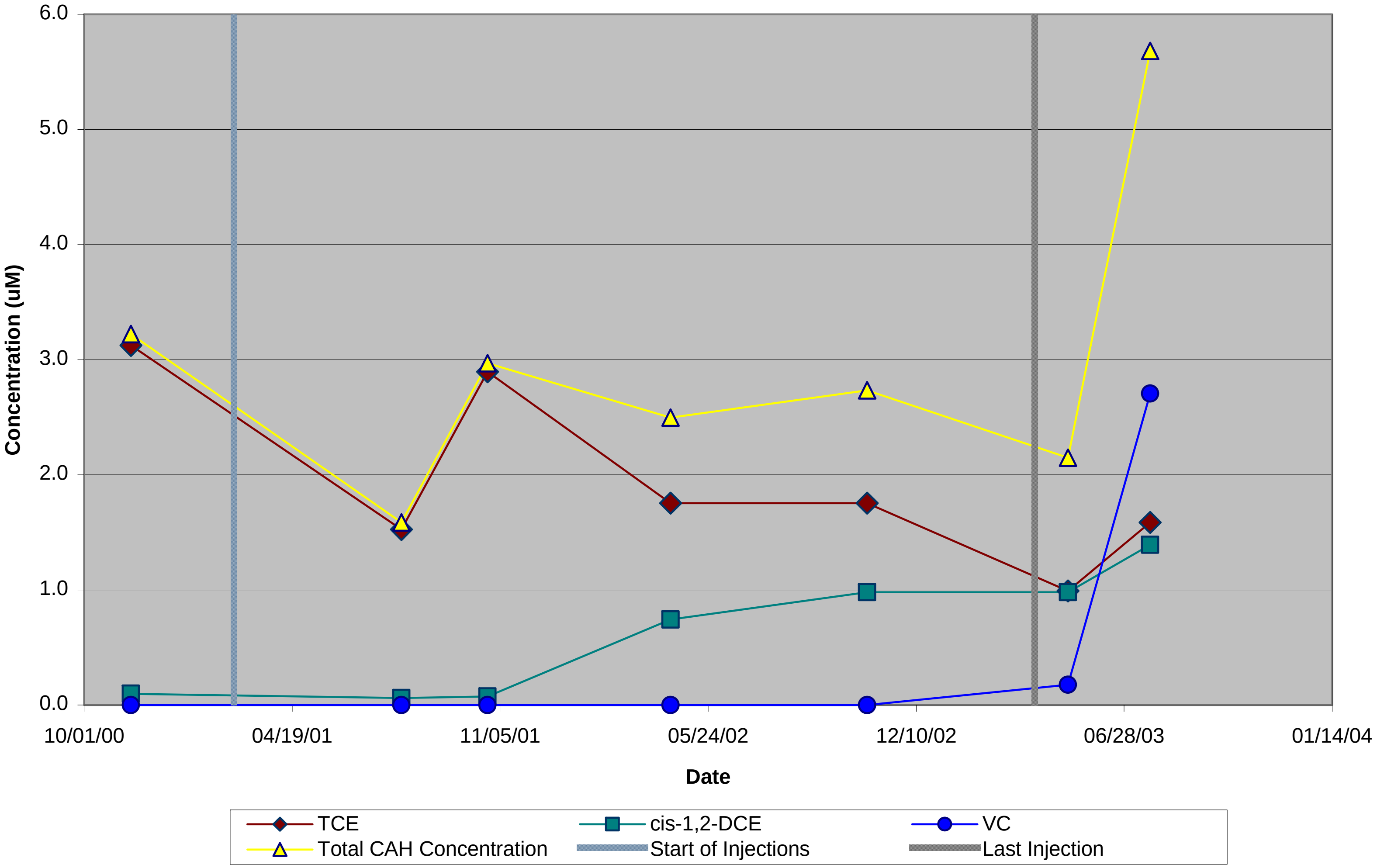


Figure 4-26 35-MW-20 VOC Trends - Molar Basis

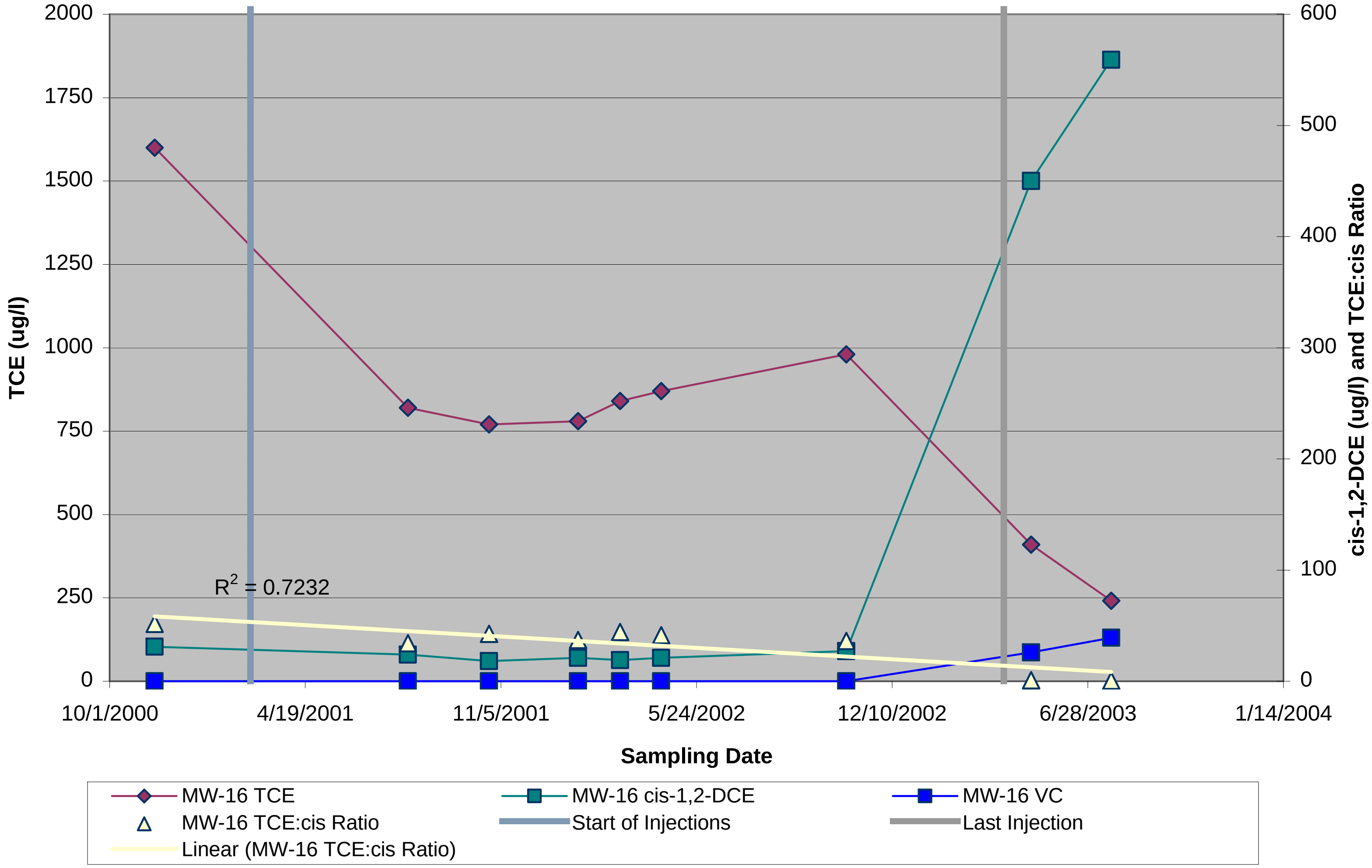


Figure 4-27 35-MW-16 CAH Trends

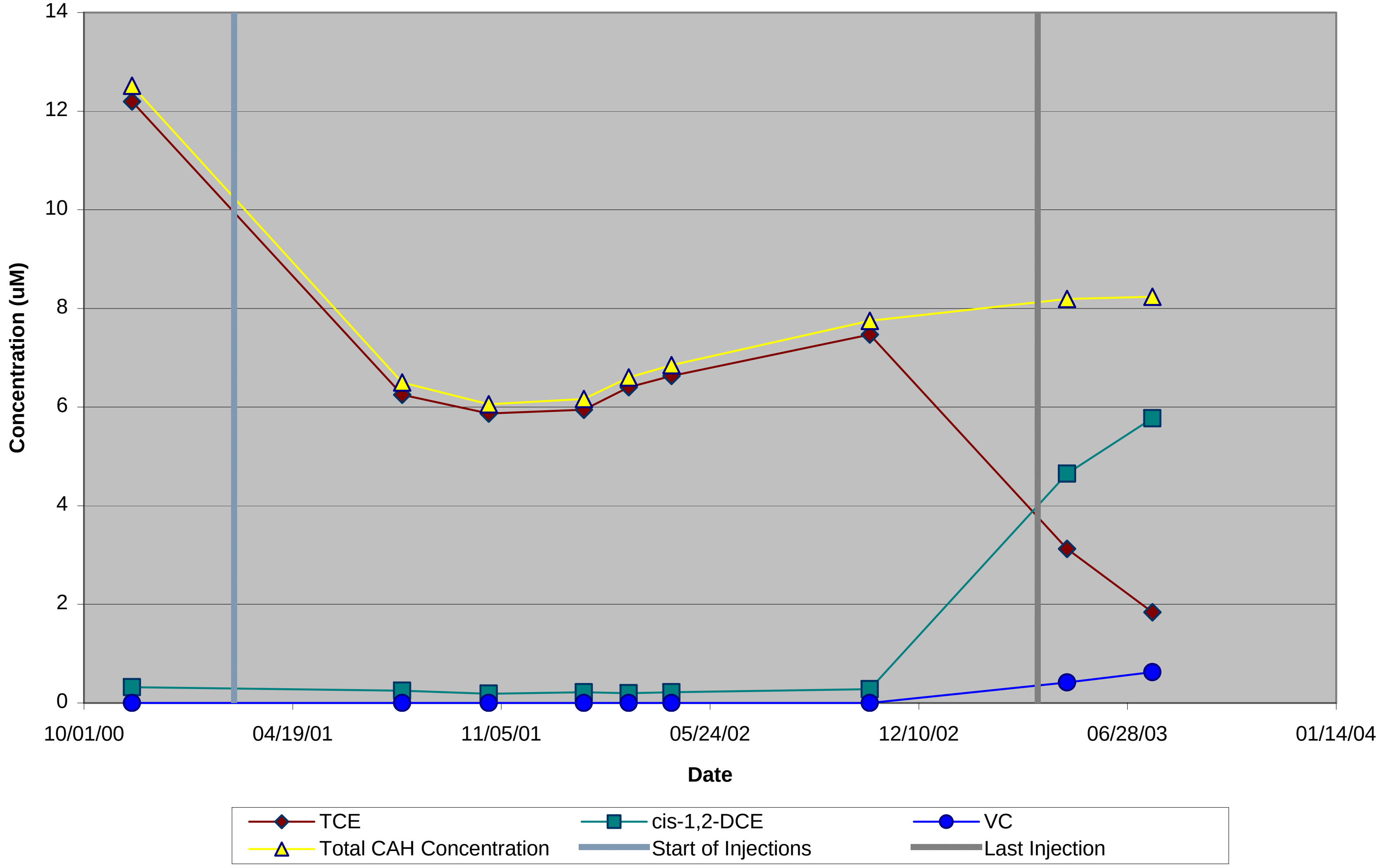


Figure 4-28 35-MW-16 VOC Trends - Molar Basis

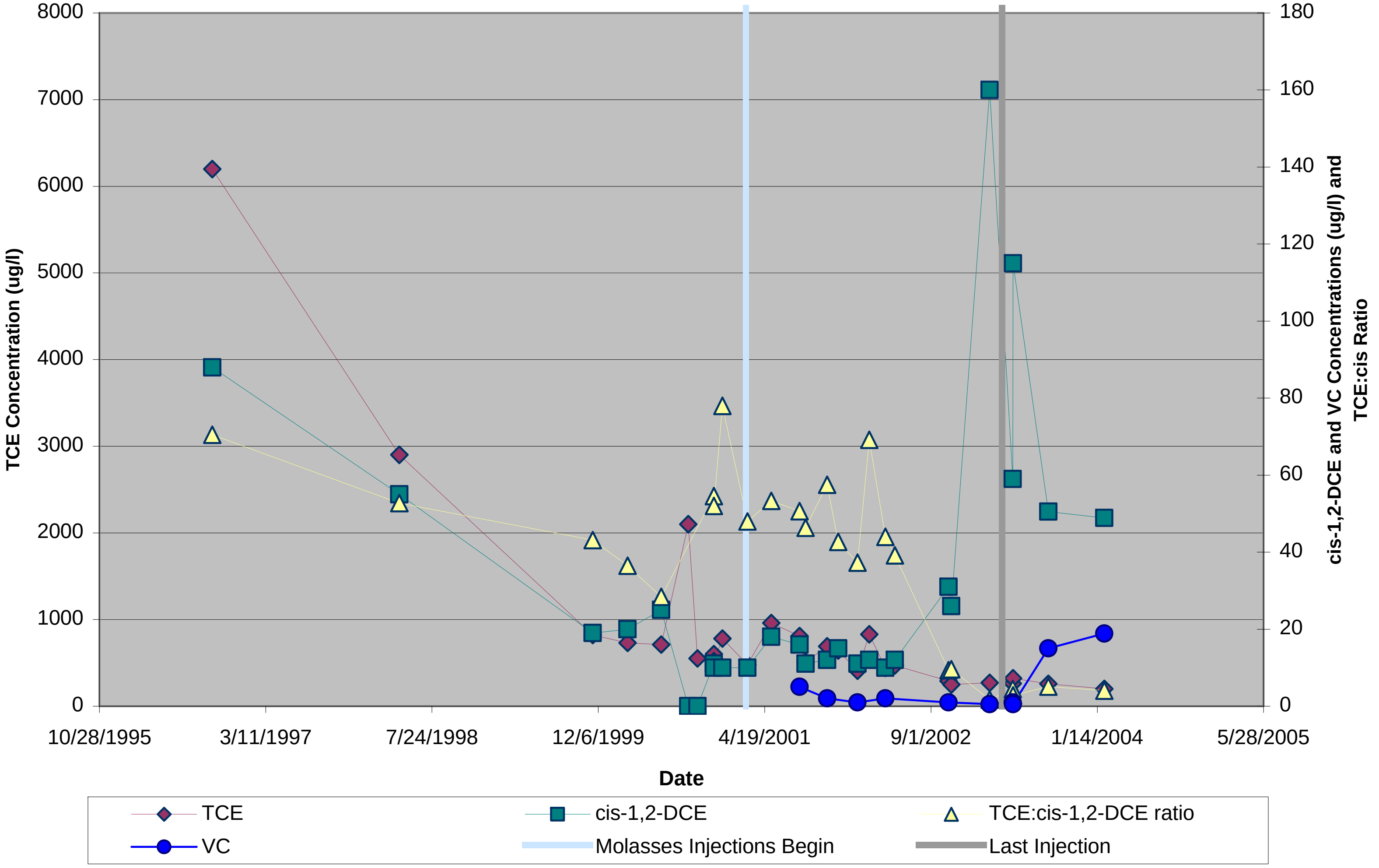


Figure 4-29 Long-Term 35-MW-7 CAH Trends

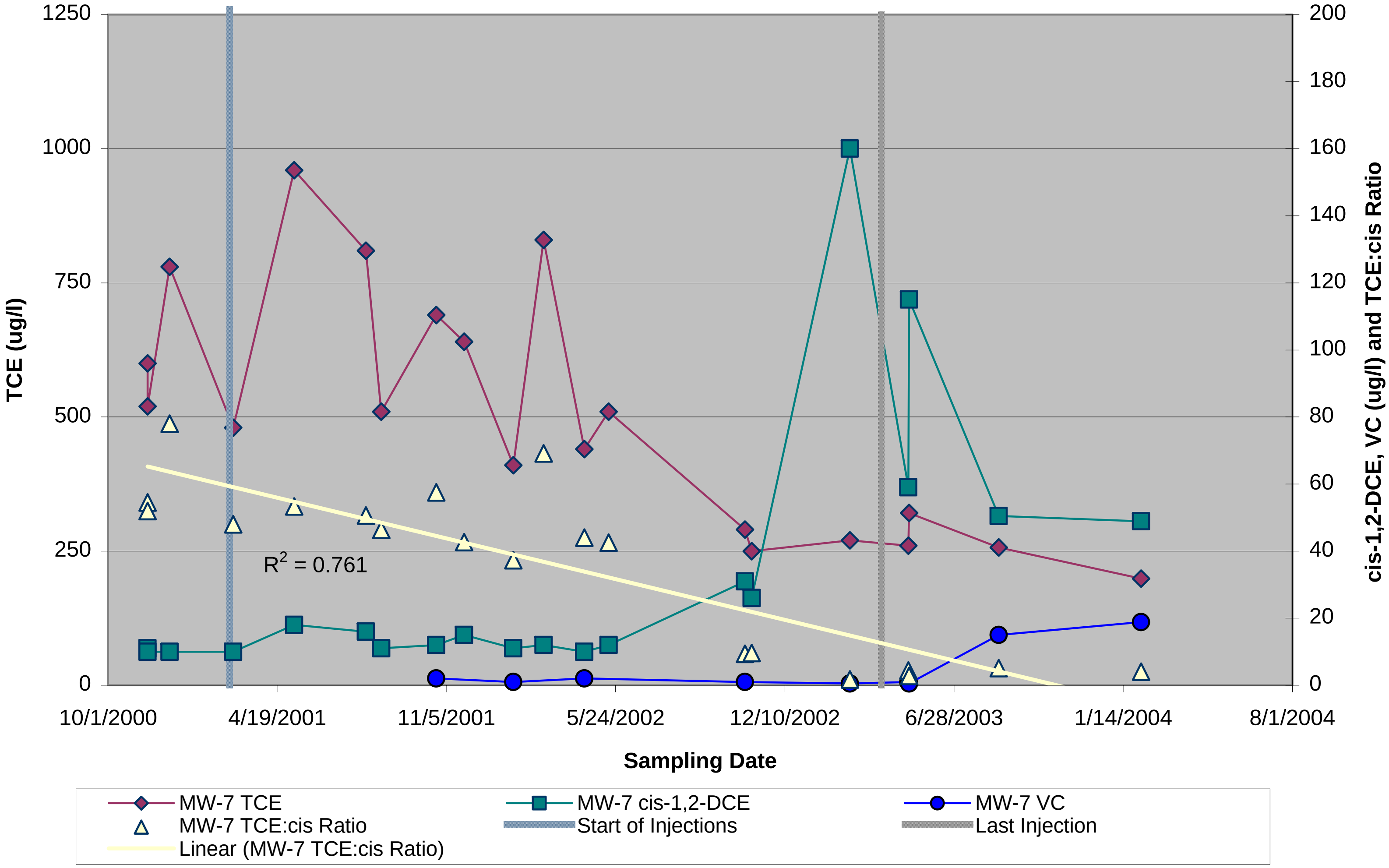


Figure 4-30 35-MW-7 CAH Trends

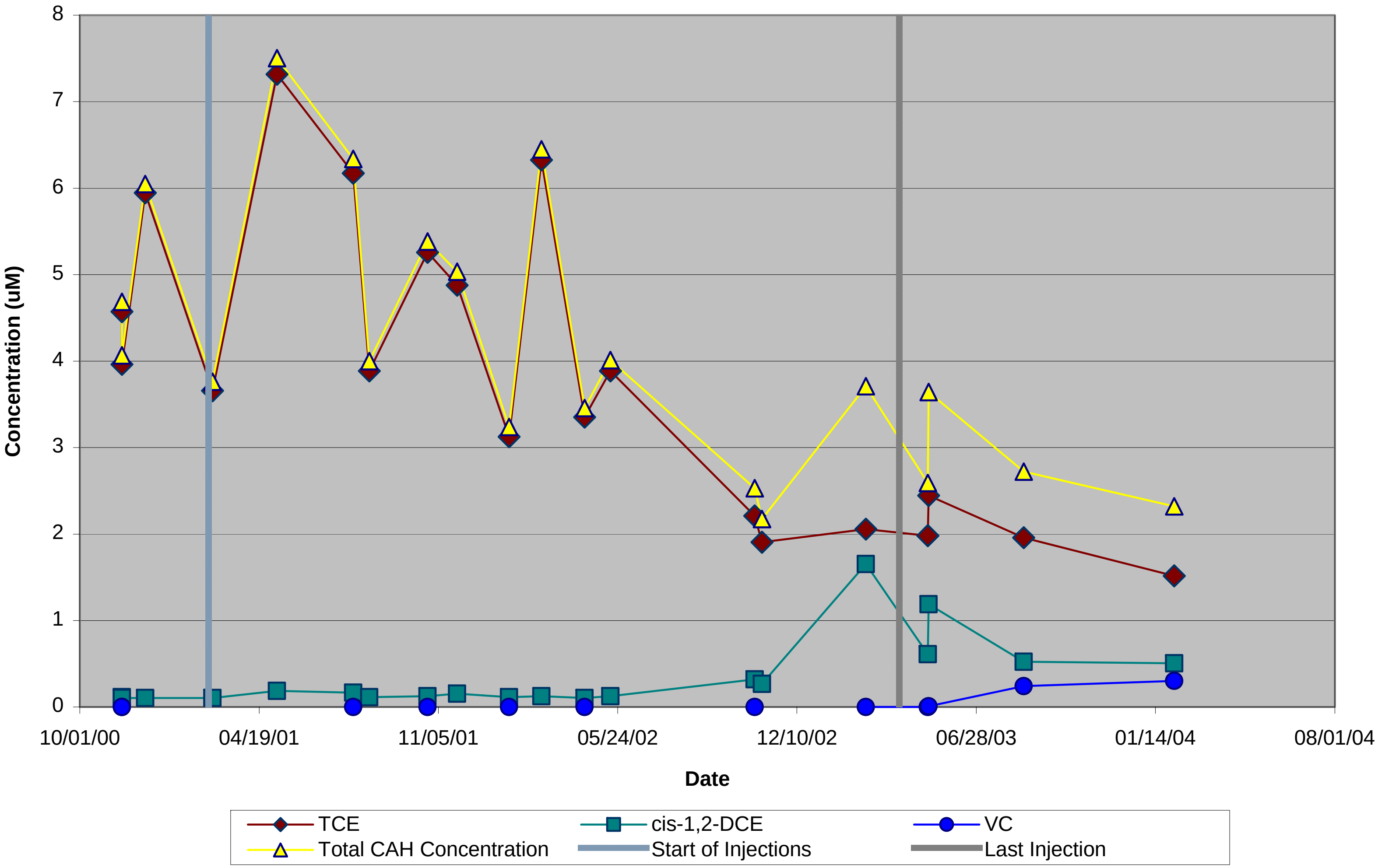


Figure 4-31 35-MV-7 VOC Trends – Molar Basis

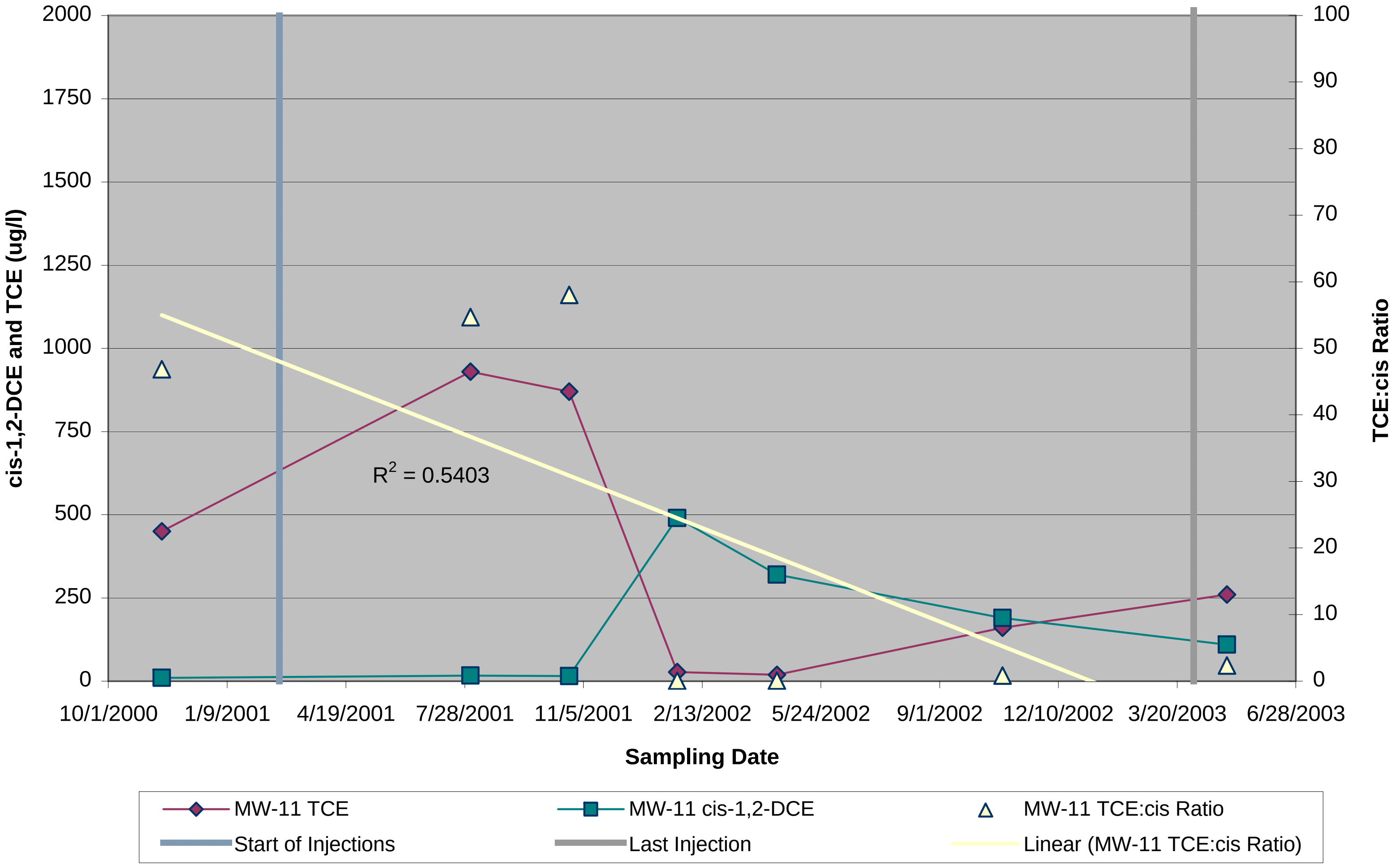


Figure 4-32 35-MW-11 CAH Trends

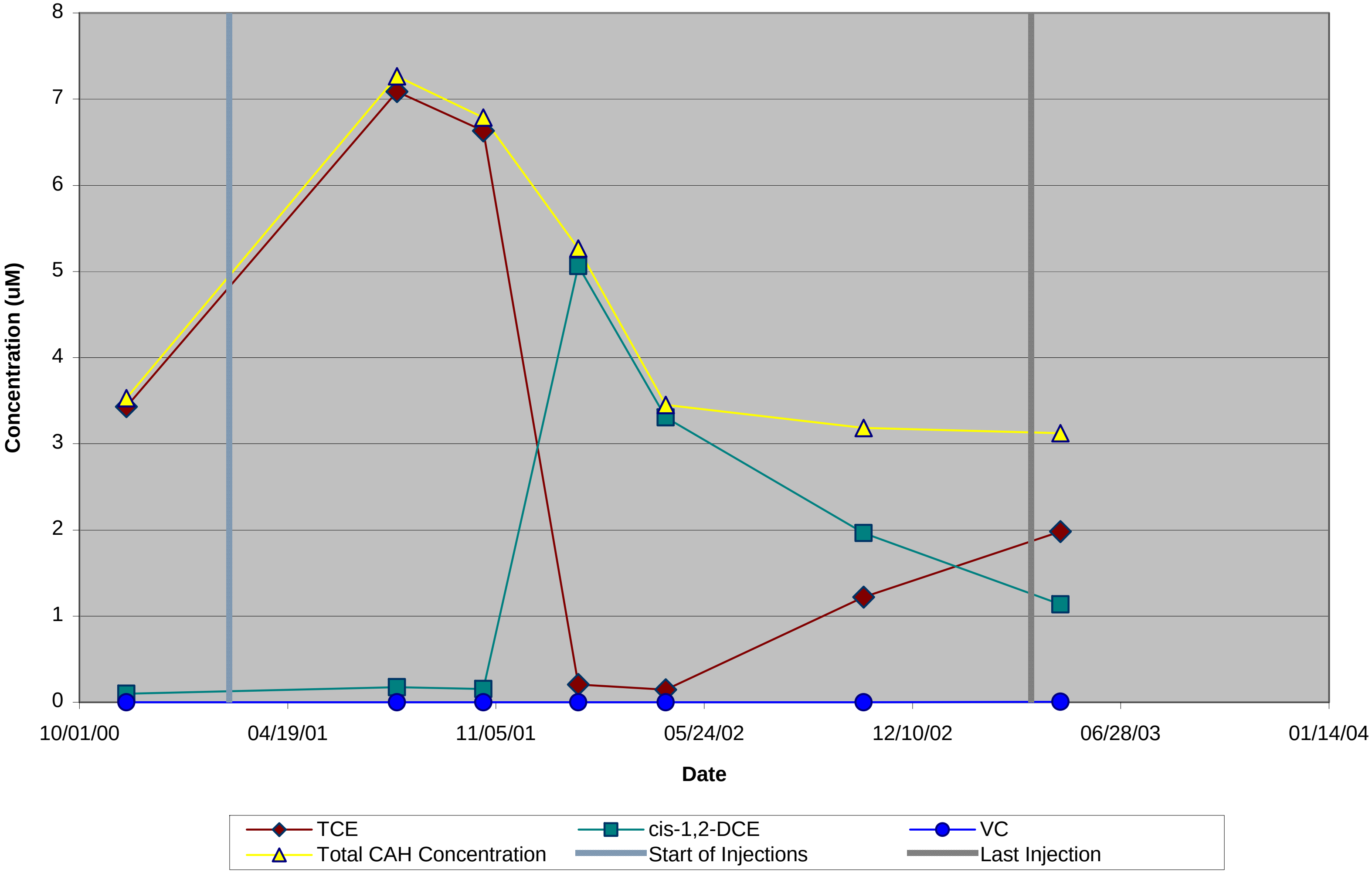


Figure 4-33 35-MW-11 VOC Trends - Molar Basis

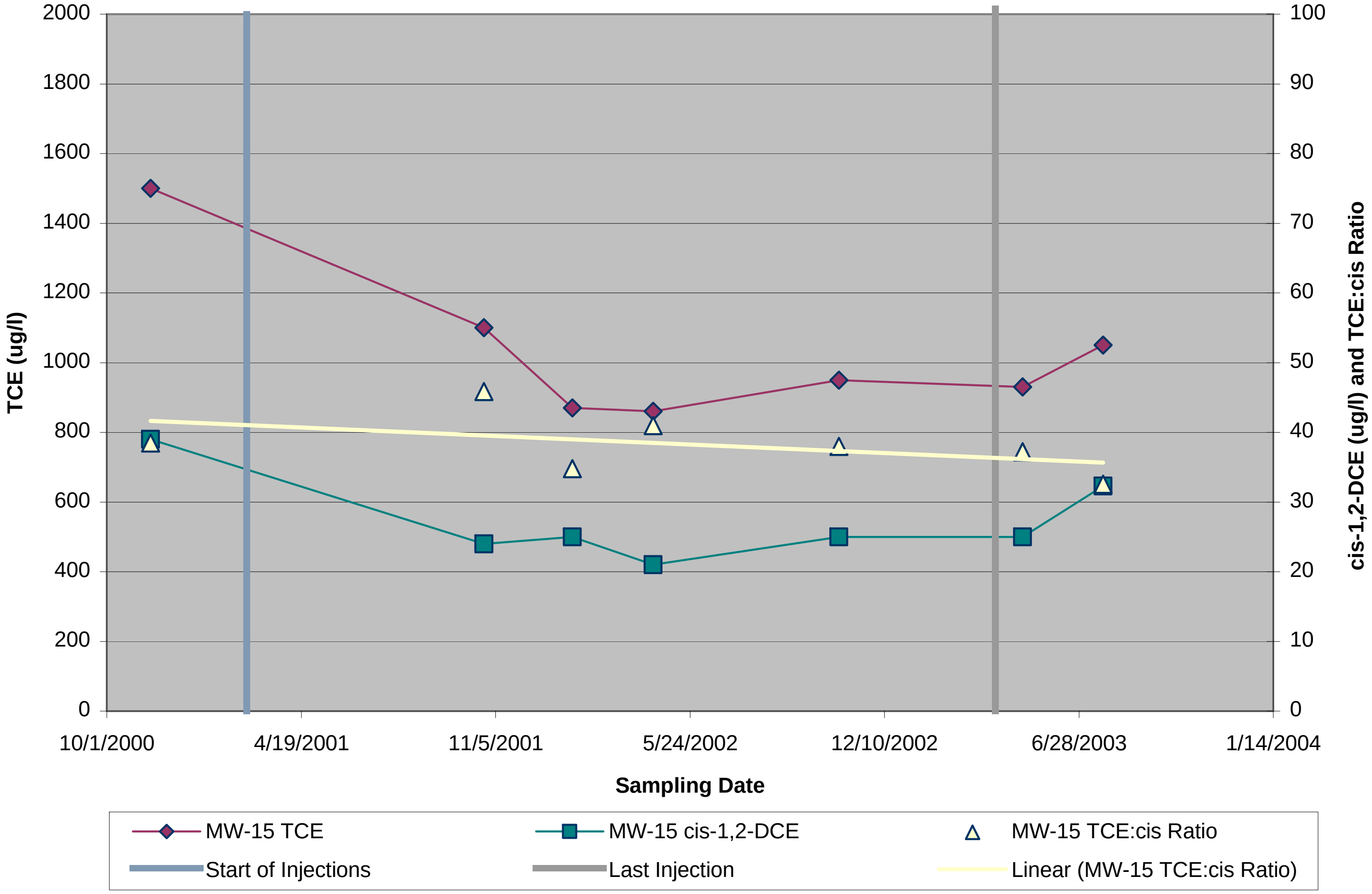


Figure 4-34 MW-15 CAH Trends

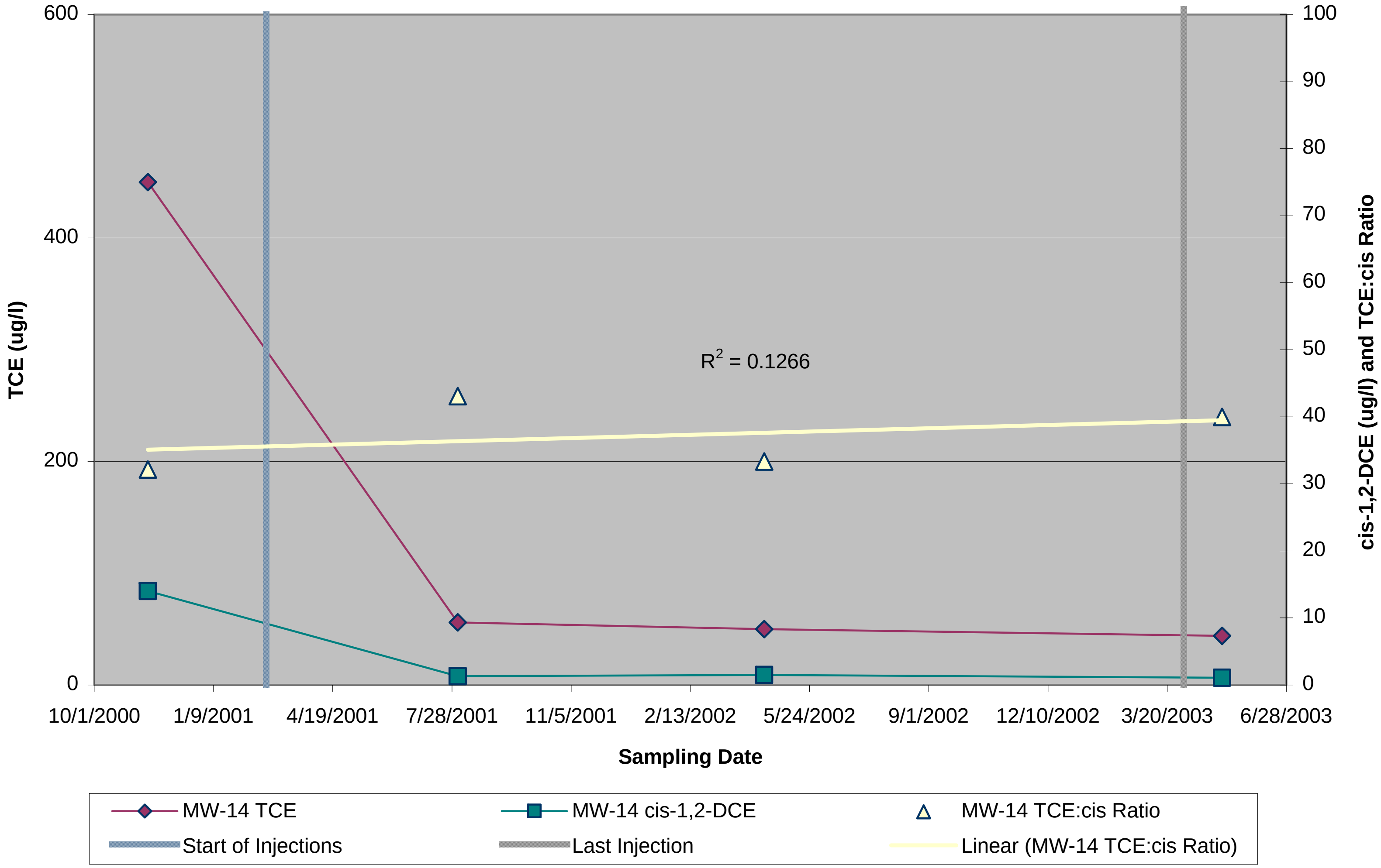


Figure 4-35 MW-14 CAH Trends

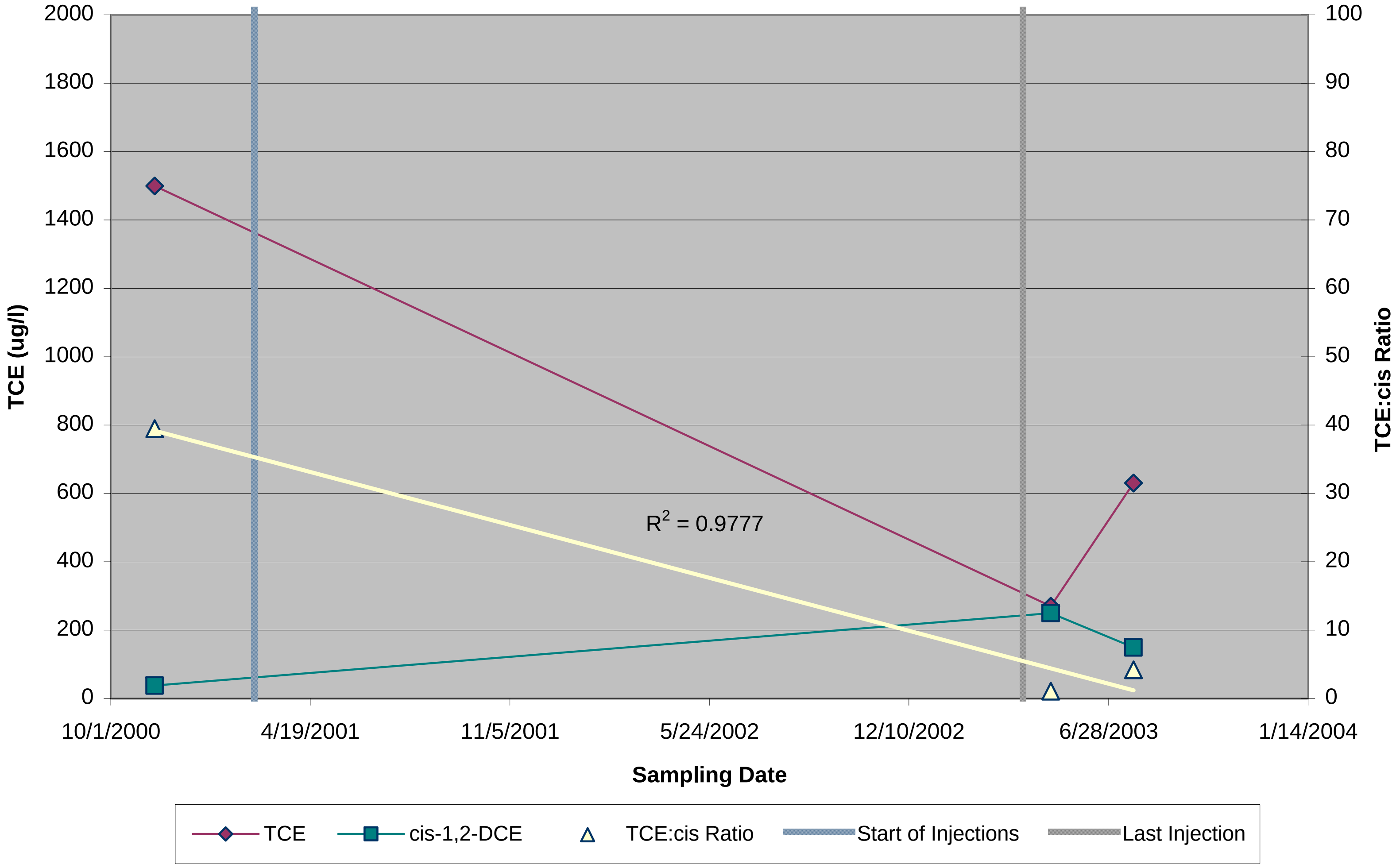


Figure 4-36 MW-19A CAH Trends

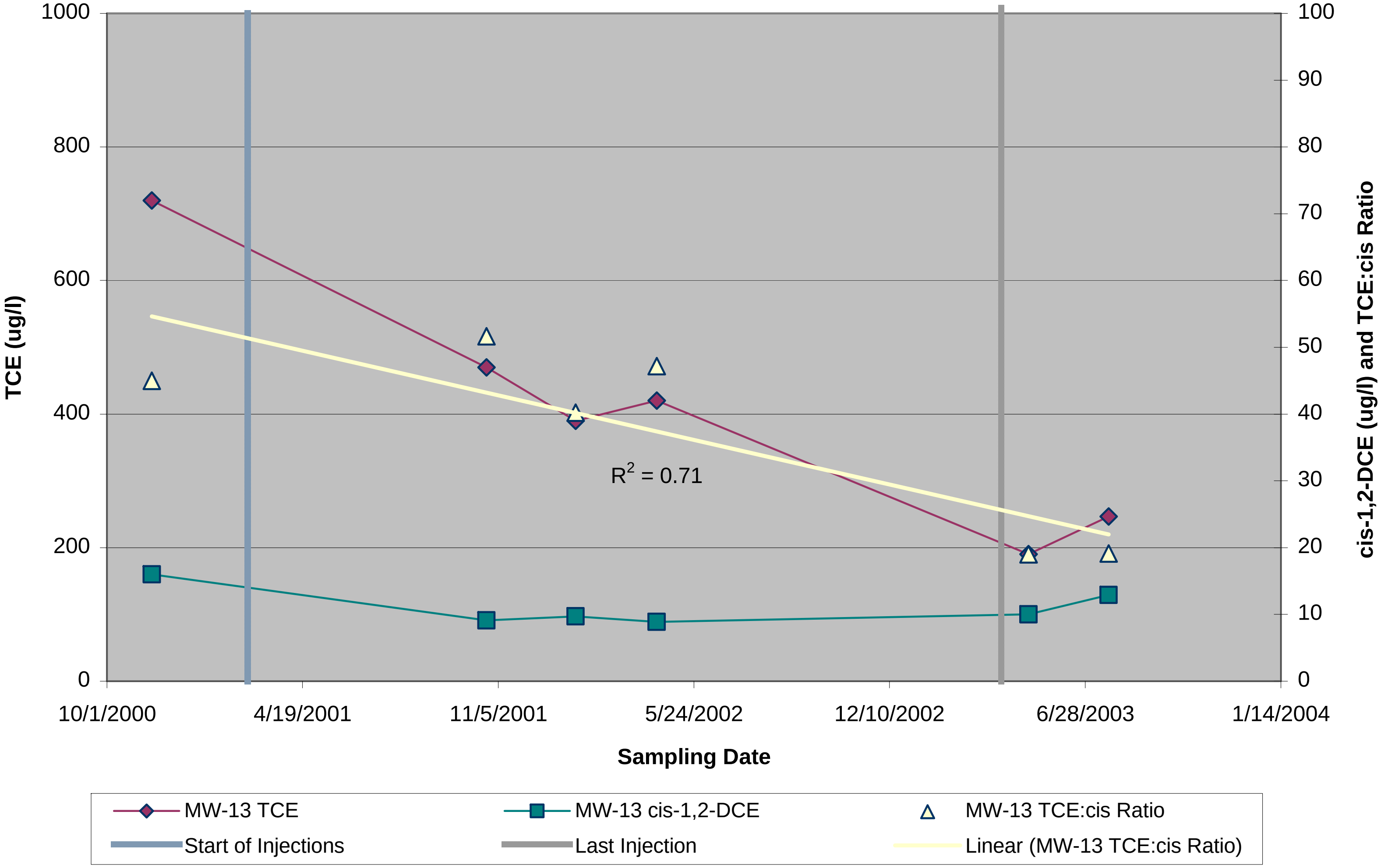


Figure 4-37 MW-13 CAH Trends

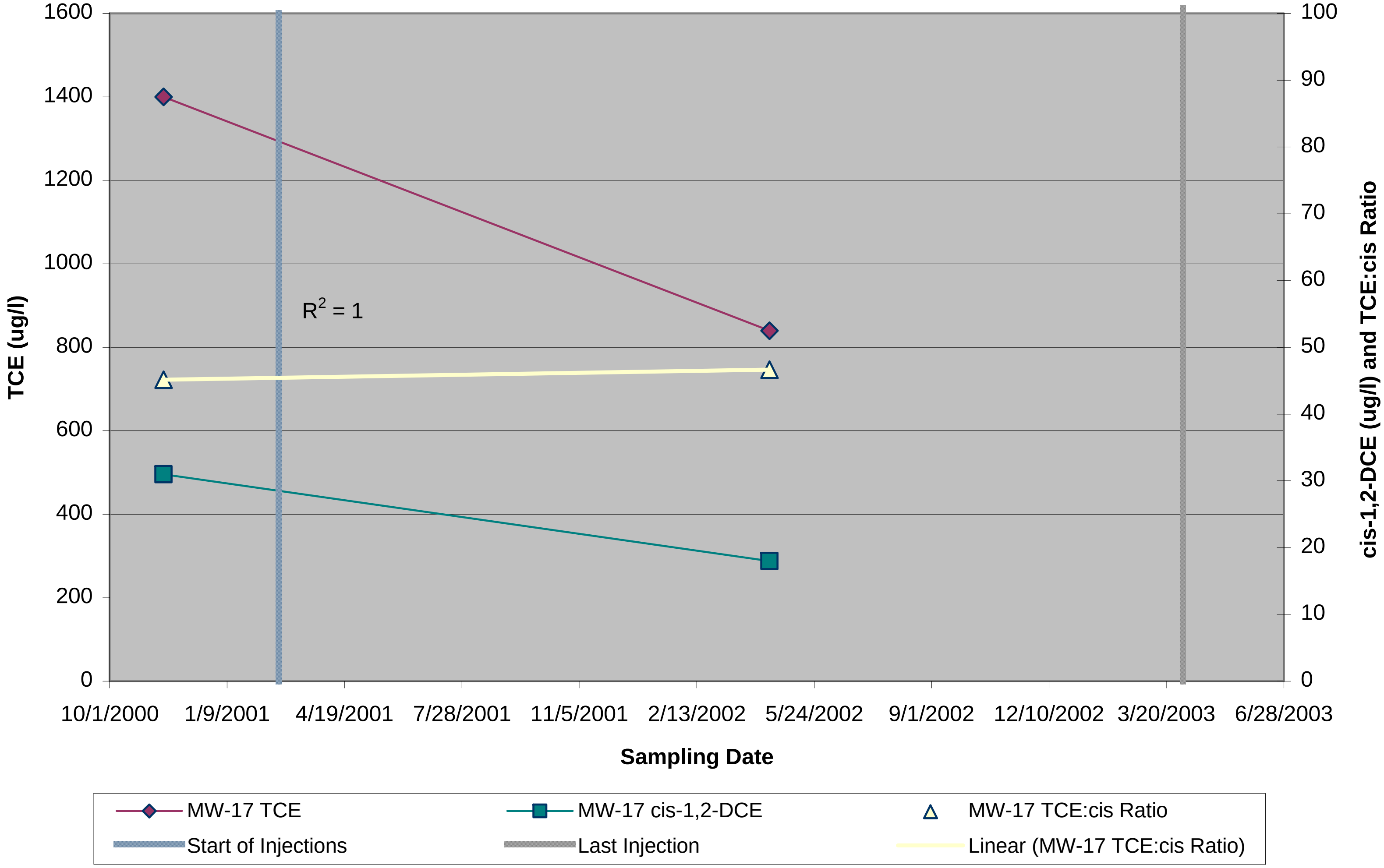


Figure 4-38 MW-17 CAH Trends

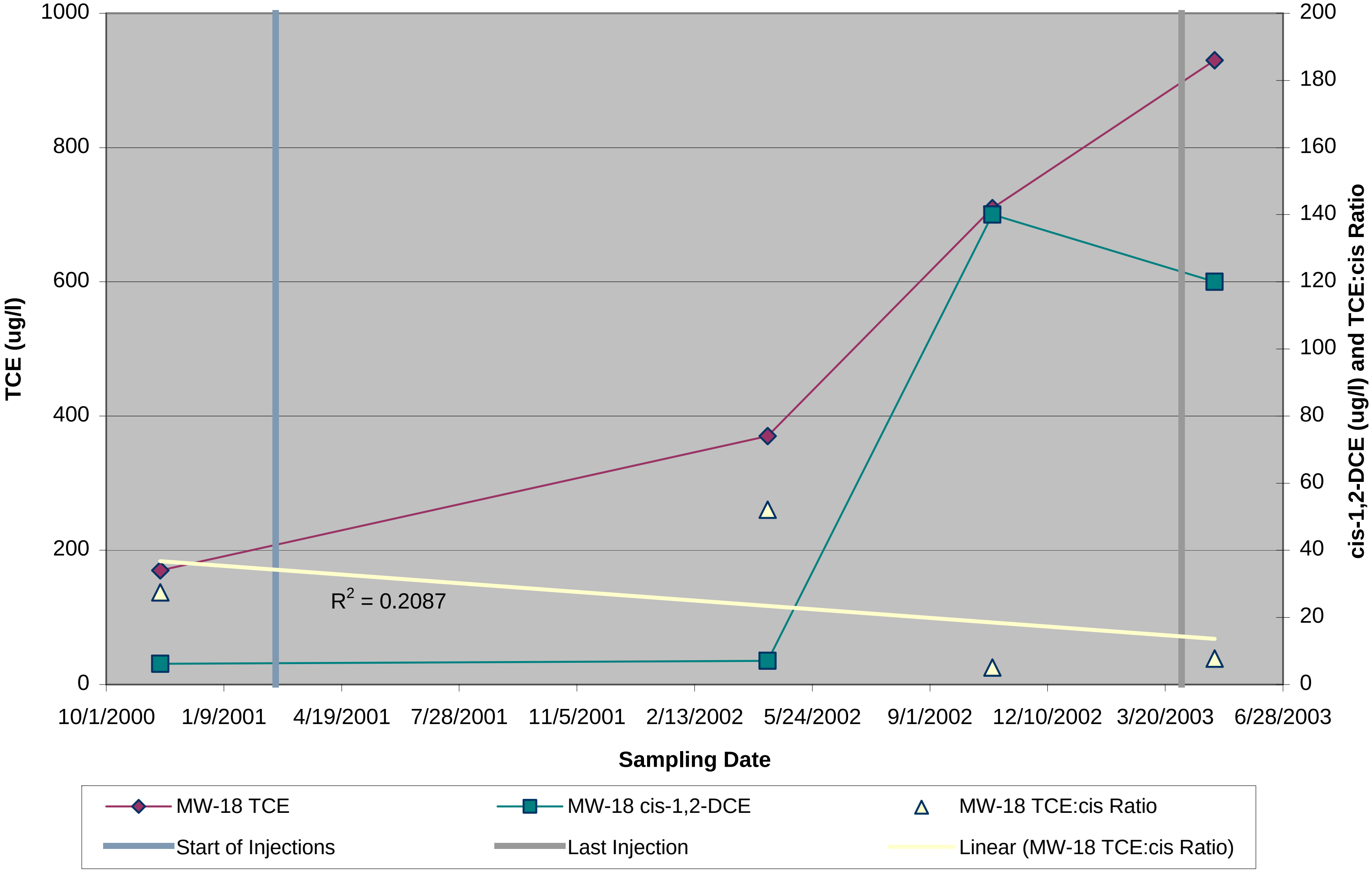


Figure 4-39 MW-18 CAH Trends

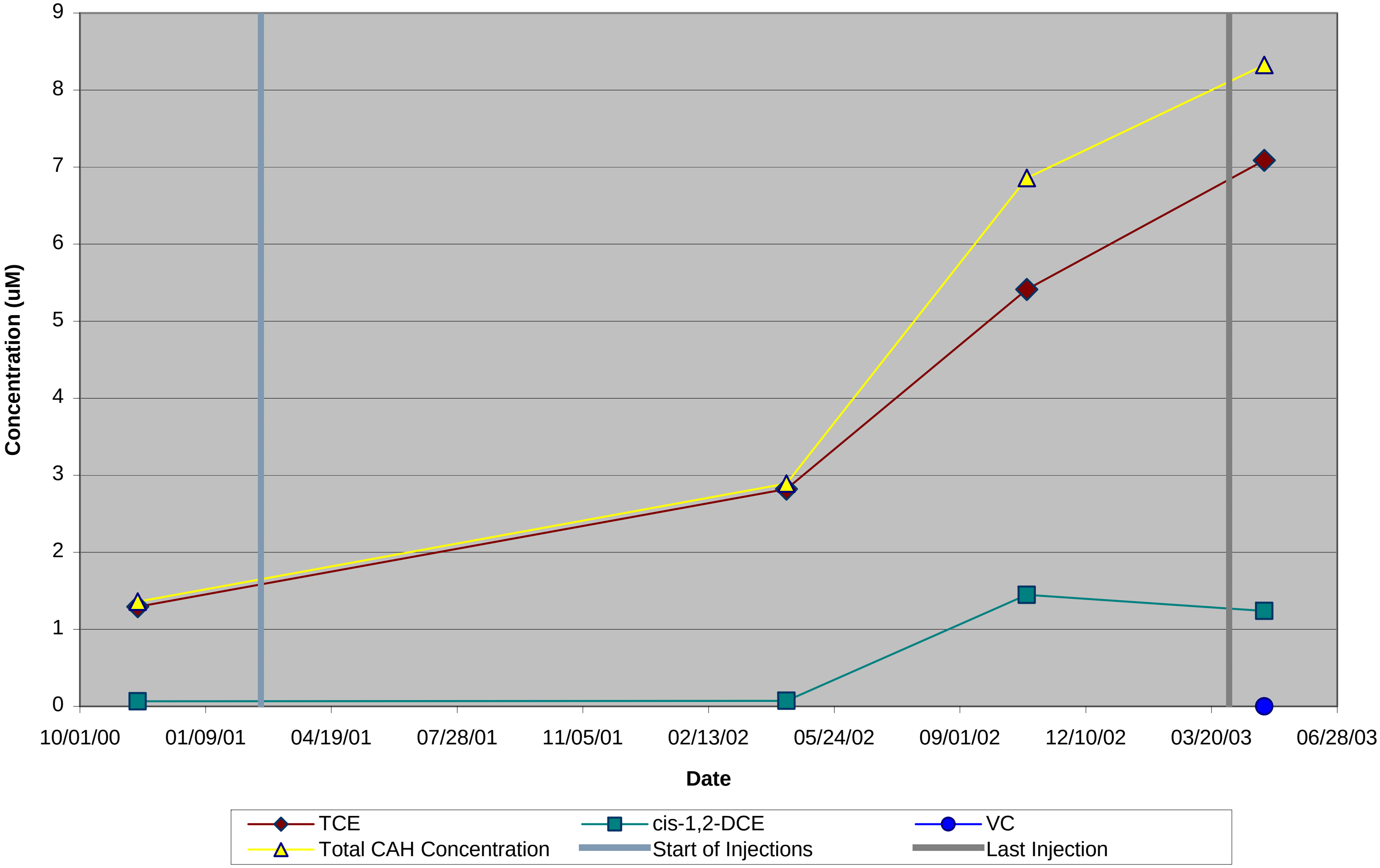


Figure 4-40 35-MW-18 VOC Trends - Molar Basis

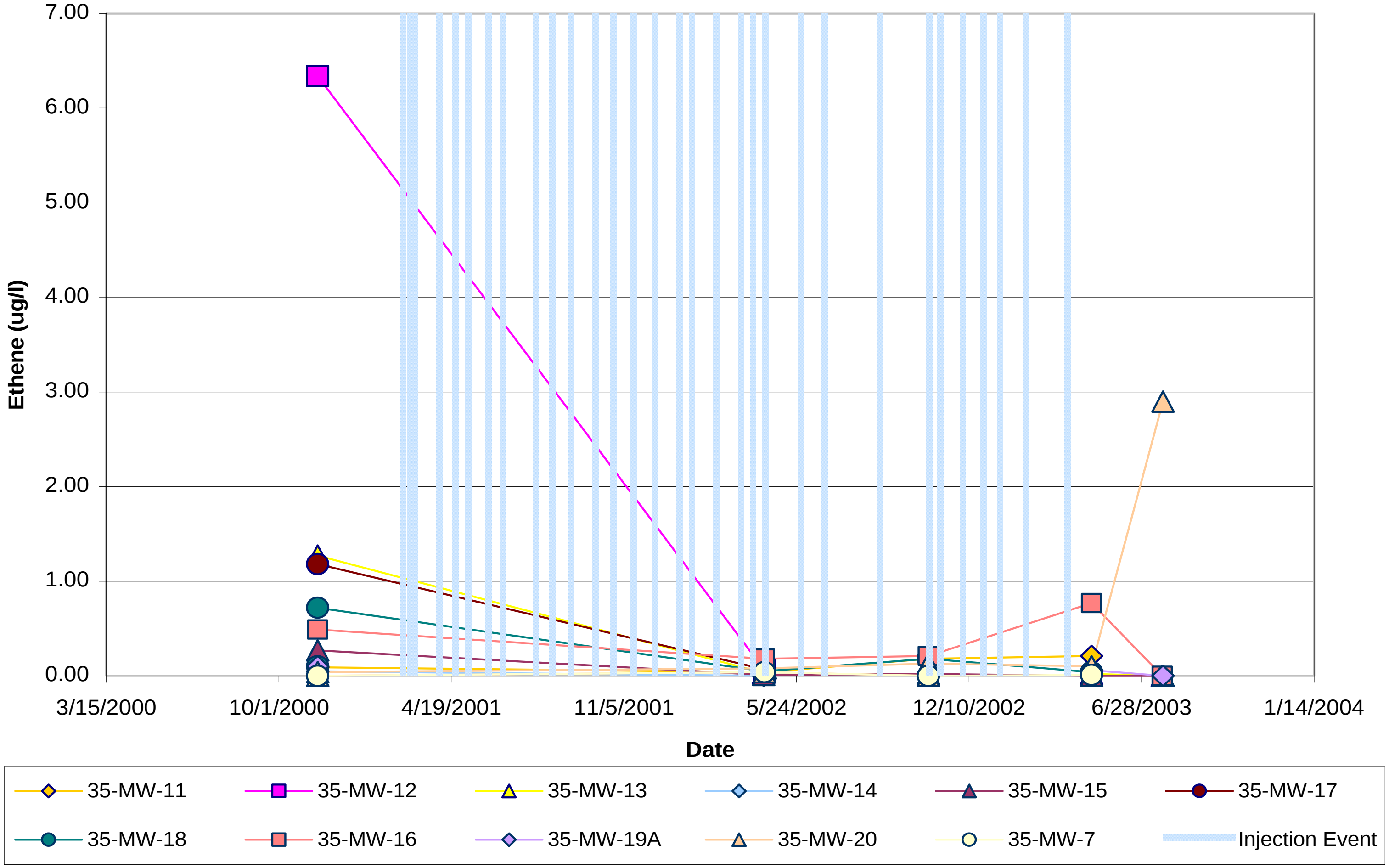


Figure 4-41 Ethene Trends

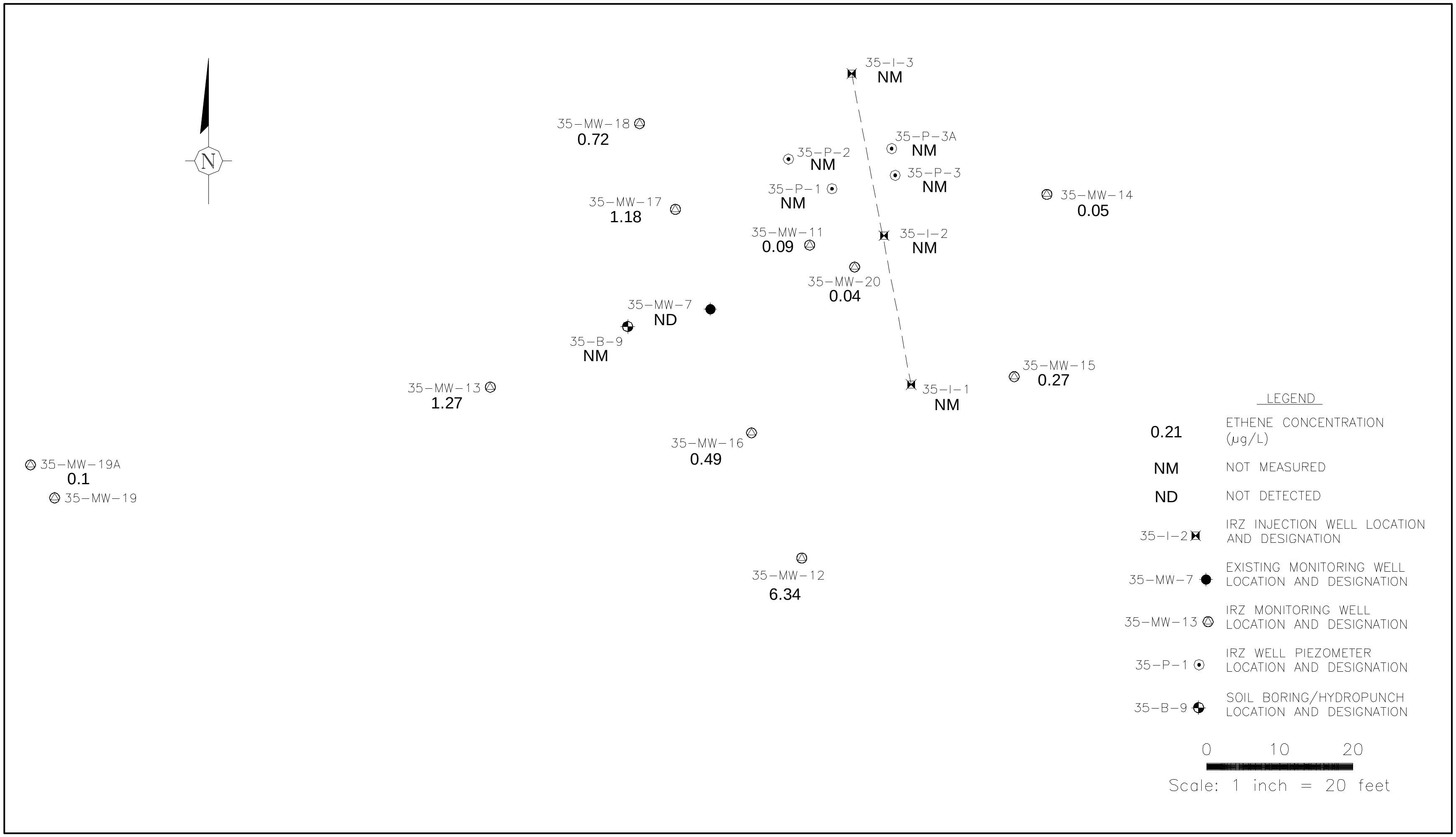


Figure 4-42 Ethene Distribution – November 2000

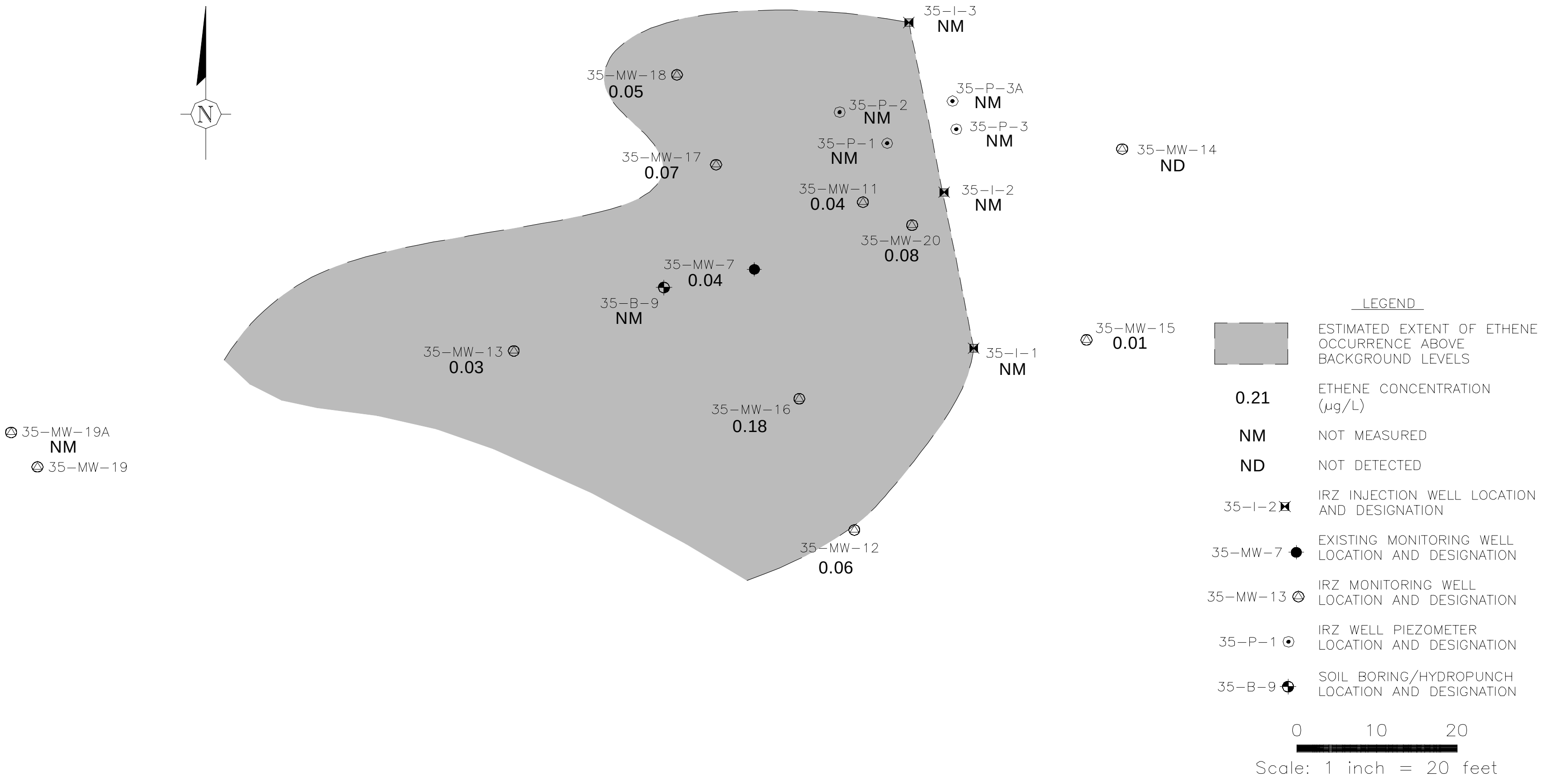


Figure 4-43 Ethene Distribution – April 2002

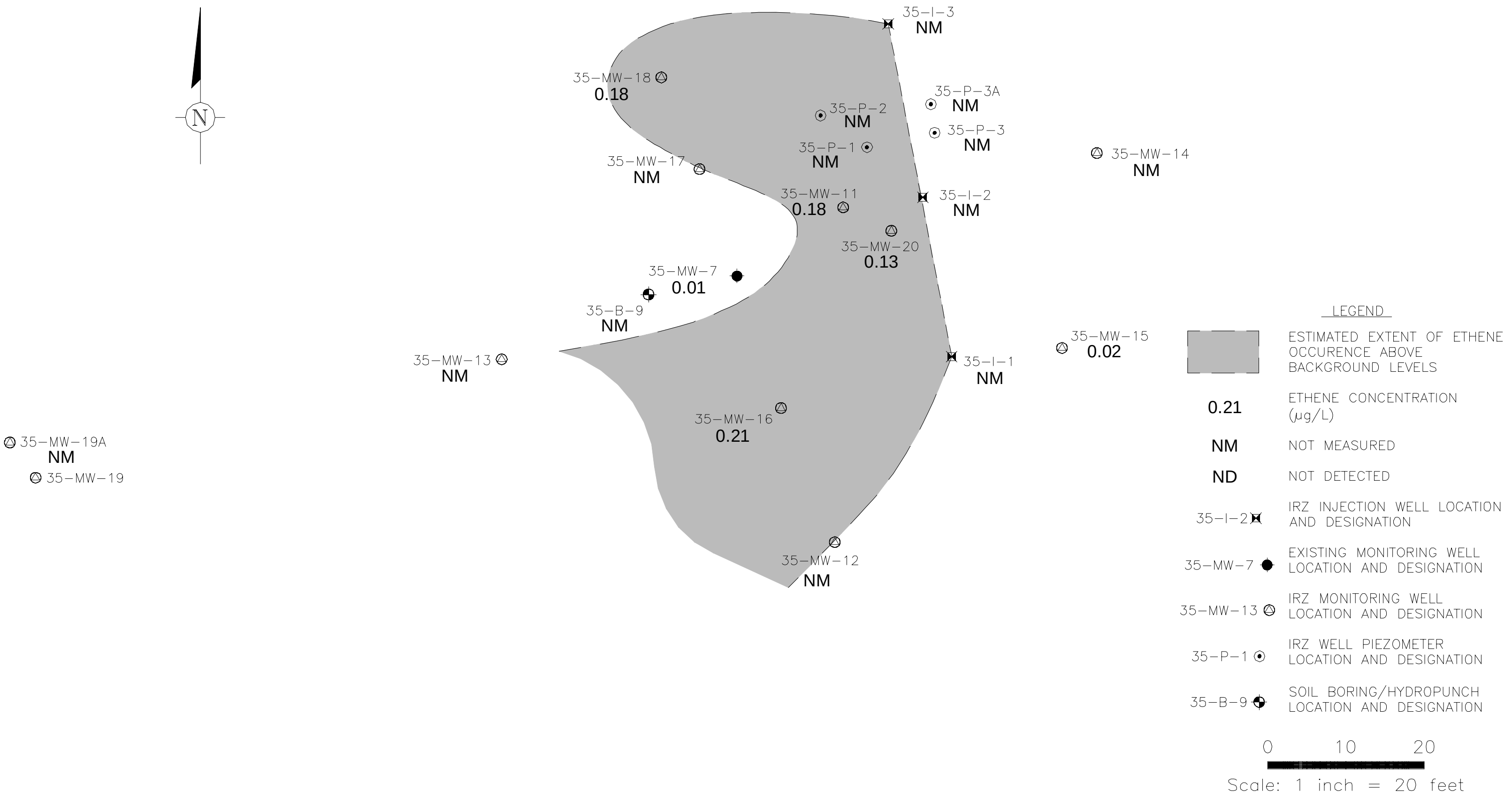


Figure 4-44 Ethene Distribution – October 2002

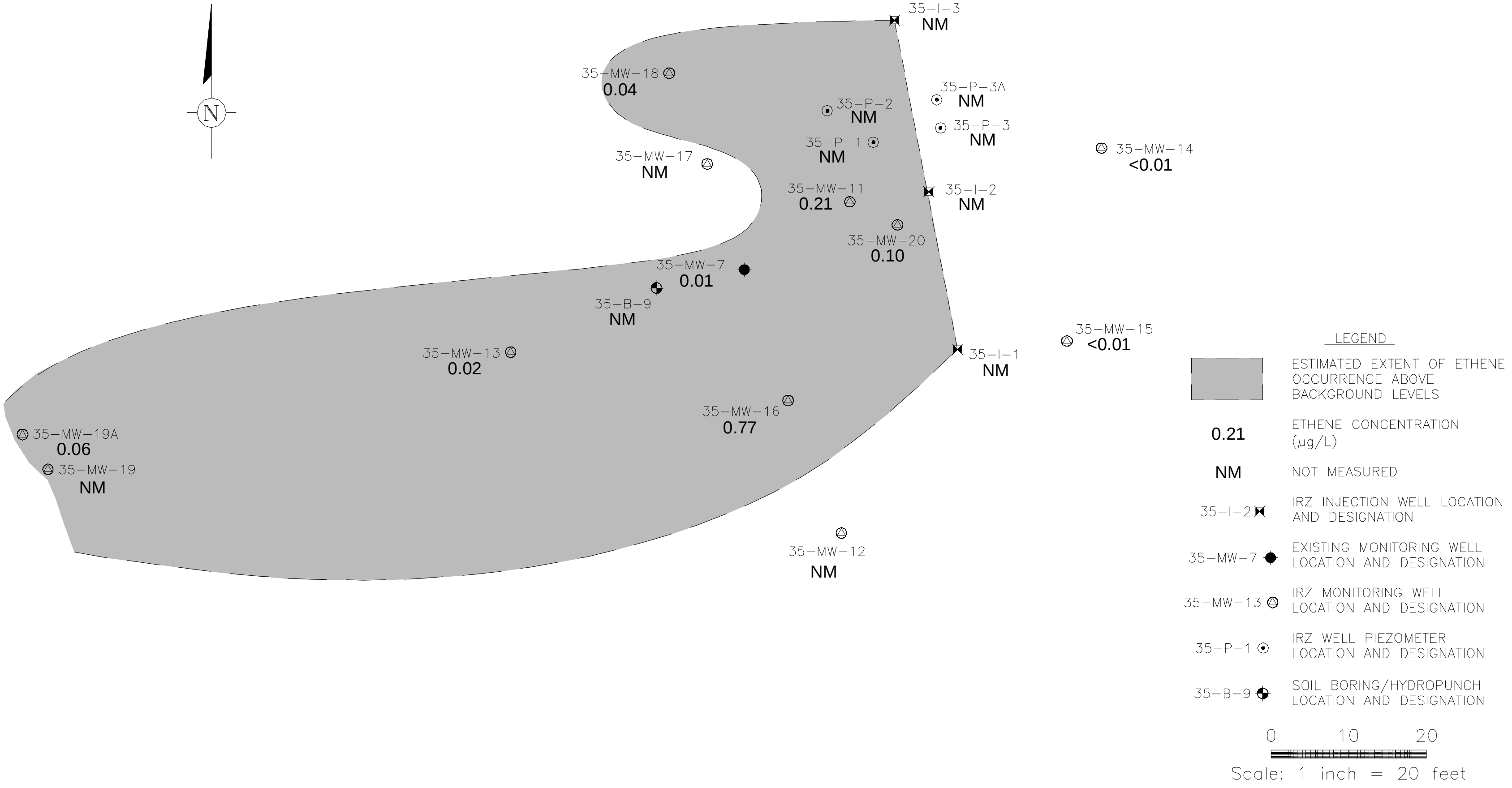


Figure 4-45 Ethene Distribution - May 2003

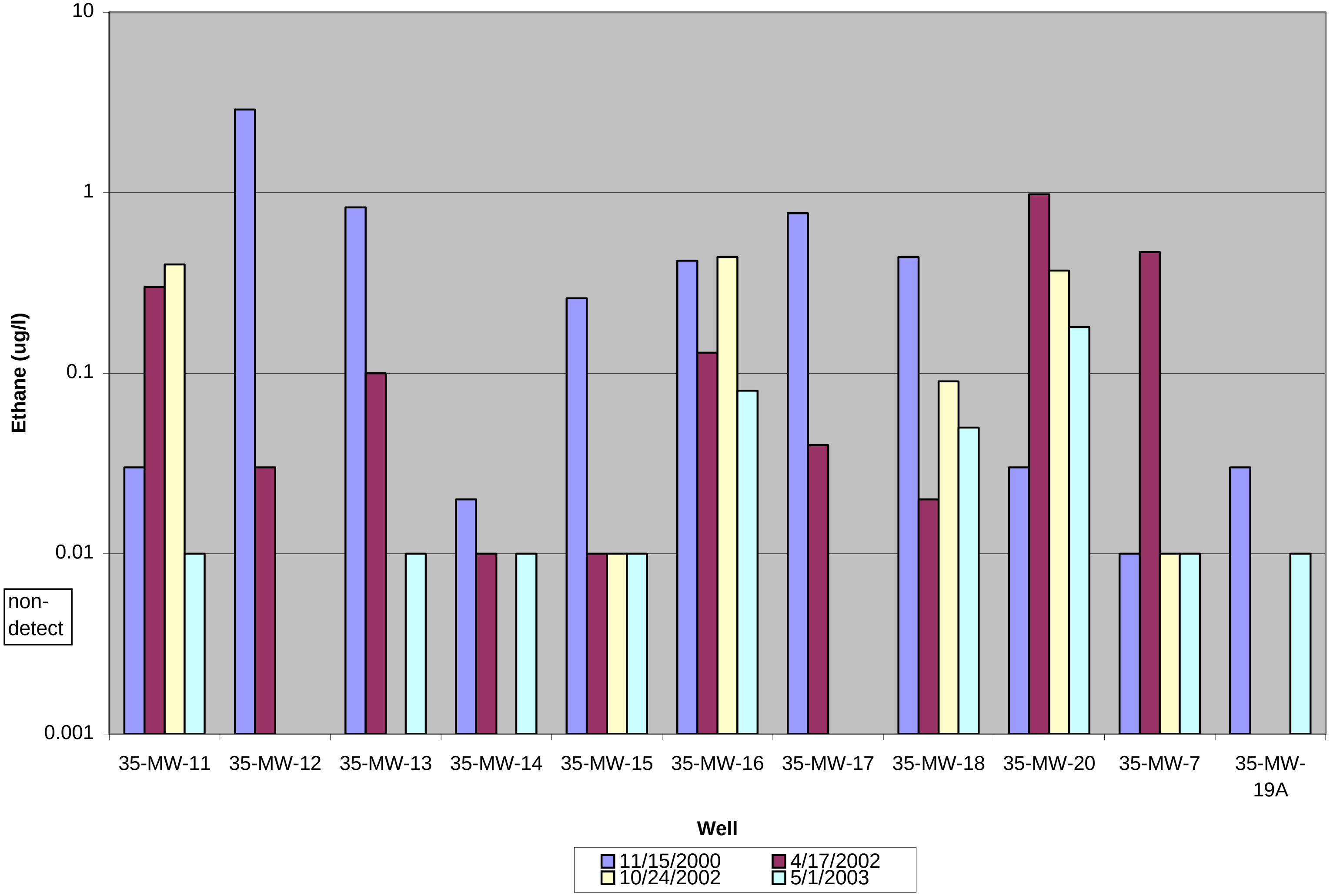


Figure 4-46 Ethane Trends

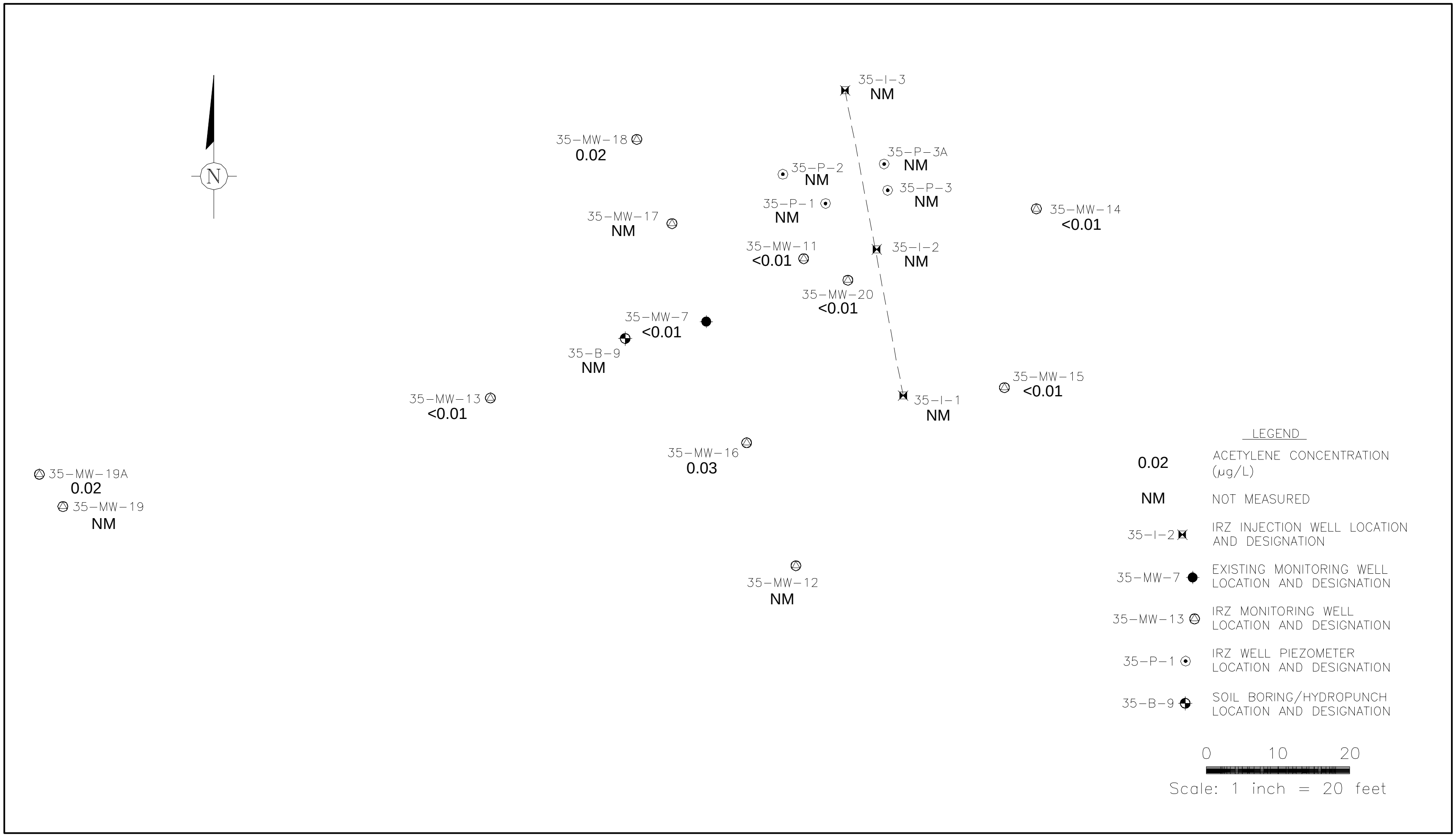


Figure 4-47 Acetylene Distribution – May 2003

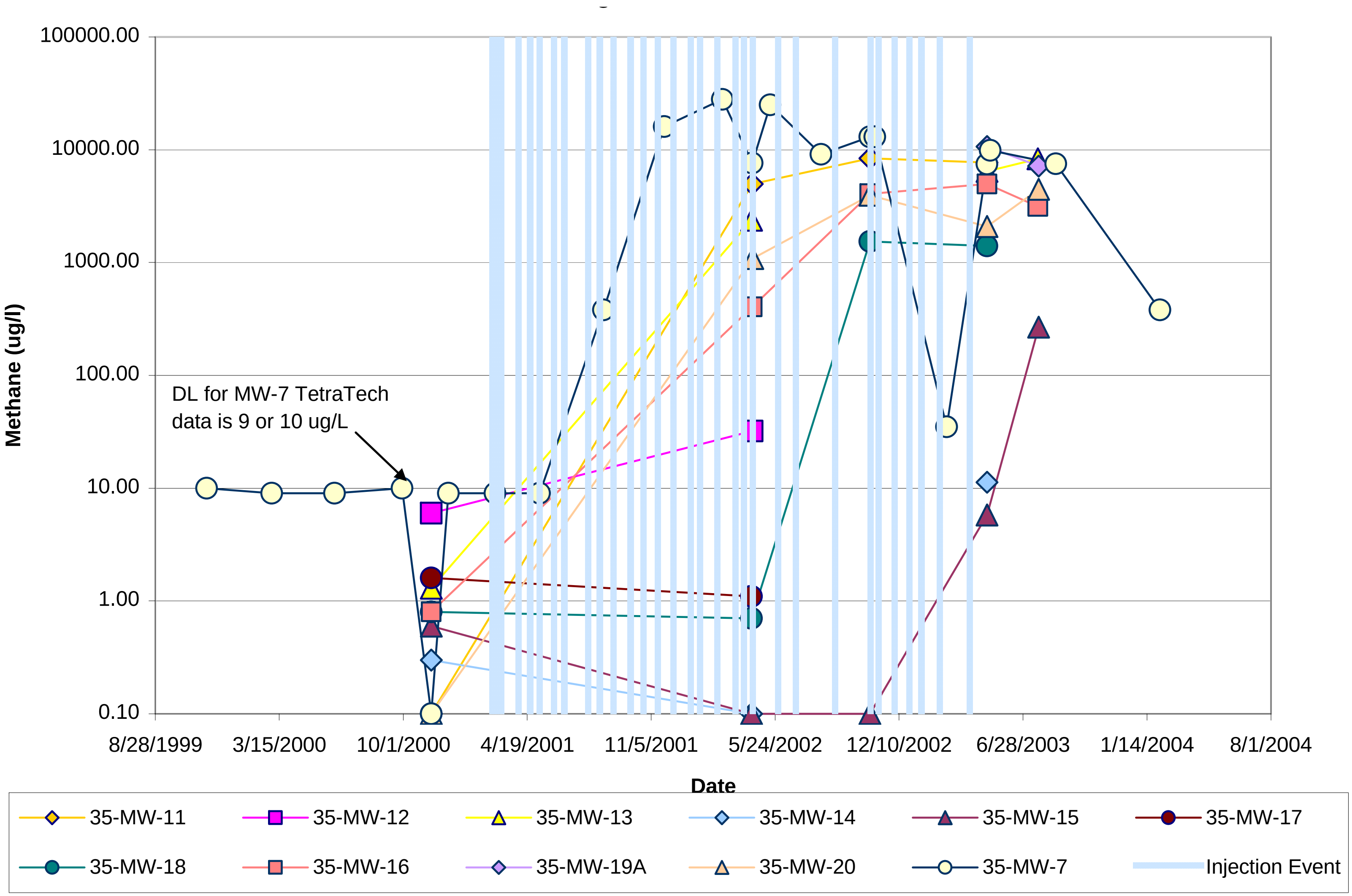


Figure 4-48 Methane Trends

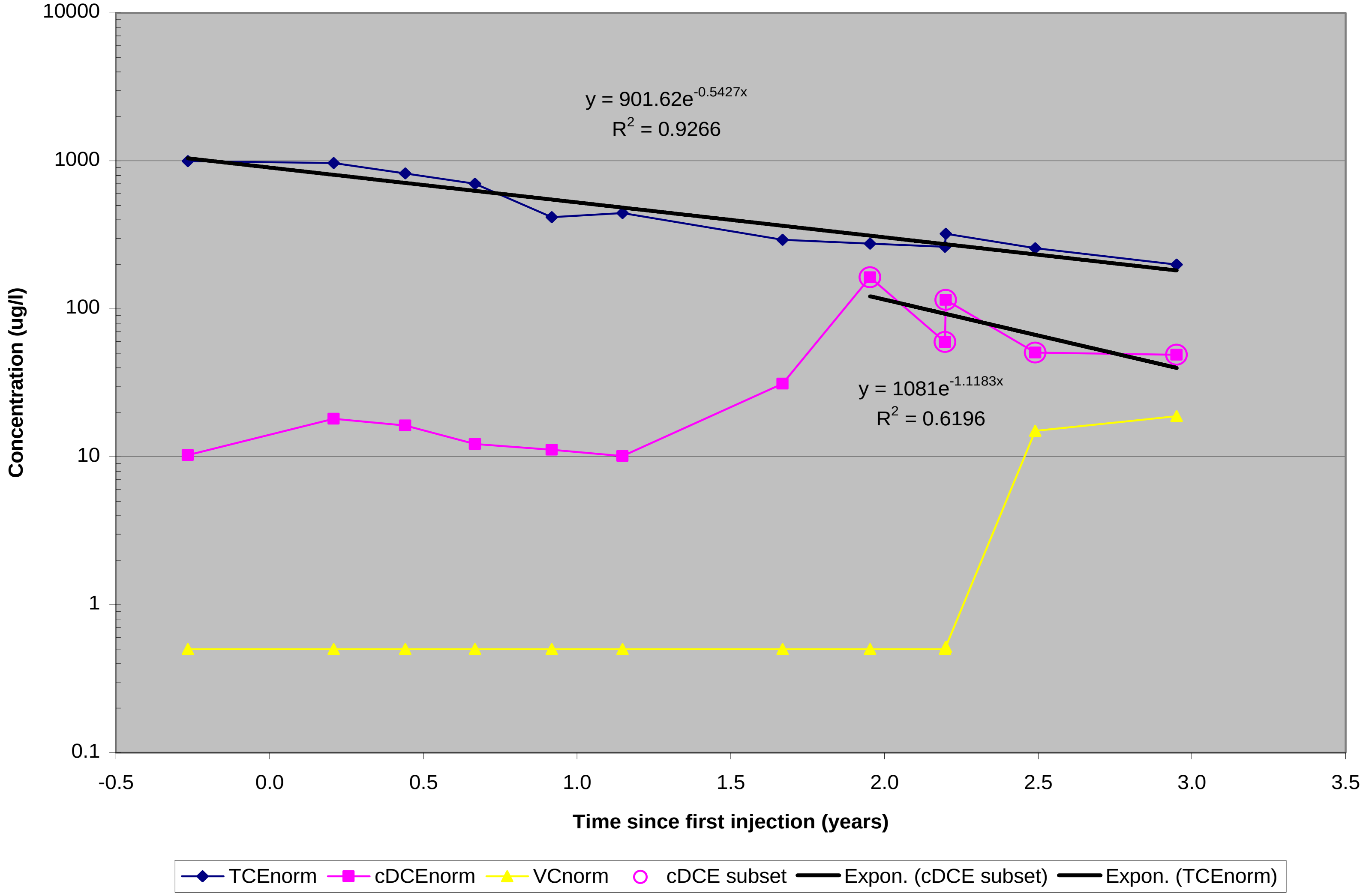


Figure 4-49 Biodegradation Rates at 35-MW-7 During Demonstration

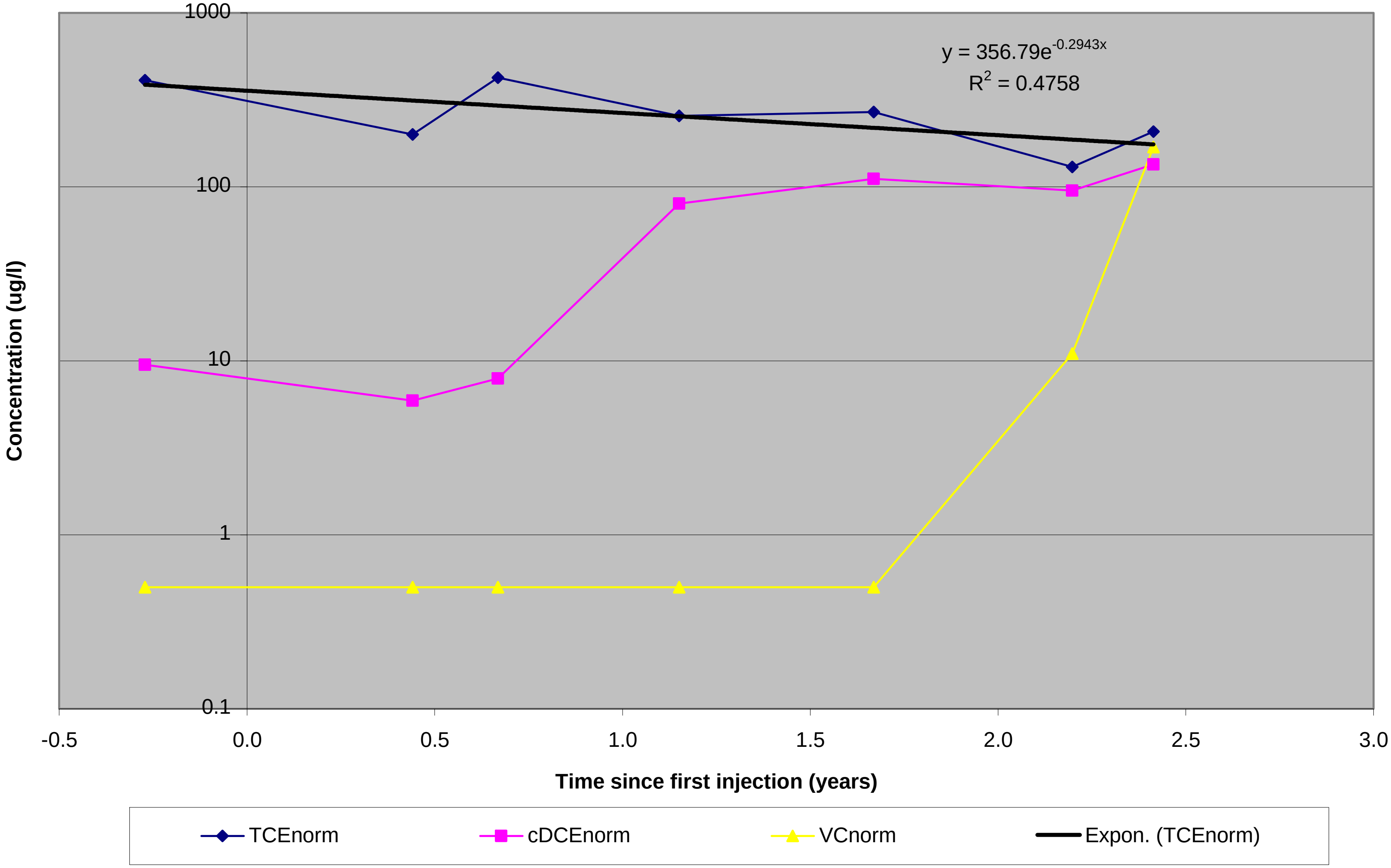


Figure 4-50 Biodegradation Rates at 35-MW-20

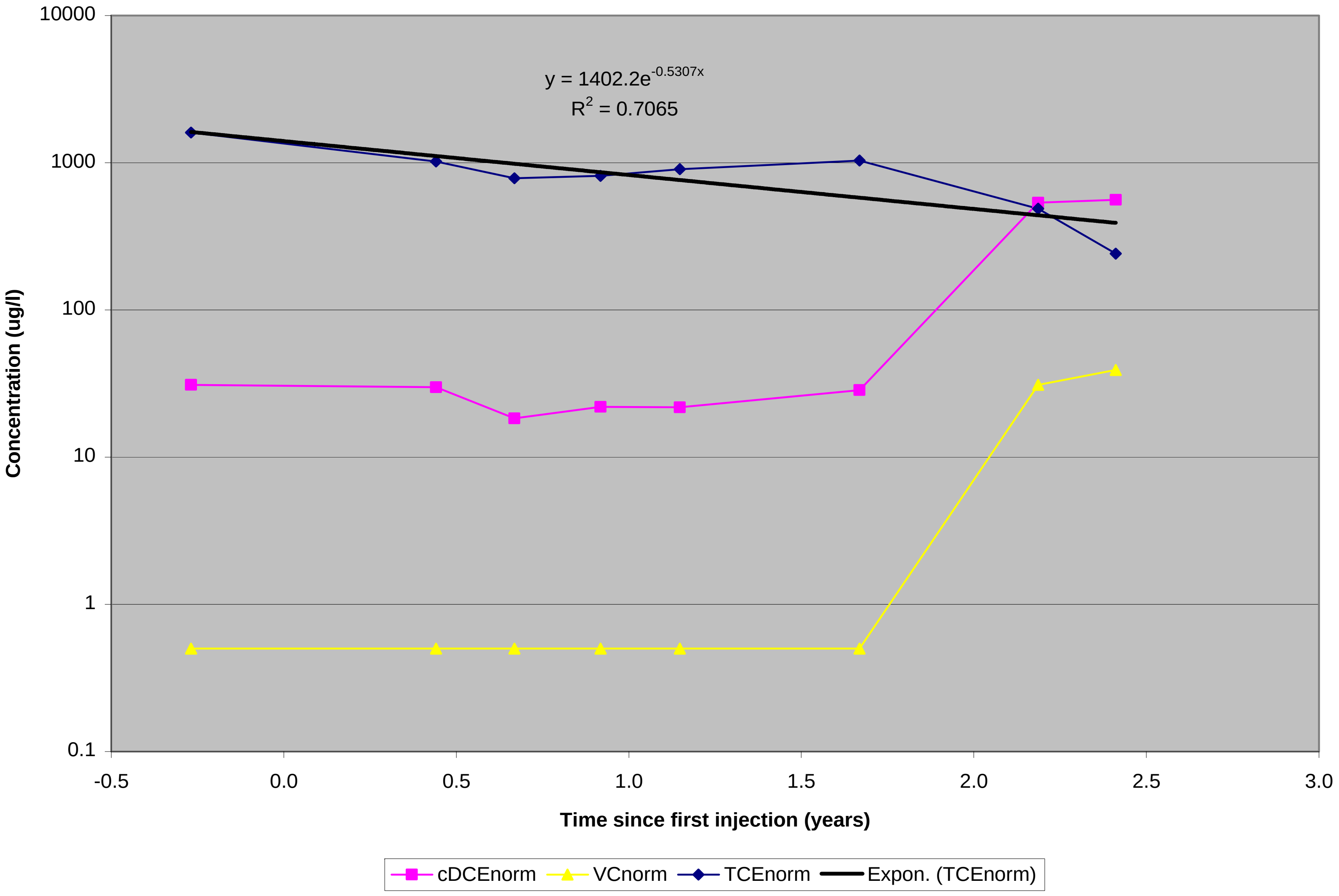


Figure 4-51 Biodegradation Rates at 35-MW-16

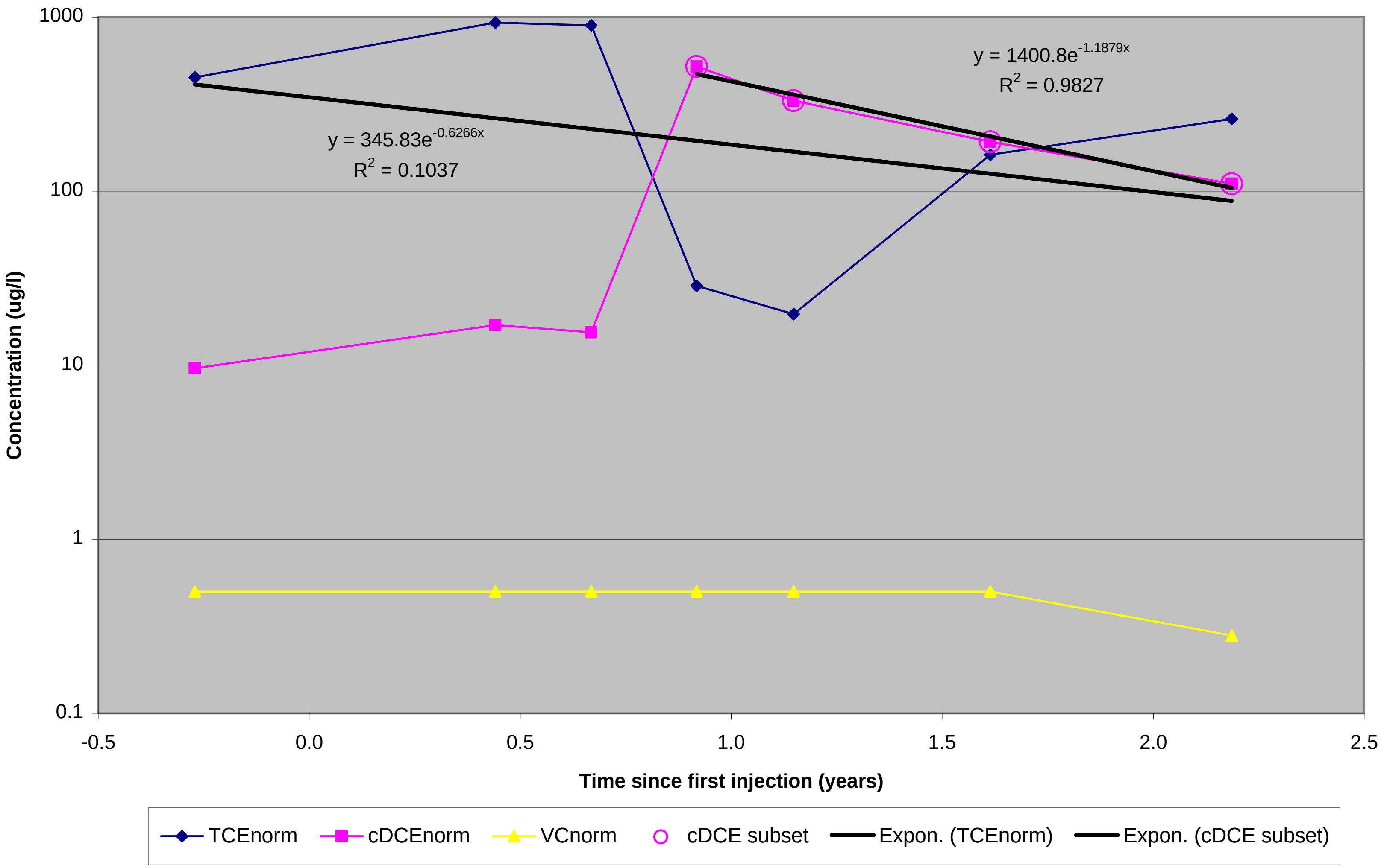


Figure 4-52 Biodegradation Rates at 35-MW-11

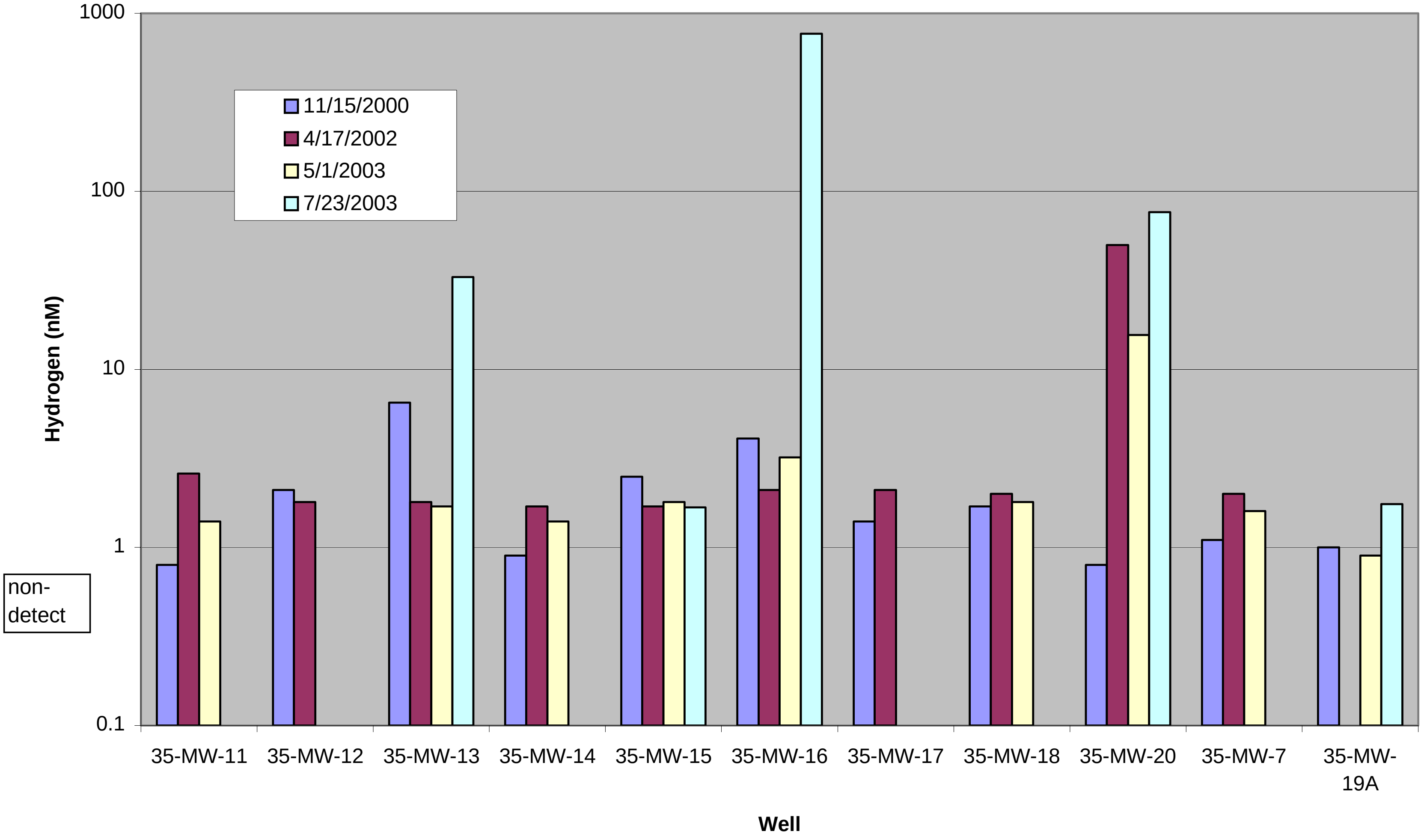


Figure 4-53 Hydrogen Trends – Log Scale

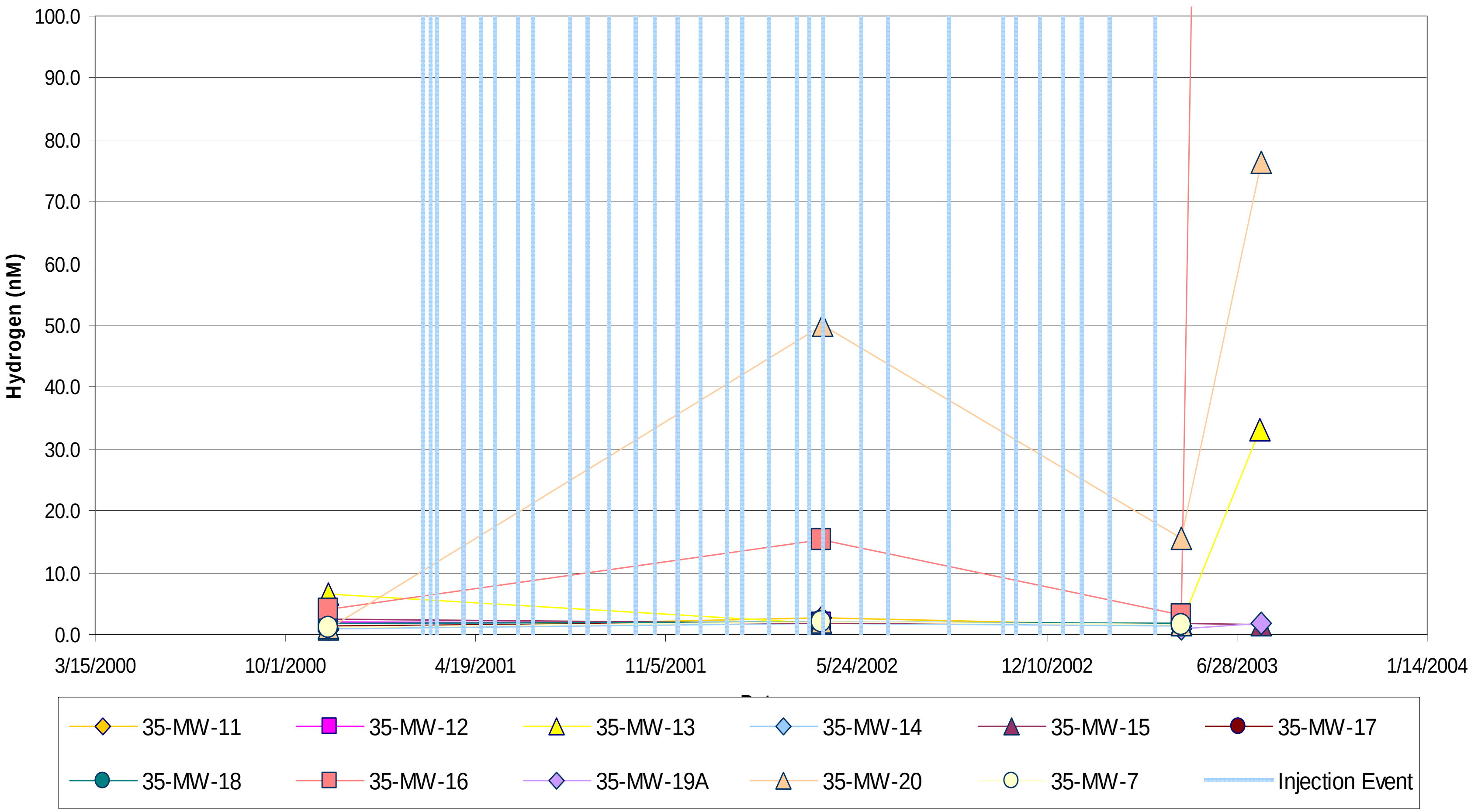
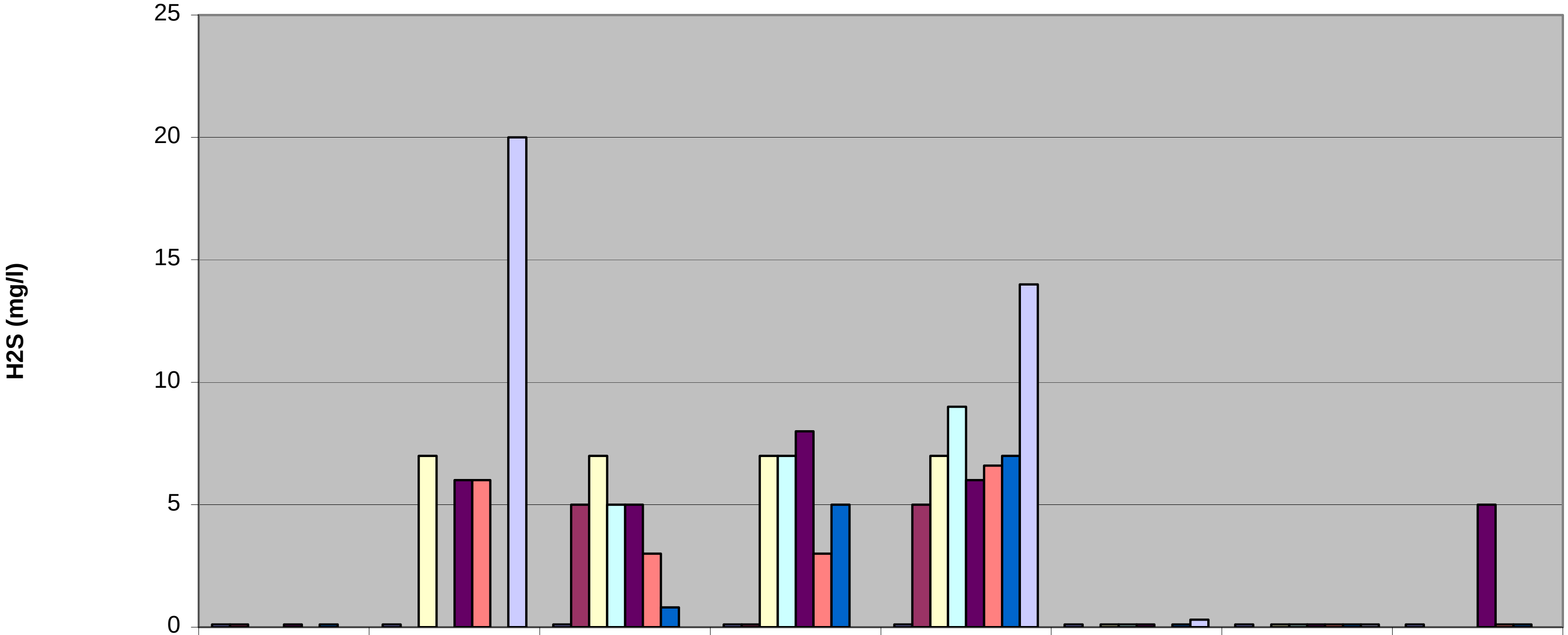


Figure 4-54 Hydrogen Trends – Linear Scale



	MW-14	MW-20	MW-11	MW-7	MW-16	MW-13	MW-15	MW-18
■ 11/15/2000	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
■ 8/2/2001	0.1		5	0.1	5			
□ 10/24/2001		7	7	7	7	0.1	0.1	
□ 1/23/2002			5	7	9	0.1	0.1	
■ 4/17/2002	0.1	6	5	8	6	0.1	0.1	5
■ 10/24/2002		6	3	3	6.6		0.1	0.1
■ 5/1/2003	0.1		0.8	5	7	0.1	0.1	0.1
□ 7/23/2003		20			14	0.3	0.1	

Well

Figure 4-55 Hydrogen Sulfide Trends

TABLES

Table 2-1 ERD Site Remediation Project Cost Elements

COST ELEMENT	COMMENTS
Costs incurred before treatment	
Engineering design	See text.
Work Plan preparation	Also include submittal and editing required for regulatory acceptance; permit preparation. Include costs for bid solicitation for subcontractors.
Mobilization and preparatory work	Includes mobilization for injection well installation and system construction. May also include installation of additional monitoring wells if the preexisting network is inadequate.
Well installation	Surface and subsurface structures at the facility may interfere with well design and placement. Proper planning and design can minimize these costs.
Treatment costs	
Field supervision	Oversight of subcontractors for drilling, laboratory analyses, etc.
Injection system	Manual batch loading of molasses into the injection well array can be performed using relatively low cost injection systems that may be truck or trailer mounted (see section 2.1 of this report and sections 4 and 6 of the protocol document, Suthersan 2002) . If a permanent injection set-up is required, additional capital costs will be incurred, including a system enclosure, permanent mixing tank/equipment, automated injection pumps and valving, and controls. Additional costs for this type of system may include below grade piping to transfer the solution from the enclosure to the wells and provision of utilities (water and electric). However, a portion of the costs associated with the more permanent installation will be off-set by the lower labor and field expense costs associated with the manual batch injections.
Substrate (food grade carbohydrate)	As mentioned in the text and in the protocol, these costs are relatively low on a per pound basis but can become substantial if a site requires high doses due to high flow or electron acceptor load. Feed rates are discussed in detail in protocol sections 4.3,4.5 and 5.3 (Suthersan 2002)
Labor, O&M	Automated loading of molasses into the injection well array will require more control equipment, but will reduce operations and maintenance costs.
Sampling and sample analysis	Labor required to collect groundwater samples from the treatment area. as well as costs for shipping, analysis and data interpretation should be included.
Utility costs	The main requirement should be a readily available source of potable water, preferably with a large flow rate near the site. Fuel for vehicles and electrical power or gasoline for pumps is also likely to be required but in small quantity.
Other costs	These include disposal of drill cuttings and purge water. During application of ERD, process waste is limited to disposal of contaminated groundwater generated during well purging.
Interim reporting	Technical performance and financial interim reports are normally required
After treatment costs	
Final reporting	Reports documenting system performance must be prepared for site closure.
Demobilization (equipment, material, and personnel.	Must include labor and subcontractor costs required to remove any equipment or surface facilities associated with the demonstrations. It must be assessed if injection and monitoring wells need to be removed/abandoned. Some site restoration can typically be anticipated.

Table 2-2 Summary of Reagent Cost Ranges for Selected Soluble Carbohydrates

Reagent	**Range of Costs (Per Pound of TOC)**	
	Low	**High**
Molasses (Food Grade)	$ 0.25	$ 0.60
Corn Syrup	$ 0.25	$ 0.44
Whey (Powder)	$ 1.17	$ 1.33
Sodium Lactate	$ 1.25	$ 1.46

Source: Suthersan et al., 2002

Table 3-1 Performance Objectives

Type of Performance Objective	**Primary Performance Criteria**	**Expected Performance (Metric)**	**Actual Performance Objective Met?**
Qualitative	1. Technology Evaluation - Gather information (for estimation of long-term treatment effectiveness, life span and costs) to use in a protocol for use of ERD technology for CAHs at DoD facilities	Collection of extensive performance data	Yes
Quantitative	2. Reduce Time to Remediate - Demonstrate the ability of ERD to remediate contaminants in the subsurface over a relatively short time period	1 to 5 years in typical full-scale applications	Not clearly demonstrated due to duration of test; rates were more rapid than NA, but slower than many other applications of ERD
Quantitative	3. Contaminant Reduction (%) - Reduce total CAH concentrations from baseline levels of a) >200 ppb b) 50 to 200 ppb c) <50 ppb	a) 80% in 1 year b) 75% in 1 year c) 50% in 1 year	Objective was not met for total CAHs within target time. Individual compounds were reduced by ≥80% at specific wells by the post-treatment period: 85% TCE reduction at 35-MW-16 and 80% at 35-MW-7
Qualitative	4. Prevent "Stalling" - Demonstrate that degradation of CAHs by ERD does not stall at undesirable by-products (cis-DCE and/or VC)	Reduction of cis-DCE, VC after initial production, production of ethene	Yes for cis-DCE in limited area; VC and ethene levels have not progressed far enough to completely evaluate. However, progression from TCE degradation to DCE degradation and on to VC is occurring
Type of Performance Objective	**Secondary Performance Criteria**	**Expected Performance (Metric)**	**Actual Performance Objective Met?**
Quantitative	5. Geochemistry Manipulation - Demonstrate the ability of ERD to enhance the anaerobic and reducing environment in groundwater where anaerobic conditions prevail	DO to <1 mg/L ORP <50 mV	Yes; anaerobic environment created within a large reactive zone
Quantitative	6. Contaminant Mobility - Evaluate the ability of ERD to desorb CAHs from aquifer materials	Presence of "spike" in concentration after initial injections	Yes in limited area, but mostly not applicable; primarily a dissolved phase, low-TOC plume
Quantitative	7. Contaminant Reduction (Rate) - Evaluate degradation rates before & after treatment	Calculate k	Yes

Type of Performance Objective	**Secondary Performance Criteria**	**Expected Performance (Metric)**	**Actual Performance Objective Met?**
Qualitative	8. System Performance Optimization - Determine optimal strengths and frequency of reagent delivery for the site	Injection Wells: pH > 4 DO < 1.0 mg/L -400 mV < ORP < -250 mV 500 mg/L < TOC < 9,000 mg/L Sp. Cond. 10x increase Mon. Wells: pH > 5.0 DO < 1.0 mg/L ORP < -200 mV TOC > 50 mg/L Sp. Cond. 20-50% increase	Variable, but generally yes; continuously "tuned" system to metrics, determined required strength, frequency of injections; addition of buffer improved control
Quantitative	9. Hazardous Materials	Potentially hazardous materials limited to soil cuttings from well drilling and purge water	Yes; no other haz. materials generated
Qualitative	10. Reliability	No significant reliability issues anticipated	Yes
Qualitative	11. Ease of Use	Field implementation (substrate delivery) requires an environmental technician with 40 Hour HAZWOPER training, and office support from degreed scientists or engineers	Yes
Qualitative	12. Versatility	ERD can be used for other applications (e.g., metals, perchlorate) and under variable site conditions	N/A (though this is true, there were no other COCs at this site
Qualitative	13. Maintenance	Maintenance limited to occasional well development, normal equipment maintenance by technician	Yes
Qualitative	14. Scale-Up Constraints	Scale-up potential determined	Yes, but have not yet done

Table 3-2 Suitability of Vandenberg AFB Site Screening Characteristics for IRZ Implementation

Site Characteristic	Suitable for IRZ	Unsuitable for IRZ	Vandenberg AFB
Aquifer hydraulic conductivity	> 1 ft/day	<0.01 ft/day	0.9 to 3.8 ft/day
Groundwater velocity	30 ft/year - 5 ft/day	< 30 ft/year, > 5 ft/day	0.11 to 0.46 ft/day
pH	6.0 – 8.0	< 5.0, > 9.0	6-7
Natural attenuation of CAHs	Slow, complete degradation, or stalled degradation	No degradation	Slow
DNAPL presence	None, or emulsified, sorbed, or residuals	IRZ not appropriate for targeting pooled DNAPL at this point in technology development	No DNAPL known to be present
Sulfate	< 700 ppm		200-300 ppm
Redox	Aerobic or borderline	Anaerobic with sufficient TOC	Aerobic (DO >1 mg/l) and oxidizing (ORP > 300 mV)
Depth of Target Zone		>50 feet can become expensive (as also true with other technologies)	45 feet
CAH concentration	Non-toxic	Toxic	Non-toxic

Table 3-3 Summary of K Estimates

Well	K (ft/day)	Method	Source
35-MW-3	0.045	Soil Sample	RI (Tetra Tech, 1999)
35-MW-4	0.000021	Slug Test	RI (Tetra Tech, 1999)
35-MW-5	0.1665	Slug Tests (averaged)	RI (Tetra Tech, 1999)
35-MW-7	1.023	Slug Tests (averaged)	RI (Tetra Tech, 1999)
35-MW-8	111.5	Slug Test	RI (Tetra Tech, 1999)
35-I-2	0.92 to 3.83	Step-Drawdown Test	ARCADIS tests

Table 3-4 Demonstration Milestones

Event	Date
ARCADIS well installations and soil sampling	August-October 2000
Step-drawdown test	August 29, 2000
Baseline groundwater sampling	September-November 2000
First substrate injection	February 22, 2001
Start of buffering	October 24-25, 2002
Last substrate injection	April 3, 2003
Post-demonstration monitoring	May 2003; additional event planned for mid-2004
EPA-Ada evaluations	July 22-23, 2003; additional work planned with AFCEE/COE in 2004
Sampling events by base contactor, Tetra Tech, at 35-MW-7	Typically semiannually, most recently in May 2003 and February 2004

Table 3-5 Groundwater Analytical Parameters

Parameter	Analytical Method	Concentration Units Reported In	Volume, Container, Preservative & Storage Requirements	Hold Time	Parameter Included also In Abbreviated Monitoring Events?	Location of test/ Firm
Temperature	ARCADIS SOP D1 (based on EPA 170.1)	Degrees C	NA	Analyze immediately	Y	ARCADIS in the field
ORP	See appendix 'field procedures' & 'instrument calibration procedures'	mV	NA	Analyze immediately	Y	ARCADIS in the field
Dissolved Oxygen	ARCADIS SOP D5 (Based on EPA 360.1)	mg/L	NA	Analyze immediately	Y	ARCADIS in the field
PH	ARCADIS SOP D2 (based on EPA 150.1)	S.U.	NA	Analyze immediately	Y	ARCADIS in the field
Specific Conductance	ARCADIS SOP D3 based on standard methods for examination of water & wastewater, 15th edition method 205 & USEDA method 120.1	microsiemens/cm	NA	Analyze immediately	Y	ARCADIS in the field
Alkalinity	310.1	mg/L	250 mL Glass or plastic Cool to 4 °C	14 days	N	STL

Parameter	Analytical Method	Concentration Units Reported In	Volume, Container, Preservative & Storage Requirements	Hold Time	Parameter Included also In Abbreviated Monitoring Events?	Location of test/ Firm
Nitrate	300.0A	mg/L	250 mL Glass or plastic Cool to 4 °C	48 hours	N	STL
Nitrite	300.0A	mg/L	250 mL Glass or plastic Cool to 4 °C	48 hours	N	STL
Sulfate	300.0A	mg/L	100 mL Glass or plastic Cool to 4 °C	28 days	N	STL
Chloride	300.0A	mg/L	250 mL Glass or plastic	28 days	N	STL
Methane, Ethane, Ethene	Modified RSK-175, WA 1.02	ug/l	Glass VOA vials	7 days	N	Vaportech
Carbon Dioxide	WA 2.01 modified	mg/l	Glass VOA vials	7 days	N	Vaportech
Chemical Oxygen Demand	410.4 or 410.1	mg/L	250 mL Glass or Plastic Cool to 4 °C H_2SO_4 to pH<2	28 days	N	STL
Biochemical Oxygen Demand	405.1	mg/L	100 mL Glass or plastic Cool to 4 °C	48 hours	N	STL

Parameter	**Analytical Method**	**Concentration Units Reported In**	**Volume, Container, Preservative & Storage Requirements**	**Hold Time**	**Parameter Included also In Abbreviated Monitoring Events?**	**Location of test/ Firm**
Total Organic Carbon (TOC)	415.1	mg/L	100 mL Glass or Plastic Cool to 4 °C H_2SO_4 to pH<2	28 days	Y	STL
Dissolved Total Organic Carbon	415.1	mg/L	100 mL Glass or Plastic Cool to 4 °C H_2SO_4 to pH<2	28 days	Y	STL
Ammonia	350.1	mg/L	500 mL Glass or Plastic Cool to 4 °C H_2SO_4 to pH<2	28 days	N	STL
Sulfide	Color Chart/ Effervescence of H_2S (Hach Kit 25378-00)	mg/L	500 mL Glass or Plastic Cool to 4 °C H_2SO_4 to pH<2	7 days	Y	ARCADIS in the field
Total Iron	6010B and CHEMetrics kit in field	ug/L	1 L Glass or plastic HNO_3 to pH<2	6 months	N	STL, Also in field by ARCADIS
Total Manganese	6010B and CHEMetrics kit in field based on APHA 314C and CHEMetrics kit in field	ug/L	1 L Glass or plastic HNO_3 to pH<2	6 months	N	STL, Also in field by ARCADIS

Parameter	Analytical Method	Concentration Units Reported In	Volume, Container, Preservative & Storage Requirements	Hold Time	Parameter Included also In Abbreviated Monitoring Events?	Location of test/ Firm
Dissolved Iron	6010B and CHEMetrics kit in field	ug/L	1 L Glass or plastic HNO_3 to pH<2	6 months	N	STL, Also in field by ARCADIS
Dissolved Manganese	6010B and CHEMetrics kit in field (APHA 314C)	ug/L	1 L Glass or plastic HNO_3 to pH<2	6 months	N	STL, Also in field by ARCADIS
CAHs	8260	ug/L	VOA vials, no headspace HCl to pH<2; Cool to 4 °C	14 days	Y	STL
Hydrogen	RSK-196	nM/L	Special; see text Re: dissolved gas sampling	28 days	N	Vaportech
Bromide	300.0	mg/l	250 ml plastic or glass unpreserved	28 days	Y	STL

Table 3-6 Soil Analytical Parameters

Parameter	Analytical Method	Concentration Units Reported In	Container & Preservative Requirements	Hold Time	Parameter Included also In Abbreviated Monitoring Events?	Location of test
Total Organic Carbon (TOC)	9060	mg/kg	None specified	28 days	Y	STL
CAHs	8260	ug/kg	4 oz Glass with teflon lined septa; store @ 4 °C	14 days	Y	STL
Grain Size	ASTM D-422	% passing	500 mL wide mouth glass or plastic (purchased by field crew)	None	Y	ECS

Table 3-7 Summary of Well Construction Data, Site 35, Vandenberg Air Force Base

Well ID	Date Constructed	Drilling Contractor	Consultant	Well Diameter (inches)	Screen Slot Size (inches)	Well Depth (ft bgs)	Screen Top (ft bgs)	Screen Bottom (ft bgs)	Sisquoc Fm. (Shale) Depth (ft bgs)	Northing	Easting	Grade Elevation (ft amsl)	Top of the casing Elevation (ft amsl)	Well Depth Elevation (ft amsl)	Screen Top Elevation (ft amsl)	Screen Bottom Elevation (ft amsl)	Bedrock Elevation (ft amsl)	Depth to Water (11/14/00) (ft btoc)	Ground Water Elevation (11/14/00) (ft amsl)
35-I-1	10/11/00	West Hazmat	AG&M	2	0.020	45.00	32.00	42.00	45.00	2131300.198	5792513.814	408.8	410.96	363.80	376.80	366.80	363.80	13.71	397.25
35-I-2	8/8/00	S/G Testing	AG&M	2	0.020	44.50	32.50	42.50	43.00	2131320.549	5792510.118	409.9	412.45	365.40	377.40	367.40	366.90	15.27	397.18
35-I-3	10/12/00	West Hazmat	AG&M	2	0.020	45.50	32.00	42.00	44.00	2131342.703	5792505.702	410.7	413.14	365.20	378.70	368.70	366.70	16.28	396.86
35-P-1	9/16/00	SCAPS	AG&M	0.75	0.020	37.50	27.50	37.50	37.50	2131326.950	5792502.989	409.8	412.45	372.30	382.30	372.30	372.30	15.55	396.90
35-P-2	9/15/00	SCAPS	AG&M	0.75	0.020	38.30	28.30	38.30	38.30	2131330.969	5792497.144	409.8	412.16	371.50	381.50	371.50	371.50	15.48	396.68
35-P-3	9/16/00	SCAPS	AG&M	0.75	0.020	18.40	8.40	18.40	NA	2131328.789	5792511.635	410.2	412.59	391.80	401.80	391.80	NA	13.99	398.60
35-P-3A	10/12/00	West Hazmat	AG&M	2	0.020	45.50	32.00	42.00	43.00	2131332.443	5792511.155	410.4	412.74	364.90	378.40	368.40	367.40	15.83	396.91
35-MW-7	2/11/98	West Hazmat	TetraTech	4	0.010	46.50	32.30	42.30	41.00	2131310.500	5792486.383	408.0	410.54	361.50	375.70	365.70	367.00	14.27	396.27
35-MW-11	8/8/00	S/G Testing	AG&M	2	0.020	44.50	32.50	42.50	42.00	2131319.264	5792499.952	409.1	411.83	364.60	376.60	366.60	367.10	15.00	396.83
35-MW-12	9/15/00	SCAPS	AG&M	0.75	0.020	41.70	31.70	41.70	40.00	2131276.505	5792498.874	406.9	409.57	365.20	375.20	365.20	366.90	13.28	396.29
35-MW-13	9/15/00	SCAPS	AG&M	0.75	0.020	42.06	32.06	42.06	40.00	2131299.861	5792456.307	406.7	409.08	364.64	374.64	364.64	366.70	13.89	395.19
35-MW-14	8/9/00	S/G Testing	AG&M	2	0.020	44.50	32.50	42.50	42.00	2131326.200	5792532.364	410.7	413.22	366.20	378.20	368.20	368.70	15.74	397.48
35-MW-15	9/16/00	SCAPS	AG&M	0.75	0.020	42.66	32.66	42.66	40.00	2131301.296	5792527.910	409.8	412.37	367.14	377.14	367.14	369.80	14.97	397.40
35-MW-16	9/15/00	SCAPS	AG&M	0.75	0.020	41.70	31.70	41.70	40.00	2131293.621	5792492.009	407.2	409.92	365.50	375.50	365.50	367.20	13.80	396.12
35-MW-17	9/13/00	SCAPS	AG&M	0.75	0.010	41.00	31.00	41.00	40.80	2131324.147	5792481.599	408.4	410.93	367.40	377.40	367.40	367.60	14.78	396.15
35-MW-18	9/13/00	SCAPS	AG&M	0.75	0.010	41.00	31.00	41.00	41.00	2131335.869	5792476.707	408.8	411.66	367.80	377.80	367.80	367.80	15.44	396.22
35-MW-19	9/13/00	SCAPS	AG&M	0.75	0.010	20.00	10.00	20.00	NA	2131284.733	5792396.761	403.0	405.95	383.00	393.00	383.00	NA	15.43	390.52
35-MW-19A	10/11/00	West Hazmat	AG&M	2	0.020	45.00	32.00	42.00	39.00	2131289.231	5792393.473	403.0	405.38	358.00	371.00	361.00	364.00	12.28	393.10
35-MW-20	8/9/00	S/G Testing	AG&M	2	0.020	44.50	32.50	42.50	42.00	2131316.269	5792506.102	409.4	411.82	364.90	376.90	366.90	367.40	14.82	397.00
35-H-A*	9/18/00	SCAPS	AG&M	0.75	0.020	48.00	38.00	48.00	NR	2131511.031	5792727.887	412.1	NA	364.14	374.14	364.14	NA	NA	NA
35-H-1B*	9/18/00	SCAPS	AG&M	0.75	0.020	41.60	31.60	41.60	NR	2131364.715	5792776.580	420.0	NA	378.37	388.37	378.37	NA	NA	NA
35-H-1C*	9/18/00	SCAPS	AG&M	0.75	0.020	41.60	31.60	41.60	NR	2131294.918	5792806.573	420.2	NA	378.59	388.59	378.59	NA	NA	NA
35-H-2B*	9/18/00	SCAPS	AG&M	0.75	0.020	40.20	30.20	40.20	NR	2131125.310	5792606.512	409.2	NA	368.99	378.99	368.99	NA	NA	NA
35-H-2C*	9/18/00	SCAPS	AG&M	0.75	0.020	41.80	31.80	41.80	NR	2131038.456	5792668.997	409.1	NA	367.27	377.27	367.27	NA	NA	NA

Notes:

ft bgs - Feet below ground surface

ft btoc - Feet below top of casing

ft amsl - Feet above mean sea level

NA - Not applicable

NR - Not recorded

* Temporary well - abandoned September 19, 2000

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Table 3-8 History Log of Demonstration

Week	Dates (from - to)		Event
1	2/19/2001	2/25/2001	Initial injection, pre- and post-Br-/TOC monitoring 2-22-01
2	2/26/2001	3/4/2001	Injection #2 3-2-01
3	3/5/2001	3/11/2001	Process monitoring #1 w/TOC, Br-, injection #3 3-8-01
4	3/12/2001	3/18/2001	
5	3/19/2001	3/25/2001	Process monitoring #2 w/TOC, Br- 3-22-01
6	3/26/2001	4/1/2001	
7	4/2/2001	4/8/2001	Injection #4 into I-2 only #1, process monitoring #3 w/TOC, Br- 4-5-01
8	4/9/2001	4/15/2001	
9	4/16/2001	4/22/2001	
10	4/23/2001	4/29/2001	Redevelopment of wells I1 and I3 along with TOC and Br monitoring of the redevelopment water,
11	4/30/2001	5/6/2001	
12	5/7/2001	5/13/2001	Injection #6 into I-1 and I-2 (#1), process monitoring #4 w/TOC and Br 5-9-01.
13	5/14/2001	5/20/2001	
14	5/21/2001	5/27/2001	
15	5/28/2001	6/3/2001	6/1/01 Sample Br and TOC in I-3 only, then Injected # 7in I-1 and I-2 only (#2)
16	6/4/2001	6/10/2001	
17	6/11/2001	6/17/2001	
18	6/18/2001	6/24/2001	6/18/01 Process Monitoring #5 in Numerous Wells, Injection #8 in I-1 and I-2 only (#3)
19	6/25/2001	7/1/2001	
20	7/2/2001	7/8/2001	
21	7/9/2001	7/15/2001	Process monitoring #6 primarily on injection wells (#1) 7-10-01.
22	7/16/2001	7/22/2001	
23	7/23/2001	7/29/2001	7-26-01 Molasses injection #9 into I-2 only (#3), water-only injection #1 into wells I-1 and I-3 .
24	7/30/2001	8/5/2001	8-2-01 Abbreviated monitoring #1.
25	8/6/2001	8/12/2001	
26	8/13/2001	8/19/2001	8-14-01 Molasses injection #10 into I-1 and I-2 only (#4). Process monitoring #7 primarily on injection wells (#2).
27	8/20/2001	8/26/2001	
28	8/27/2001	9/2/2001	
29	9/3/2001	9/9/2001	9-5-01 Molasses injection #11 into I-2 and I-3 (50 gallons only into I-3).
30	9/10/2001	9/16/2001	
31	9/17/2001	9/23/2001	
32	9/24/2001	9/30/2001	
33	10/1/2001	10/7/2001	10-3-01 Injection #12 into I-2 only (#4). Process monitoring #8.
34	10/8/2001	10/14/2001	
35	10/15/2001	10/21/2001	
36	10/22/2001	10/28/2001	10-24-01 Abbreviated Monitoring #2, Water only injection into I-1, molasses injection #13 into I-2 only (#5)
37	10/29/2001	11/4/2001	
38	11/5/2001	11/11/2001	
39	11/12/2001	11/18/2001	11-16-01 Injection #14 into I-1 only (#1). Process monitoring #9 on injection wells only (#3).
40	11/19/2001	11/25/2001	
41	11/26/2001	12/2/2001	
42	12/3/2001	12/9/2001	
43	12/10/2001	12/16/2001	12-11-01 Injection #15 into I-2 only (#6) with no water push. Process monitoring #10 on injection wells only (#4).
44	12/17/2001	12/23/2001	
45	12/24/2001	12/30/2001	
46	12/31/2001	1/6/2002	
47	1/7/2002	1/13/2002	1/8/02 Injection event #16: full injection into I-2, half injections into I-1 and I-3. Process monitoring #11 on injection wells only (#5).
48	1/14/2002	1/20/2002	
49	1/21/2002	1/27/2002	1/23/02 Injection event #17: full injection into I-2 only (#7). Abbreviated monitoring #3.
50	1/28/2002	2/3/2002	

Table 3-8 History Log of Demonstration - continued

Week	Dates (from - to)		Event
51	2/4/2002	2/10/2002	2/6/02 process monitoring #12 on injection wells (#6) and MW-20 only.
52	2/11/2002	2/17/2002	
53	2/18/2002	2/24/2002	2/20/02 Injection event #18: full injection into I-2 only (#8). Process monitoring #13 on injection wells (#7) and MW-20 only.
54	2/25/2002	3/3/2002	
55	3/4/2002	3/10/2002	3/7/02 process monitoring #14 on selected wells.
56	3/11/2002	3/17/2002	
57	3/18/2002	3/24/2002	3/21/02 Injection event #19: half injection into I-3, water push into I-1
58	3/25/2002	3/31/2002	
59	4/1/2002	4/7/2002	4/4/02 Injection event #20: half injection into 1-2; process monitoring #15 on selected wells.
60	4/8/2002	4/14/2002	
61	4/15/2002	4/21/2002	4/18/02 Injection event #21: half injection into I-1 and I-3; process monitoring #16; full midpoint monitoring.
62	4/22/2002	4/28/2002	
63	4/29/2002	5/5/2002	
64	5/6/2002	5/12/2002	5/8/02 pH measurement of Injection wells. All too low to inject.
65	5/13/2002	5/19/2002	
66	5/20/2002	5/26/2002	
66	5/27/2002	6/2/2002	5-29-02 Injection event #22: full injection into I-2 and half injection into I-3; process monitoring #17 on key wells.
67	6/3/2002	6/9/2002	
68	6/10/2002	6/16/2002	
69	6/17/2002	6/23/2002	
70	6/24/2002	6/30/2002	6-26-02 Injection event #23: half injection into I-2. Process monitoring #18 on key wells.
71	7/1/2002	7/7/2002	
72	7/8/2002	7/14/2002	
73	7/15/2002	7/21/2002	7-19-02 Process monitoring #19 on injection wells only (#8). pHs too low to inject.
74	7/22/2002	7/28/2002	
75	7/29/2002	8/4/2002	
76	8/5/2002	8/11/2002	
77	8/12/2002	8/18/2002	
78	8/19/2002	8/25/2002	
79	8/26/2002	9/1/2002	8/29/2002 Process monitoring #20, Injection event #24: half injection into all wells.
80	9/2/2002	9/8/2002	
81	9/9/2002	9/15/2002	
82	9/16/2002	9/22/2002	
83	9/23/2002	9/29/2002	
84	9/30/2002	10/6/2002	10/4/02 Process monitoring #21, TOC/Br key wells. Water push on I-3 only.
85	10/7/2002	10/13/2002	
86	10/14/2002	10/20/2002	
87	10/21/2002	10/27/2002	10/24-25/02 Abbreviated monitoring #4, injection #25 into all wells with buffer.
88	10/28/2002	11/3/2002	
89	11/4/2002	11/10/2002	11/7/2002 Injection event #26: double injection with buffer into I-1 and I-2; water/buffer push only into I-3. Process monitoring #22.
90	11/11/2002	11/17/2002	
91	11/18/2002	11/24/2002	
92	11/25/2002	12/1/2002	
93	12/2/2002	12/8/2002	12/3/02 Injection event #27: double injection with buffer attempted into all wells; difficult injection into I-1, so reallocated 60 gal to I-2. PM#23
94	12/9/2002	12/15/2002	
95	12/16/2002	12/22/2002	
96	12/23/2002	12/29/2002	12/26/02 Injection event #28: full injection with water/buffer push into all wells. PM#24
97	12/30/2002	1/5/2003	
98	1/6/2003	1/12/2003	
99	1/13/2003	1/19/2003	1/15/03 Injection event #29: double injection with buffer into all wells. PM#25
100	1/20/2003	1/26/2003	

Table 3-8 History Log of Demonstration - continued

Week	Dates (from - to)		Event
101	1/27/2003	2/2/2003	
102	2/3/2003	2/9/2003	2-5-03 Process monitoring #26 on most wells. 2-6-03 Aborted injection due to faulty pump.
103	2/10/2003	2/16/2003	2-14-03 PM on injection wells, double injection with buffer into wells 1 & 3, single injection w/buffer and water push into well 2. Injection event #30.
104	2/17/2003	2/23/2003	
105	2/24/2003	3/2/2003	
106	3/3/2003	3/9/2003	
107	3/10/2003	3/16/2003	
108	3/17/2003	3/23/2003	
109	3/24/2003	3/30/2003	
110	3/31/2003	4/6/2003	4-3-03 double injection w/buffer into I-1 and I-3, single injection with buffer into I-2, PM on injection wells. Injection event #31.
111	4/7/2003	4/13/2003	
112	4/14/2003	4/20/2003	
113	4/21/2003	4/27/2003	
114	4/28/2003	5/4/2003	
115	5/5/2003	5/11/2003	5-1 and 5-5-03 final round, full process monitoring.
116	5/12/2003	5/18/2003	
117	5/19/2003	5/25/2003	
118	5/26/2003	6/1/2003	
119	6/2/2003	6/8/2003	
120	6/9/2003	6/15/2003	
121	6/16/2003	6/22/2003	
122	6/23/2003	6/29/2003	
123	6/30/2003	7/6/2003	
124	7/7/2003	7/13/2003	
125	7/14/2003	7/20/2003	
126	7/21/2003	7/27/2003	7/22 and 7/23 EPA Ada samples six wells
127	7/28/2003	8/3/2003	

Table 4-1 Performance Criteria

Performance Criteria	Description	Primary or Secondary
Technology Evaluation	Gather information to use in a protocol for use of IRZ technology for CAHs at DoD facilities	Primary
Reduce Time to Remediate	Demonstrate the ability of ERD to remediate contaminants in the subsurface over a relatively short time period	Primary
Contaminant Reduction	Reduction of baseline levels of CAHs, primarily TCE and cis-1,2-DCE at Vandenberg AFB	Primary
	Enhancement of CAH degradation rates	Secondary
Prevent "Stalling"	Demonstrate that degradation of CAHs by ERD does not stall at undesirable by-products (cis-DCE and/or VC)	Primary
Geochemistry Manipulation	Demonstrate the ability of ERD to create the anaerobic and reducing environment where aerobic conditions prevail	Secondary
Contaminant Mobility	a. Evaluate the ability of ERD to desorb CAHs from aquifer materials	Secondary
	b. Evaluate the propensity of ERD to mobilize metals	Secondary
System Performance Optimization	Determine optimal strengths and frequency of reagent delivery for the site	Secondary
Hazardous Materials	Identify any hazardous materials introduced or generated by ERD technology	Secondary
Reliability	Identify potential problems that may cause system shutdowns	Secondary
Ease of Use	Describe the number of people, skill level(s) and safety training required to perform injections and monitoring	Secondary
Versatility	Describe whether ERD can be used for other applications and under other site conditions	Secondary
Maintenance	Identify operations and maintenance requirements and level of training required to implement O&M	Secondary
Scale-Up Constraints	Identify engineering constraints associated with scaling up an ERD system	Secondary

Table 4-2 Expected Performance and Performance Confirmation Methods

Performance Criteria	Expected Performance Metric (Pre-Demonstration)	Performance Confirmation Method	Actual (Post-Demonstration)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Technology Evaluation	Collection of extensive performance data	Body of data from 11 monitoring wells conforms to demonstration plan	Performance data collection plan was met with few exceptions
Prevent "Stalling"	Reduction of cis-DCE, VC after initial production, production of ethene	CAH and ethene data from wells in the reactive zone	Cis-DCE peaked and fell at some reactive zone wells; VC production began recently. Evidence of continuing ethene production
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Reduce Time to Remediate	1 to 5 years in typical full-scale applications	Evidence of contaminant reductions (% and rates) and ethene production	In the 2-year pilot, observed significant contaminant reductions and ethene production (see Sections 4.3.3.5 and 4.3.7.1), suggesting that remediation time of 5 years or less may be attainable, though a quantitative determination was not possible
Contaminant Reduction (%)	Total CAH concentrations reduced by at least 80% in 1 year	CAH data from 35-MW-16, 35-MW-7, 35-MW-20 and 35-MW-11, from baseline sampling through present	Total molar CAH reductions ranged from 12-66%, TCE reductions were 42-74% at end of active treatment (see Table 4-17d). Individual TCE reductions were ≥80% at specific wells in post-treatment period. Cis-DCE and VC generally increased indicating incomplete treatment. More rapid, complete treatment would require more intensive substrate delivery (see Section 4.3.7.1)

Performance Criteria	**Expected Performance Metric (Pre-Demonstration)**	**Performance Confirmation Method**	**Actual (Post-Demonstration)**
SECONDARY CRITERIA (Performance Objectives) (Qualitative)			
System Performance Optimization	Injection Wells: pH > 4.0 DO < 1.0 mg/L -400 mV < ORP < -250 mV 500 mg/L < TOC < 9000 mg/L Sp. Cond. 10x increase Mon. Wells: pH > 5.0 DO < 1.0 mg/L ORP < -200 mV TOC > 50 mg/L Sp. Cond. 20-50% increase	Performance monitoring data evaluated before each injection event to determine optimal strengths and frequency of reagent delivery for the site	An anaerobic environment was created within the reactive zone; low buffering capacity of aquifer caused variability in performance criteria that was mitigated following the addition of a buffer (see Section 4.3.7.2). Strength and frequency of injection discussed in Sections 4.3.2.1 and 4.3.7.2
Reliability	No significant reliability issues anticipated	Field records	Met performance metric; minor corrective actions needed for equipment maintenance and optimization of injection well performance (Section 3.5.1)
Ease of Use	Field implementation (substrate delivery) requires an environmental technician with 40-hr HAZWOPER training, and office support from degreed scientists or engineers	Experience from demonstration operation and other site applications	Met performance metric for substrate delivery. Geologist required for permanent well installations.
Versatility	ERD can be used for other applications (e.g., metals, perchlorate) and under variable site conditions	Experience from other site applications	Versatility discussed in Sections 1.1, 2.1.1

Performance Criteria	Expected Performance Metric (Pre-Demonstration)	Performance Confirmation Method	Actual (Post-Demonstration)
Maintenance	Maintenance limited to occasional well development, normal equip. maintenance by technician	Field records	Met performance metric; maintenance issues discussed in Section 3.5.1
Scale-Up Constraints	Primary scale-up issues anticipated to be efficacy of manual batch injection mode and area of influence determination	Experience from demonstration operation and other site applications	Scale-up hasn't occurred at this site, but batch injection successful, area of influence determined in Section 4.3.6.1. Scale-up issues and cost implications are discussed in Section 6.3 and in Section 5.7 of the protocol document (Suthersan, 2002)
SECONDARY CRITERIA (Performance Objectives) (Quantitative)			
Geochemistry Manipulation	Monitoring well: DO to <1 mg/L ORP <200 mV	Performance monitoring data evaluated before each injection event	A sufficient anaerobic environment was created within the reactive zone, though substrate delivery was heterogeneous and thus the shape of the downgradient reactive zone was irregular (see Section 4.3.7.2)
Geochemistry Manipulation	Monitoring well: TOC >50 mg/l	Performance monitoring data evaluated before each injection event	Sustained TOC >50 was observed at 35-MW-20 and 35-MW-16. Such TOC levels were briefly observed but not sustained at 35-MW-11 and 35-MW-7.
Contaminant Mobility	Presence of "spike" in concentration after initial injections	CAH data for wells 35-MW-7, 35-MW-11, 35-MW-16 and 35-MW-20	In some wells, modest spikes observed in TCE concentrations after active treatment began (see Section 4.3.7.2)
Contaminant Reduction (Rate)	Calculate k	k determined from long-term pre-demonstration data at 35-MW-7 and from data trends at 35-MW-7, 35-MW-11, 35-MW-16 and 35-MW-20	Calculated k (see Section 4.3.3.5)

Performance Criteria	**Expected Performance Metric (Pre-Demonstration)**	**Performance Confirmation Method**	**Actual (Post-Demonstration)**
Hazardous Materials	Potentially hazardous materials limited to soil cuttings from well drilling and purge water	Field records, analyses of soil cuttings and purge water	Purge water treated in a licensed treatment system, cuttings from soil borings characterized and disposed of off-site

Table 4-3 Results of Soil Analyses

Parameter	**VAN-SS-I2-25/35**	**VAN-SS-I2-25/35 Dup**	**VAN-SS-MW-11-25/35**	**VAN-SS-MW-11-20-40**	**VAN-SS-I2-20-40**	**VAN-SS-I2-20-40 Dup**	**Laboratory**
VOCs (ug/Kg)							
Acetone	6.7 JB	8.9 JB	9.8 JB	NA	NA	NA	Severn Trent
Trichloroethene	61	40	13	NA	NA	NA	Severn Trent
Total Organic Carbon (mg/Kg)	NA	NA	<2000	NA	<2000	<2000	Severn Trent
Moisture (%)	13.4	12.9	16.6	NA	13.8	13.4	Severn Trent
Moisture (%)	NA	NA	NA	12.9	16.2	13.0	ECS Ltd.
Soil Description	NA	NA	NA	Light yellowish brown poorly graded sand with silt	Light yellowish brown silty sand	Light yellowish brown silty sand	ECS Ltd.
USCS Group	NA	NA	NA	SP-SM	SM	SM	ECS Ltd.

Notes:

Samples collected August 2000 from well boring for 35-MW-11

B - Detected in blank

J - Estimated result - less than reporting limit

Table 4-4 Groundwater Results for Full Baseline Monitoring Event, November 14-17, 2000

Analyte	Units	35-MW-14	35-MW-15	35-MW-20	35-MW-11	35-MW-18	35-MW-17	35-MW-7	35-MW-16	35-MW-12	35-MW-13	35-MW-19A
Volatile Organic Compounds												
1,1-Dichloroethane	ug/L	<10	<33	<10	<10	<8	<50	<20	<67	<67	<29	<100
1,1-Dichloroethene	ug/L	<10	<33	<10	<10	<8	<50	<20	<67	<67	<29	<100
cis-1,2-Dichloroethene	ug/L	14	39	9.5	9.6J	6.2J	31J	11J	31J	39J	16J	38J
trans-1,2-Dichloroethene	ug/L	<5	<17	<5	<5	<4	<25	<10	<33	<33	<14	<50
Trichloroethene	ug/L	450	1500	410	450	170	1400	600	1600	1900	720	1500
Vinyl Chloride	ug/L	<20	<67	<20	<20	<16	<100	<40	<130	<130	<57	<200
Dissolved Gases												
Carbon Dioxide	mg/L	44.2	73.5	65.4	55.8	92.1	79.8	76.3	78.1	52.5	71.9	60.4
Ethane	ug/L	0.02	0.26	0.03	0.03	0.44	0.77	<0.01	0.42	2.89	0.83	0.03
Ethene	ug/L	0.05	0.27	0.04	0.09	0.72	1.18	<0.01	0.49	6.34	1.27	0.1
Hydrogen	nM/L	0.9	2.5	0.8	0.8	1.7	1.4	1.1	4.1	2.1	6.5	1
Methane	ug/L	0.3	0.6	<0.2	<0.2	0.8	1.6	<0.2	0.8	6	1.3	<0.2
Nitrogen	mg/L	12.3	11.8	11.6	12	12.1	11.3	11.3	12.2	11.5	11.5	10.9
Dissolved Oxygen - Field	mg/L	4.8	2.78	3.24	2.79	2.5	1.94	3.79	2.75	2.15	3.6	1.68
Oxygen - Lab	mg/L	2.41	1.41	2.22	2.09	1.45	1.39	1.88	1.71	2.47	2	1.48
Field Parameters												
pH	su	6.61	6.22	6.25	6.38	6.17	6.22	6.25	6.2	6.35	6.23	6.23
Oxidation Reduction Potential	mV	418	429	439	439	411	337	432	378	351	370	443
Conductance	µS/cm or µmhos/cm	1364	1416	1401	1429	1648	1473	1505	1435	1348	1473	1465
Inorganics and Other Lab Parameters												
Alkalinity	mg/L	143	101	105	126	101	113	101	104	95.8	101	108
Ammonia as N	mg/L	<0.1	0.13	<0.1	<0.1	0.19	0.12	0.13	0.2	0.37	0.1	0.087
Bromide	mg/L	0.81	1.2	0.83	0.83	0.57	0.71	0.59	0.7	0.7	0.66	1.1
Chloride	mg/L	160	192	150	147	147	182	164	188	182	178	189
Iron, Total - Field	mg/L	0	0	0	0	0	0	0	0	0	0	0
Iron, Total - Lab	mg/L	0.21	13	0.13	0.11	8.3	39	0.018	29	85.3	100	0.29
Iron, Soluble - Field	mg/L	0	0	0	0	0	0	0	0	0	0	0
Iron, Dissolved - Lab	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	0.038	<0.1	<0.1	0.024	0.027	<0.1
Manganese, Total - Field	mg/L	0	0	0	0	0	0	0	0	0	0	0
Manganese, Total - Lab	mg/L	0.0081	0.025	0.002	0.0056	0.021	0.11	0.0027	0.041	0.11	0.15	0.025
Manganese, Dissolved - Lab	mg/L	0.0072	0.0029	0.0015	0.0055	0.0096	0.045	0.002	0.008	0.015	0.012	0.021
Nitrate	mg/L	6.4	10.3	6.2	6	4.7	7.8	6.8	11.3	10.3	7.7	9.5
Nitrite	mg/L	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	<0.5	<0.5	2.6	<0.5	<0.5
Sulfate - Lab	mg/L	252	239	292	279	306	242	290	229	183	260	250
Sulfide - Field	mg/L	0	0	0	0	0	0	0	0	0	0	0
Dissolved Organic Carbon	mg/L	5.6	7.3	5.1	6.9	13.9	4.6	5.2	16.9	14.1	5.1	7.3
Total Organic Carbon	mg/L	4.3	4.1	4.5	4.7	4.8	4.2	4.6	4.1	3.7	5.8	4.1
Biochemical Oxygen Demand	mg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Chemical Oxygen Demand	mg/L	23.8	28.1	18.6	20.9	47.9	20.2	20.9	62.4	52.8	21.5	28.1

Notes:
Analytical methods detailed in ARCADIS (2000)
J - Estimated
NM - ot measured
NS - Not sampled
< - Indicates constituent was not detected at the reporting limit indicated

Table 4-5 Groundwater Results for Full Midpoint Monitoring Event, April 16-18, 2002

Analyte	Units	35-MW-14	35-MW-15	35-MW-20	35-MW-11	35-MW-18	35-MW-17	35-MW-7	35-MW-16	35-MW-12	35-MW-13	35-MW-19A
Volatile Organic Compounds												
1,1-Dichloroethane	ug/L	<1	<4	<5	<10	<1	<4	<10	<50	<40	<10	NS
1,1-Dichloroethene	ug/L	<1	<4	<5	0.49J	<1	<4	<2	<4	<5	<2	NS
cis-1,2-Dichloroethene	ug/L	1.5	21	72	320	7.1	18	10	21	33J	8.9	NS
trans-1,2-Dichloroethene	ug/L	<0.5	<2	<2.5	0.59	<0.5	<2	<1	<2	36	<1	NS
Trichloroethene	ug/L	50J	860J	230J	19J	370J	840J	440J	870J	1600J	420J	NS
Vinyl Chloride	ug/L	<2	<8	<10	<2	<2	<8	<4	<8	<10	<4	NS
Dissolved Gases												
Carbon Dioxide	mg/L	40.6	71.5	816.0E	426.6E	98.3	75.2	237.4	636.7E	68.6	118.9	NS
Ethane	ug/L	<0.01	<0.01	0.98	0.30	0.02	0.04	0.47	0.13	0.03	0.10	NS
Ethene	ug/L	<0.01	0.01	0.08	0.04	0.05	0.07	0.04	0.18	0.06	0.03	NS
Hydrogen	nM/L	1.7	1.7	50	2.6	2	2.1	2	15.3	1.8	1.8	NS
Methane	ug/L	<0.2	<0.2	1086	4977	0.7	1.1	7608	405	32.1	2375	NS
Nitrogen	mg/L	7.8	9.8	1.0	0.9	12.5	7.1	3.2	5.4	9.0	9.6	NS
Dissolved Oxygen - Field	mg/L	5.34	1.59	0.23	0.17	1.91	1.43	0.11	0.18	1.94	0.26	NS
Oxygen - Lab	mg/L	2.21	1.43	<0.15	<0.15	0.35	0.96	0.16	0.20	1.58	0.19	NS
Field Parameters												
pH	su	6	5.68	4.34	5.73	5.7	5.67	5.89	4.74	5.85	5.61	NS
Oxidation Reduction Potential	mV	191	195	-101	-164	-101	38	-203	-91	188	33	NS
Conductance	µS/cm or µmhos/cm	1332	1654	2907	1762	1407	1728	1475	1658	1480	1708	NS
Inorganics and Other Lab Parameters												
Alkalinity	mg/L	137	117	283	544	146	115	328	309	102	134	NS
Ammonia as N	mg/L	0.076	0.04	0.31	26.5	0.052	0.047	0.067	0.26	0.032	0.038	NS
Bromide	mg/L	0.54	0.8	18.2	5.8	4.8	0.76	1.8	6.5	0.78	0.85	NS
Chloride	mg/L	130	169	248	172	133	160	156	207	179	158	NS
Iron, Total - Field	mg/L	0	0	9	4	2.8	0	2	8.2	0	0	NS
Iron, Total - Lab	mg/L	1.1	0.25	143	53.2	3.3	1.1	5.8	13	1.5	1.5	NS
Iron, Soluble - Field	mg/L	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NS
Iron, Dissolved - Lab	mg/L	<0.1	0.24	135	48.5	2.2	0.16	1.6	11.6	<0.1	0.065	NS
Manganese, Total - Field	mg/L	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NS
Manganese, Total - Lab	mg/L	0.0036	0.0003	0.73	1.1	0.16	0.0055	0.4	0.13	0.006	0.011	NS
Manganese, Dissolved - Lab	mg/L	0.0013J	0.0031J	0.78	0.99J	0.17J	0.0064J	0.36J	0.11J	0.0041J	0.015J	NS
Nitrate	mg/L	5.1	9.3	2.4	<0.5	9.3	8.5	0.2	0.2	11.7	7	NS
Nitrite	mg/L	<0.5	<0.5	<2.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NS
Sulfate - Lab	mg/L	322	382	147	12.1	303	409	145	6.5	247	418	NS
Sulfide - Field	mg/L	0	0	6	5	5	0	8	6	0	0	NS
Dissolved Organic Carbon	mg/L	4.4J	4.4J	2000	185	21.2	4.6J	18.1J	606J	4.3J	11.9J	NS
Total Organic Carbon	mg/L	4.5	4.4	2110	182	18.1	4.8	18.2	594	4.2	11.5	NS
Biochemical Oxygen Demand	mg/L	<2	<2	4480	222	23.9	<2	27.3	822	<2	11	NS
Chemical Oxygen Demand	mg/L	8.1	10.4	5750	446	46.2	9.1	63.8	1520	15.3	20.8	NS

Notes:
Analytical methods detailed in ARCADIS (2000)
J - Estimated
NM - ot measured
NS - Not sampled
< - Indicates constituent was not detected at the reporting limit indicated

Table 4-6 Groundwater Results for Full Final Monitoring Event, May 1-5, 2003

Analyte	Units	35-MW-14	35-MW-15	35-MW-20	35-MW-11	35-MW-18	35-MW-17	35-MW-7	35-MW-16	35-MW-12	35-MW-13	35-MW-19A
Volatile Organic Compounds												
1,1-Dichloroethane	ug/L	<1	<3.3	<2.5	<1	<3.3	NS	<1	<10	NS	<1	<2
1,1-Dichloroethene	ug/L	<1	<3.3	0.78J	0.8J	<3.3	NS	1.3	<10	NS	<1	0.8J
cis-1,2-Dichloroethene	ug/L	1.1	25	95	110	120	NS	59	450	NS	10	250
trans-1,2-Dichloroethene	ug/L	<0.5	0.61J	0.41J	0.5	1.7	NS	0.42J	<5	NS	0.16J	0.83J
Trichloroethene	ug/L	44	930	130	260	930	NS	260	410	NS	190	270
Vinyl Chloride	ug/L	<2	<6.7	11	0.28J	<6.7	NS	<2	26	NS	<2	<4
Dissolved Gases												
Carbon Dioxide	mg/L	64.6	85.3	539.7E	546.3E	106.3	NS	272.1	732.8E	NS	182.7	385.5
Ethane	ug/L	<0.01	<0.01	0.18	<0.01	0.05	NS	<0.01	0.08	NS	<0.01	<0.01
Ethene	ug/L	<0.01	<0.01	0.1	0.21	0.04	NS	0.01	0.77	NS	0.02	0.06
Hydrogen	nM/L	1.4	1.8	15.6	1.4	1.8	NS	1.6	3.2	NS	1.7	0.9
Methane	ug/L	11.3	5.8	2084.5	7698.5	1403.5	NS	7473.9	4969.6	NS	6434.1	10681.3
Nitrogen	mg/L	10.3	9.1	0.7	1.5	9.5	NS	3.9	1.2	NS	5.9	5.1
Dissolved Oxygen - Field	mg/L	5.03	1.48	0.24	0.22	0.42	0.48	0.28	0.19	1.27	0.24	0.23
Oxygen - Lab	mg/L	2.67	1.31	<0.15	0.19	<0.15	NS	0.26	<0.15	NS	0.98	<0.15
Acetylene	mg/L	<0.01	<0.01	<0.01	<0.01	0.02	NS	<0.01	0.03	NS	<0.01	0.02
Field Parameters												
pH	su	5.78	5.76	4.31	5.28	5.49	5.58	5.31	5.23	5.64	5.22	5.44
Oxidation Reduction Potential	mV	177	155	-98	-6	114	164	-54	-132	144	74	-158
Conductance	µS/cm or µmhos/cm	1514	1795	3423	1147	1939	2001	1879	1853	1579	2083	1680
Inorganics and Other Lab Parameters												
Alkalinity	mg/L	140	110	650	290	140	NS	230	510	NS	110	320
Ammonia as N	mg/L	<0.5	<0.5	13	0.2	0.039	NS	0.19	0.14	NS	<0.5	0.12
Bromide	mg/L	0.64	0.88	25	1.8	0.82	0.99	2	15	0.86	0.88	2.4
Chloride	mg/L	130	170J	280	110	150	NS	160	220	NS	150J	170J
Iron, Total - Field	mg/L	0	0	NM	6	0.3	0	2.4	4.4	0.2	0.2	4.8
Iron, Total - Lab	mg/L	0.39	0.087	83	12	0.43	NS	17	17	NS	0.059	5.9
Iron, Soluble - Field	mg/L	0.1	0.8	NM	10	0.5	0.1	10	10	0.2	0.2	6
Iron, Dissolved - Lab	mg/L	<0.1	<0.1	84	11	0.21	NS	18	18	NS	0.03	5.9
Manganese, Dissolved - Field	mg/L	0	0	NM	0	0.4	0	0.2	0.2	0	0	6
Manganese, Total - Lab	mg/L	0.0029	0.003	0.47	0.16	0.24	NS	0.56	0.18	NS	0.003	0.17
Manganese, Dissolved - Lab	mg/L	0.0015	0.00091J	0.45	0.15	0.23J	NS	0.53	0.16	NS	0.004	0.16J
Nitrate	mg/L	5.5	10	1.4	0.25	7.2	NS	<0.5	2.7	NS	8.6	4.9
Nitrite	mg/L	<0.5	<0.5	<1	<0.5	<0.5	NS	<0.5	<0.5	NS	<0.5	<0.5
Sulfate - Lab	mg/L	360	420J	31	150	520J	NS	400	9.5	NS	550J	210J
Sulfide - Field	mg/L	0	0	NM	0.8	0	0	5	7	0	0	6
Dissolved Organic Carbon	mg/L	5.1	6.5	1600	9.4	5	NS	14	460	NS	6.6	15
Total Organic Carbon	mg/L	3.6	4.1J	1700	17J	4.4J	4.5	13	430J	3.8	4.7J	14J
Biochemical Oxygen Demand	mg/L	0.5	0.5	3000	<10	0.51	NS	9	69	NS	1.8	8.6
Chemical Oxygen Demand	mg/L	20	30	22	11	19	NS	40	910	NS	3.1	5.2
Total Dissolved Solids	mg/L	880J	1100	3300J	690	1200	NS	1200J	1300	NS	1200	980

Notes:

Analytical methods detailed in ARCADIS (2000)

J - Estimated

NM - ot measured

NS - Not sampled

< - Indicates constituent was not detected at the reporting limit indicated

Table 4-7 Results of Groundwater Hydrosparge Analysis

Volatile Organic Compounds (ug/L)	**35-MW-7** NR	**35-MW-12** 41.7 ft	**35-MW-13** 42.1 ft	**35-MW-15** 42.7 ft	**35-MW-16** 41.7 ft	**35-MW-17** 41.0 ft	**35-MW-18** 41.0 ft	**35-MW-19** 20.0 ft
Trichloroethene (TCE)	2500	4000	1200	2300	2300	3500	230	500
Dichloroethene (DCE)	ND	ND	ND	ND	ND	ND	8.7	ND
Tetrachloroethene (PCE)	ND	ND	ND	ND	ND	ND	6.6	ND
Carbon Tetrachloride (CT)	ND	ND	ND	ND	ND	ND	4.5	ND
Aromatics	ND	ND	ND	ND	ND	ND	5.7	ND

Volatile Organic Compounds (ug/L)	**35-P-1** 37.5 ft	**35-P-2** 38.3 ft	**35-P-3** 18.6 ft	**35-H-A** 48.0 ft	**35-H-1B** 41.6 ft	**35-H-1C** 41.6 ft	**35-H-2B** 40.2 ft	**35-H-2C** 41.8 ft
Trichloroethene (TCE)	250	240	ND	3.6	1000	5000	<1	<1
Dichloroethene (DCE)	ND	3.2	ND	ND	10	ND	ND	ND
Tetrachloroethene (PCE)	ND	ND	ND	ND	ND	ND	ND	ND
Carbon Tetrachloride (CT)	ND	ND	ND	ND	ND	ND	ND	ND
Aromatics	ND	ND	ND	ND	ND	ND	ND	ND

Notes:
Samples collected August 2000 from well boring for 35-MW-11
VOC rsults reported in ug/L

B - Detected in blank
J - Estimated result - less than reporting limit
NR - Not reported
ND - Not detected

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Table 4-8 Summary of Metals Data, Full Final Monitoring Event, May 1-5, 2003

Dissolved																							
Analyte (mg/L)	**MCL or Other Std.**	**35-MW-14**		**35-MW-15**		**35-MW-20**		**35-MW-11**		**35-MW-18**		**35-MW-17**		**35-MW-7**		**35-MW-16**		**35-MW-12**		**35-MW-13**		**35-MW-19A**	
Aluminum	36 (PRG)	0.1	U	0.1	U	1.4		0.038	B	0.1	U	NS		0.1	U	0.024	B	NS		0.1	U	0.024	B
Antimony	0.006	0.01	U	0.01	U	0.0052	B	0.01	U	0.0037	B	NS		0.01	U	0.01	U	NS		0.01	U	0.01	U
Arsenic	0.01 (effective 1/06)	0.005	U	0.015	U	0.036		0.006	B	0.015	U	NS		0.015	U	0.029		NS		0.015	U	0.01	U
Barium	2	0.068		0.12	J	0.31		0.031	J	0.11	J	NS		0.08		0.17	J	NS		0.14	J	0.04	J
Beryllium	0.004	0.002	U	0.005	U	0.005	U	0.005	U	0.005	U	NS		0.005	U	0.005	U	NS		0.005	U	0.005	U
Cadmium	0.005	0.005	U	0.005	U	0.005	U	0.005	U	0.005	U	NS		0.005	U	0.005	U	NS		0.005	U	0.005	U
Calcium	---	30		28	J	98		18	J	36	J	NS		30		40	J	NS		38	J	21	J
Chromium	0.1	0.01	U	0.01	U	0.049		0.01	U	0.01	U	NS		0.01	U	0.0072	B	NS		0.01	U	0.01	U
Cobalt	0.73 (PRG)	0.01	U	0.01	U	0.01		0.01	U	0.01	U	NS		0.01	U	0.0018	B	NS		0.01	U	0.01	U
Copper	1.3	0.0027	B	0.0019	B	0.0018	B	0.01	U	0.0019	B	NS		0.0016	B	0.0016	B	NS		0.0017	B	0.001	B
Iron	11 (PRG)	0.1	U	0.1	U	84		11		0.21		NS		18		18		NS		0.03	B	5.9	
Lead	0.015	0.003	U	0.003	U	0.003	U	0.003	U	0.003	U	NS		0.003	U	0.003	U	NS		0.003	U	0.003	U
Magnesium	---	31		28		82		18		38		NS		33		42		NS		38		20	
Manganese	0.88 (PRG)	0.0015	B	0.00091	B J	0.45		0.15	J	0.23	J	NS		0.53		0.16	J	NS		0.004	B J	0.16	J
Mercury	0.002	0.0002	U	0.000061	B J	0.00012	B	0.000045	B J	0.000049	B J	NS		0.0002	U	0.00014	B J	NS		0.000049	B J	0.000059	B J
Nickel	.73 (PRG)	0.0065	B	0.0068	B	0.064		0.04	U	0.0084	B	NS		0.0069	B	0.028	B	NS		0.0088	B	0.0069	B
Potassium	---	1.3	B	1.4	B	220		2.9	B	1.4	B	NS		1.7	B	18		NS		1.6	B	1.4	B
Selenium	0.05	0.011		0.0062	B	0.012	B	0.015	U	0.0055	B	NS		0.015	U	0.015	U	NS		0.0084	B	0.015	U
Silver	0.18 (PRG)	0.01	U	0.01	U	0.00092	B	0.01	U	0.01	U	NS		0.01	U	0.01	U	NS		0.01	U	0.01	U
Sodium	---	240		290		470		190		290		NS		310		330		NS		300		270	
Thallium	0.002	0.01	U	0.01	U	0.01	U	0.01	U	0.01	U	NS		0.01	U	0.01	U	NS		0.01	U	0.01	U
Vanadium	0.26 (PRG)	0.0046	B	0.0034	B	0.081		0.0052	B	0.0026	B	NS		0.0054	B	0.016		NS		0.0027	B	0.0043	B
Zinc	11 (PRG)	0.05		0.02	U	0.027		0.02	U	0.02	U	NS		0.018	B	0.0082	B	NS		0.02	U	0.02	U

Total																							
Analyte (mg/L)	**MCL or Other Std.**	**35-MW-14**		**35-MW-15**		**35-MW-20**		**35-MW-11**		**35-MW-18**		**35-MW-17**		**35-MW-7**		**35-MW-16**		**35-MW-12**		**35-MW-13**		**35-MW-19A**	
Aluminum	36 (PRG)	0.34		0.25		1.6		0.048	B	0.1		NS		0.03	B	0.038	B	NS		0.078	B	0.044	B
Antimony	0.006	0.01	U	0.0047	B	0.01	U	0.01	U	0.01	U	NS		0.01	U	0.0041	B	NS		0.01	U	0.0037	B
Arsenic	0.01 (effective 1/06)	0.015	U	0.015	U	0.036		0.0057	B	0.015	U	NS		0.015	U	0.032		NS		0.015	U	0.015	U
Barium	2	0.067		0.12		0.33		0.03		0.11		NS		0.085		0.16		NS		0.14		0.039	
Beryllium	0.004	0.005	U	0.005	U	0.005	U	0.005	U	0.005	U	NS		0.005	U	0.00077	B	NS		0.005	U	0.005	U
Cadmium	0.005	0.00066	B	0.0014	B	0.005	U	0.005	U	0.005	U	NS		0.0048	B	0.005	U	NS		0.00065	B	0.005	U
Calcium	---	25		30		93		17		39		NS		28		39		NS		41		21	
Chromium	0.1	0.01	U	0.01	U	0.052		0.01	U	0.01	U	NS		0.0026	B	0.0073	B	NS		0.01	U	0.0021	B
Cobalt	0.73 (PRG)	0.01	U	0.0013	B J	0.01		0.00072	B J	0.0012	B J	NS		0.01	U	0.0038	B J	NS		0.01	U	0.00088	B J
Copper	1.3	0.0018	B	0.0012	B	0.0033	B	0.01	U	0.0014	B	NS		0.012		0.0044	B	NS		0.0014	B	0.0074	B
Iron	11 (PRG)	0.39		0.087	B	83		12		0.43		NS		17		17		NS		0.059	B	5.9	
Lead	0.015	0.003	U	0.003	U	0.003	U	0.003	U	0.003	U	NS		0.003	U	0.003	U	NS		0.003	U	0.003	U
Magnesium	---	29		30		82		19		41		NS		32		44		NS		41		22	
Manganese	0.88 (PRG)	0.0029	B	0.003	B	0.47		0.16		0.24		NS		0.56		0.18		NS		0.003	B	0.17	
Mercury	0.002	0.00005	B J	0.000028	B	0.00025	J	0.0002	U	0.0002	U	NS		0.000054	B J	0.00018	B	NS		0.0002	U	0.000018	B
Nickel	.73 (PRG)	0.0066	B	0.0089	B	0.07		0.0048	B	0.0092	B	NS		0.0053	B	0.032	B	NS		0.0095	B	0.0097	B
Potassium	---	0.83	B	1.6	B	220		3.3		1.8	B	NS		1.5	B	18		NS		1.8	B	1.2	B
Selenium	0.05	0.015	U	0.015	U	0.0063	B	0.015	U	0.015	U	NS		0.015	U	0.015	U	NS		0.015	U	0.015	U
Silver	0.18 (PRG)	0.00073	B	0.01	U	0.0012	B	0.01	U	0.01	U	NS		0.00085	B	0.01	U	NS		0.01	U	0.01	U
Sodium	---	230		320		460		200		320		NS		310		360		NS		330		290	
Thallium	0.002	0.01	U	0.01	U	0.01	U	0.01	U	0.01	U	NS		0.01	U	0.01	U	NS		0.01	U	0.01	U
Vanadium	0.26 (PRG)	0.0051	B	0.0043	B	0.089		0.0042	B	0.0045	B	NS		0.0052	B	0.017		NS		0.0035	B	0.0052	B
Zinc	11 (PRG)	0.018	B	0.0097	B	0.039		0.02	U	0.011	B	NS		0.033		0.02	U	NS		0.016	B	0.0096	B

Notes:

Samples collected May 1-5, 2003

Analytical methods - SW846 Methods 6010B and 7470

B - Detected in blank

J - Estimated

U - Undetected at the reporting limit listed

MCL - Federal Maximum Contaminant Level for drinking water

PRG - US EPA Region 9 Preliminary Remedial Goal for tap water (provided where no MCL exists)

NS - Not sampled

Shading indicates exceedance of listed standard

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Table 4-9 Bromide Tracer Data Summary

Well ID	11/15/00	03/08/01	03/22/01	04/05/01	05/09/01	06/18/01	07/10/01	08/02/01	08/13/01	10/03/01
35-I-1	NS	142	NS	113	26.5	4.2	114	NS	0.29	58.3
35-I-2	NS	52.9	NS	NS	4	4	6.5	NS	8.1	8.7
35-I-3	NS	142	NS	175	109	2.8	71.7	NS	12.9	61.4
35-MW-7	0.59	0.83	1.2	1.2	0.96	0.89	NS	3.1	NS	4.2
35-MW-11	0.83	0.57	1.6	1	0.76	0.6	NS	1.9	NS	NS
35-MW-12	0.7	NS	NS	NS	NS	0.64	NS	NS	NS	1.6
35-MW-13	0.66	NS	NS	NS	NS	NS	NS	NS	NS	NS
35-MW-14	0.81	0.5	1.2	NS	NS	NS	NS	0.27	NS	NS
35-MW-15	1.2	0.91	NS	NS	NS	NS	NS	NS	NS	NS
35-MW-16	0.7	NS	NS	NS	NS	82.2	8.1	35.4	NS	7.6
35-MW-17	0.71	NS	NS	NS	NS	NS	NS	NS	NS	0.1
35-MW-18	0.57	NS	NS	NS	NS	NS	NS	NS	NS	0.84
35-MW-19A	1.1	NS	NS	NS	NS	NS	NS	NS	NS	NS
35-MW-20	0.83	8.8	31	35.2	44.4	38.1	33	208	NS	3.9

Well ID	10/24/01	01/23/02	04/16/02	06/26/02	10/04/02	10/24/02	12/03/02	12/26/02	02/05/03	05/01/03
35-I-1	NS	NS	NS	NS	NS	NS	NS	NS	NS	160
35-I-2	NS	NS	NS	NS	NS	NS	NS	NS	NS	35
35-I-3	NS	NS	NS	NS	NS	NS	NS	NS	NS	120
35-MW-7	2.6	2.5	1.8	2	1.9	1.5	1.5	NS	2	2
35-MW-11	5.4	10	5.8	4.4	2	1.8	2.4	2.2	1.4	1.8
35-MW-12	NS	NS	0.78	NS	NS	NS	NS	NS	NS	0.86
35-MW-13	0.81	1.9	0.85	NS	NS	NS	NS	NS	0.8	0.88
35-MW-14	NS	NS	0.54	NS	NS	NS	NS	NS	NS	0.64
35-MW-15	0.67	1.1	0.8	NS	NS	0.77	NS	NS	NS	0.88
35-MW-16	3.3	7.8	6.5	5.4	13	9.7	NS	10	11	15
35-MW-17	NS	NS	0.76	NS	NS	NS	NS	NS	NS	0.99
35-MW-18	NS	NS	4.8	0.59	0.82	0.73	NS	NS	0.61	0.82
35-MW-19A	NS	NS	NS	NS	NS	NS	NS	NS	1.6	2.4
35-MW-20	18.5	NS	18.2	NS	18	26	NS	68	36	25

NS = Not sampled

Results reported in mg/L

Table 4-9a Dilution Calculations Using Tracer

				TCE	TCE	cis-DCE	cis-DCE	VC	VC
	Bromide	Bromide in	Dilution	Measured	Corrected	Measured	Corrected	Measured	Corrected
	(mg/L)	(mg/L)	Factor	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
35-MW-11									
11/15/00	0.83	0	**1**	450	**450**	9.6	**9.6**	0	**0**
08/02/01	1.9	0	**1**	930	**930**	17	**17**	0	**0**
10/24/01	5.4	180	**0.9700**	870	**897**	15	**15**	0	**0**
01/23/02	10	180	**0.9444**	27	**29**	490	**519**	0	**0**
04/17/02	5.8	180	**0.9678**	19	**20**	320	**331**	0	**0**
10/04/02	2	180	**0.9889**	160	**162**	190	**192**	0	**0**
05/01/03	1.8	0	**1**	260	**260**	110	**110**	0.28	**0.28**
35-MW-16									
11/16/00	0.7	0	**1**	1600	**1600**	31	**31**	0	**0**
08/02/01	35.4	180	**0.8033**	820	**1021**	24	**30**	0	**0**
10/24/01	3.3	180	**0.9817**	770	**784**	18	**18**	0	**0**
01/23/02	7.8	180	**0.9567**	780	**815**	21	**22**	0	**0**
04/17/02	6.5	180	**0.9639**	870	**903**	21	**22**	0	**0**
10/24/02	9.7	180	**0.9461**	980	**1036**	27	**29**	0.00	**0**
05/01/03	15	94	**0.8404**	410	**488**	450	**535**	26	**31**
35-MW-20									
11/15/00	0.83	0	**1**	410	**410**	10	**10**	0	**0**
08/02/01	208	0	**0**	200	**Inf**	6	**Inf**	0	**Inf**
10/24/01	18.5	180	**0.8972**	380	**424**	7	**8**	0	**0**
04/18/02	18.2	180	**0.8989**	230	**256**	72	**80**	0	**0**
10/24/02	26	180	**0.8556**	230	**269**	95	**111**	0	**0**
05/05/03	25	180	**0.8611**	130	**151**	95	**110**	11	**13**
35-MW-7									
11/17/00	0.63	0	**1**	600	**600**	11	**11**	0	**0**
11/17/00	0.59	0	**1**	520	**520**	10	**10**	0	**0**
05/09/01	0.96	180	**0.9947**	960	**965**	18	**18**	0	**0**
08/02/01	3.1	180	**0.9828**	810	**824**	16	**16**	0	**0**
10/24/01	2.6	180	**0.9856**	690	**700**	12	**12**	0	**0**
01/23/02	2.5	180	**0.9861**	410	**416**	11	**11**	0	**0**
04/17/02	1.8	180	**0.9900**	440	**444**	10	**10**	0	**0**
10/24/02	1.5	180	**0.9917**	290	**292**	31	**31**	0	**0**
02/05/03	2	94	**0.9787**	270	**276**	160	**163**	0	**0**
05/05/03	2	180	**0.9889**	260	**263**	59	**60**	0	**0**
			blue = more than 10% dilution						

Table 4-10 Biological Oxygen Demand and Chemical Oxygen Demand

Constituent	Date	35-MW-7	35-MW-11	35-MW-12	35-MW-13	35-MW-14	35-MW-15	35-MW-16	35-MW-17	35-MW-18	35-MW-20	35-MW-19A
BOD (mg/L)	11/15/00	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
	04/17/02	26.8	222	1 U	11	1 U	1 U	822	1 U	23.9	4475	NS
	05/01/03	9	1 U	NS	1.8	0.5	0.5	69	NS	0.51	3000	8.6
COD (mg/L)	11/15/00	66.6	20.9	52.8	21.5	23.8	28.1	62.4	20.2	47.9	18.6	28.1
	04/17/02	66.6	446	15.3	20.8	8.1	10.4	1520	9.1	46.2	5750	NS
	05/01/03	40	11	NS	3.1	20	30	910	NS	19	22	5.2

Notes:

Analytical methods: BOD by SW846 Method 405.1/5210B, COD by SW846 Method 410.4

NS = Not sampled

U = Undetected at the listed detection limit

Table 4-11 Summary of Biodegradation Rates Vandenberg AFB

Constituent	Well	During Treatment k (1/yr)	During Treatment R^2	During Treatment Half Life (days)	Other ERD Sites[1] k (1/yr)	Other ERD Sites[1] Half Life (days)	Published NA Rates[3] k (1/yr)	Published NA Rates[3] Half Life (days)
TCE	35-MW-7	0.5427	0.9266	466	0.98	257	0.15-2.58	98-1653
	35-MW-11	0.6266	0.1037	404	3.95	64		
	35-MW-16	0.5307	0.7065	477	3.10	82		
	35-MW-20	0.2943	0.4758	859	2.33	108		
					1.31-3.20	79-193		
					1.83-8.40	30-139		
					15.33	17		
					3.16-8.98[2]	28-80[2]		
cis-DCE	35-MW-7	1.12	0.6196	226	2.45	103	0.35-2.26	112-720
	35-MW-11	1.19	0.9829	213	3.18	80		
	35-MW-16				2.15	117		
	35-MW-20				1.26	200		
					1.46-6.21	41-173		
					15.33	17		
					0.59-1.14[2]	223-428[2]		
Vinyl Chloride	35-MW-7				2.92	87	0.35-2.26	112-720
	35-MW-11				0.95	267		
	35-MW-16				0.69	365		
	35-MW-20				1.10-5.48	46-231		
					2.33[2]	109[2]		

Notes:

See text for explanation of intervals over which rates were calculated.

[1] Rates calculated for other ARCADIS ERD sites, as published in Horst et al. (2000), Suthersan et al. (2002), and ARCADIS (2003).

[2] Hanscom AFB demonstration

[3] Published data are anaerobic, aqueous biodegradation half-lives from Howard et al. (1991), assumed to represent natural attenuation.

Table 4-12 Molasses Analysis for Inorganics

Blackstrap Molasses Analysis (US Sugar Corp., 2000)	
Weight/gallon	12.0 lbs
Calcium	0.80%
Chloride	2.10%
Cobalt	negligible
Copper	14 ppm
Iron	130 ppm
Magnesium	0.27%
Manganese	5 ppm
Nitrogen	1.01%
Phosphorus	negligible
Potassium	4.20%
Selenium	negligible
Sodium	0.09%
Sulfur	0.78%
Zinc	8 ppm

from http://www.suga-lik.com/molasses/molasses_frame.html

Table 4-13 Molasses-Water Analysis for Inorganics

Constituent	SDWA MCL	Laboratory Detection Lmt	Laboratory Analysis Mixture	Qualifier
Molasses used at a commercial site in Ohio; 10:1 water:molasses mixture				
Arsenic	0.05	0.01	0.0088	B
Barium	2	0.2	0.031	B
Cadmium	0.005	0.005	0.00053	BJ
Lead	--	0.003	0.005	
Chromium	0.1	0.01	0.0078	B
Selenium	0.05	0.005	0.028	B
Silver	0.1*	0.01	<0.01	
Mercury	0.002	0.0002	0.000077	B

Concentrations reported in milligrams per liter

Metals analysis conducted by USEPA Method 6010B

Laboratory Qualifiers:

"B" - Estimated result below laboratory method detection limit

"J" - Method blank contamination, associated method blank contains the target analyte at a reportable level

Federal Standards are SDWA MCLs or *secondary drinking water regulations

Arsenic MCL is currently 0.05 mg/L and will change to 0.01 mg/L In 2006

Table 4-14 VOCs of Secondary Concern in Groundwater

Analyte (ug/L)	MCL or Other Std.	Date	35-MW-14		35-MW-15		35-MW-20		35-MW-11		35-MW-18		35-MW-17		35-MW-7		35-MW-16		35-MW-12		35-MW-13		35-MW-19A	
2-Butanone	1900 (PRG)	11/17/00	50	U	170	U	50	U	50	U	40	U	250	U	100	U	330	U	330	U	140	U	500	U
		04/17/02	5	U	20	U	25	U	50	U	5	U	20	U	50	U	250	U	200	U	50	U	NS	
		10/24/02	NS		14	U	12	U	5	U	10	U	NS		5	U	210		NS		NS		NS	
		02/25/03*													2.5	U								
		05/01/03	5	U	17	U	740		5	U	17	U	5	U	5	U	150		5	U	5	U	13	
		05/06/03*													0.6	U								
		08/20/03*													0.3	U								
		02/04/04*																						
Acetone	610 (PRG)	11/17/00	100	U	330	U	100	U	100	U	80	U	500	U	200	U	670	U	670	U	290	U	1000	U
		04/17/02	3.7	J	29	J	560		280		14		19	J	40	J	500	U	400	U	100	U	NS	
		10/24/02	NS		28	U	140		10	U	20	U	NS		10	U	180		NS		NS		NS	
		02/25/03*													2.5	U								
		05/01/03	10	U	33	U	260		10	U	33	U	10	U	3.7	J	120		10	U	10	U	12	J
		05/06/03*													8.7									
		08/20/03*													0.7	U								
		02/04/04*													1.5	U								
Carbon disulfide	1000 (PRG)	11/17/00	10	U	33	U	10	U	10	U	8	U	50	U	20	U	67	U	67	U	29	U	100	U
		04/17/02	1	U	4	U	5	U	10	U	1	U	4	U	10	U	50	U	40	U	10	U	NS	
		10/24/02	NS		5.3		4.8		1.6		2	U	NS		0.86	J	4.7		NS		NS		NS	
		02/25/03*													0.5	U								
		05/01/03	1	U	3.3	U	1.3	J	0.36	J	3.3	U	1	U	0.24	J	3.2	J	1	U	1	U	2	U
		05/06/03*													0.48	U								
		08/20/03*													11.9	U								
		02/04/04*													0.48	U								
Chloroform	80 (total THMs)	11/17/00	10	U	33	U	10	U	10	U	8	U	50	U	20	U	67	U	67	U	29	U	100	U
		04/17/02	1	U	4	U	5	U	10	U	1	U	4	U	10	U	50	U	40	U	10	U	NS	
		10/24/02	NS		2.8	U	2.5	U	1	U	2	U	NS		1	U	2.8	U	NS		NS		NS	
		02/25/03*													0.5	U								
		05/01/03	1	U	3.3	U	2.5	U	0.17	J	0.62	J	1	U	1	U	10	U	1	U	0.18	J	2	U
		05/06/03*													0.15	U								
		07/23/03	NS		1.3		NS		NS		NS		NS		NS		1.8		NS		0.54		1.1	
		08/20/03*													0.11	U								
		02/04/04*													0.15	U								
Ethylbenzene	700	11/17/00	10	U	33	U	10	U	10	U	8	U	50	U	20	U	67	U	67	U	29	U	100	U
		04/17/02	1	U	4	U	5	U	10	U	1	U	4	U	10	U	50	U	40	U	10	U	NS	
		10/24/02	NS		2.8	U	2.5	U	1	U	2	U	NS		1	U	2.8	U	NS		NS		NS	
		02/25/03*													0.5	U								
		05/01/03	1	U	3.3	U	1.4	J	1	U	3.3	U	1	U	1	U	10	U	1	U	1	U	2	U
		05/06/03*													0.13	U								
		08/20/03*													0.11	U								
		02/04/04*													0.13	U								
Methylene chloride	4.3 (PRG)	11/17/00	10	U	33	U	10	U	10	U	8	U	50	U	20	U	67	U	67	U	29	U	100	U
		04/17/02	1	U	4	U	5	U	10	U	1	U	4	U	10	U	50	U	40	U	10	U	NS	
		10/24/02	NS		2.8	U	2.5	U	1	U	2	U	NS		1	U	2.8	U	NS		NS		NS	
		02/25/03*													0.5	U								
		05/01/03	1	U	2.2	JB	0.66	JB	1	U	2.5	JB	1	U	1	U	3.9	JB	1	U	0.25	JB	1.3	JB
		05/06/03*													3.23	U								
		08/20/03*													0.09	U								
		02/04/04*													0.13	U								

Notes:
* Sample results for these dates reported by TetraTech (all other samples collected by ARCADIS)
Analytical method - SW846 Method 8260B
B - Detected in blank
J - Estimated
U - Undetected at the reporting limit listed
MCL - Federal Maximum Contaminant Level for drinking water
PRG - US EPA Region 9 Preliminary Remedial Goal for tap water (provided where no MCL exists)
NS - Not sampled

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Table 4-15 Results for Volatile Fatty Acids Analysis

Well	Date	Pyruvic	Lactic	Formic	Acetic	Propionic	Butyric
35-MW-14	5/5/2003	<4	<1	<1	<1	<1	<1
35-MW-20	5/5/2003	<4	<1	<1	1407	493.6	516.8
35-MW-7	5/5/2003	<4	<1	<1	2.1	<1	<1

Results reported in mg/L

Table 4-16 Comparison of Technology Alternatives

	Groundwater Pump & Treat	Aquifer Sparging
Effectiveness	Rapid results (containment & mass removal) once system is deployed.	Rapid results (containment & mass removal) once system is deployed.
	Effective at dissolved phase concentration; can have a limited effect on mass removal when the majority of the mass is in sorbed or free phase.	Effective at mass removal of contaminants.
	Very effective for hydraulic containment & easily demonstrated.	Effectiveness for containment and/or plume treatment is more complex to demonstrate in short-term.
	Not effective in meeting all but the least stringent clean-up goals.	In-situ treatment allows for more effective treatment of organics such as VOCs. However, overall effectiveness limited to compounds with high Henry's Law constant or those that can degrade aerobically.
		Limited to particular geologies.
Reliability	Moderate reliability - number of fixed/engineered components increase likelihood of operational problems/failures.	In-situ nature and limited fixed components make technology very reliable.
	Fixed, engineered nature of systems severely limit flexibility and adaptability.	Fixed, engineered nature of systems severely limit flexibility and adaptability.
	Operational experience suggests systems can be plagued by reliability problems associated with non-target contaminants (i.e., fouling).	More reliable than ex-situ treatment techniques given no need to handle extracted groundwater.
	Can address wide range of contaminants (VOCs, SVOCs, metals, other inorganics, etc.).	Limited suite of compounds that can be reliable treated (see above).
Speed	Short-term - Slow speed. Fairly complex design, approval & permitting process needed for implementation.	Short-term - Moderate speed. Reasonable design & approval, limited permitting process needed for implementation.
	Long-term - Poor speed. Nature of technology requires very long time to reach closure.	Long-term - Moderate speed. Nature of technology requires some time to reach closure - especially if goals are low.
Ease of Use	Technology is very complex due to water handling, energy requirements, manpower requirements, and residuals management.	Technology is moderately complex due to energy requirements, manpower requirements. Limited residuals management.
	Health & safety concerns are moderate. Technology can cause additional routes of exposure to media.	Health & safety concerns are low. Technology does not provide additional routes of exposure to media.
	Above grade nature of treatment system can impact Site activities and/or development potential.	Above grade nature of treatment system can impact Site activities and/or development potential.

(continued)

Table 4-16 (concluded)

Chemical Oxidation	Enhanced Reductive Dechlorination
Effectiveness	**Effectiveness**
Very rapid results (mass removal) upon application of technology.	Technology will provide effective mass removal upon acclimatization of reactive zone.
Effective at mass removal of certain contaminants.	Effective at mass removal of contaminants.
Effectiveness simple to demonstrate in short-term. Long-term monitoring required to evaluate 'rebound'	Effectiveness for containment and/or plume treatment is more complex to demonstrate in short-term.
In-situ treatment allows for more effective treatment of organics such as VOCs. However, overall effectiveness limited to organic compounds. In addition, mixed organic plumes may require multiple oxidants.	In-situ treatment allows for more effective treatment of organics such as VOCs and others. Technology can also be used to treat other compounds including metals.
Reliability	**Reliability**
In-situ nature and no fixed components make technology very reliable.	In-situ nature and no fixed components make technology very reliable.
Lack of fixed, engineered systems make technology flexible & adaptable.	Lack of fixed, engineered systems make technology flexible & adaptable.
More reliable than ex-situ treatment techniques given no need to handle extracted groundwater.	More reliable than ex-situ treatment techniques given no need to handle extracted groundwater.
Limited suite of compounds that can be reliable treated (see above).	Larger suite of compounds that can be reliably treated (see above).
Speed	**Speed**
Short-term - Fast speed. Limited design, approval, & permitting process needed for implementation.	Short-term - Fast speed. Limited design, approval, & permitting process needed for implementation.
Long-term - Fast speed. Nature of technology allows for rapid treatment of constituents assuming sufficient oxidant chemical is supplied.	Long-term - Moderate speed. Nature of technology requires some time for reactive zone to fully acclimatize.
Ease of Use	**Ease of Use**
Technology is moderately complex due handling of chemicals and potential for aquifer preparation prior to treatment. However, no residuals management is required.	System design and operation require input from an experienced expert.
Health & safety concerns are high. Technology can create high temperature reactions and/or high levels of oxygen in the subsurface that need to be addressed.	Technology is very simple to implement. Limited manpower requirements, no residuals management, and no chemical handling concerns
	No appreciable health & safety concerns.
Below grade nature of technology and lack of fixed systems limit impacts to Site activities and/or development potential.	Below grade nature of technology and lack of fixed systems limit impacts to Site activities and/or development potential.

Table 4-17a Performance Monitoring Data for TCE

Well	Distance from Inj. Wells (ft)	Travel Time from Inj. Wells[a] (months)	TCE Concentration (ug/L)			Reduction %		Lag Time[c] (months)
			Initial (11/00)	Final (5/03)	Post-Final (7/03)[b]	Final (5/03)	Post-Final (7/03)[b]	
35-MW-14	25 (upgradient)	---	450	44	NS	90	NA	---
35-MW-15	15 (upgradient)	---	1500	930	1050	38	30	---
35-MW-20	8	<1	410	130	208	68	49	8 to 14
35-MW-11	13	6 to 8	450	260	NS	42	NA	11
35-MW-18	30 (little TOC influence)	14/NA	170	930	NS	Gain	NA	NA
35-MW-17	30 (no TOC influence)	NA	1400	NS	NS	NA	NA	---
35-MW-7	30	6 to 8	600*	260	198	57*	67*	20
35-MW-16	25	4	1600	410	241	74	85	20 to 27
35-MW-12	30 (cross-gradient)	---	1900	NS	NS	NA	NA	---
35-MW-13	60	11/NA	720	190	247	74	66	NA
35-MW-19A	120	NA	1500	270	630	82	58	NA

[a] Travel time is based on bromide and TOC arrival

[b] "Post-final" samples were collected in July 2003 by EPA-Ada, except for 35-MW-7, which was sampled in February 2004 by TetraTech

[c] Lag time is defined here as the time from the first injection to when effective treatment of the subject compound was observed

NA - indicates insufficient or inconclusive data

NS - no sample collected

* Average pretreatment concentration from September-December 2000 was 997.5 ug/L. “Final” and “Post-Final” reductions from this value were 74% and 80% respectively.

Table 4-17b Performance Monitoring Data for cis-DCE

Well	Distance from Inj. Wells (ft)	Travel Time from Inj. Wells[a] (months)	cis-DCE Concentration (ug/L)			Reduction %		Lag Time[c] (months)
			Initial (11/00)	Final (5/03)	Post-Final (7/03)[b]	Final (5/03)	Post-Final (7/03)[b]	
35-MW-14	25 (upgradient)	---	14	1.1	NS	92	NA	---
35-MW-15	15 (upgradient)	---	39	25	32.3	36	17	---
35-MW-20	8	<1	9.5	95	135	Gain	Gain	14 to 27
35-MW-11	13	6 to 8	9.6	110	NS	Gain	NA	14
35-MW-18	30 (little TOC influence)	14/NA	6.2	120	NS	Gain	NA	NA
35-MW-17	30 (no TOC influence)	NA	31	NS	NS	NA	NA	---
35-MW-7	30	6 to 8	11	59	48.9	Gain	Gain	28
35-MW-16	25	4	31	450	559	Gain	Gain	20-27
35-MW-12	30 (cross-gradient)	---	39	NS	NS	NA	NA	---
35-MW-13	60	11/NA	16	10	12.9	38	19	NA
35-MW-19A	120	NA	38	250	150	Gain	Gain	NA

[a] Travel time is based on bromide and TOC arrival

[b] "Post-final" samples were collected in July 2003 by EPA-Ada, except for 35-MW-7, which was sampled in February 2004 by TetraTech

[c] Lag time is defined here as the time from the first injection to when effective treatment of the subject compound was observed

NA - indicates insufficient or inconclusive data

NS - no sample collected

Table 4-17c Performance Monitoring Data for VC

Well	Distance from Inj. Wells (ft)	Travel Time from Inj. Wells[a] (months)	VC Concentration (ug/L)			Reduction %		Lag Time[c] (months)
			Initial (11/00)	Final (5/03)	Post-Final (7/03)[b]	Final (5/03)	Post-Final (7/03)[b]	
35-MW-14	25 (upgradient)	---	NS	<2	NS	NA	NA	---
35-MW-15	15 (upgradient)	---	NS	<6.7	<1	NA	NA	---
35-MW-20	8	<1	<20	11	169	Unknown	Gain	14
35-MW-11	13	6 to 8	10	0.28	NS	97	NA	20
35-MW-18	30 (little TOC influence)	14/NA	NS	<6.7	NS	NA	NA	NA
35-MW-17	30 (no TOC influence)	NA	NS	NS	NS	NA	NA	---
35-MW-7	30	6 to 8	NS	0.52	18.8	NA	NA	NA
35-MW-16	25	4	<130	26	39	Unknown	Unknown	14 to 27
35-MW-12	30 (cross-gradient)	---	NS	NS	NS	NA	NA	---
35-MW-13	60	11/NA	NS	<2	<1	NA	NA	NA
35-MW-19A	120	NA	NS	<4	<1	NA	NA	NA

a Travel time is based on bromide and TOC arrival
b "Post-final" samples were collected in July 2003 by EPA-Ada, except for 35-MW-7, which was sampled in February 2004 by TetraTech
c Lag time is defined here as the time from the first injection to when effective treatment of the subject compound was observed.
NA - indicates insufficient or inconclusive data
NS - no sample collected

Table 4-17d Performance Monitoring Data for Total Ethenes (Molar)

Well	Distance from Inj. Wells (ft)	Travel Time from Inj. Wells[a] (months)	Total Ethenes (uM)			Reduction %	
			Initial (11/00)	Final (5/03)	Post-Final (7/03)[b]	Final (5/03)	Post-Final (7/03)[b]
35-MW-14	25 (upgradient)	---	3.57	0.35	NS	90	NA
35-MW-15	15 (upgradient)	---	11.84	7.35	8.34	38	30
35-MW-20	8	<1	3.22	2.15	5.68	33	Gain
35-MW-11	13	6 to 8	3.53	3.12	NS	12	NA
35-MW-18	30 (little TOC influence)	14/NA	1.36	8.33	NS	Gain	NA
35-MW-17	30 (no TOC influence)	NA	10.99	NS	NS	NA	NA
35-MW-7	30	6 to 8	4.38	2.59	2.32	41	47
35-MW-16	25	4	12.52	8.19	8.24	35	34
35-MW-12	30 (cross-gradient)	---	14.88	NS	NS	NA	NA
35-MW-13	60	11/NA	5.65	1.55	2.01	73	64
35-MW-19A	120	NA	11.83	4.64	6.35	61	46

[a] Travel time is based on bromide and TOC arrival

[b] "Post-final" samples were collected in July 2003 by EPA-Ada, except for 35-MW-7, which was sampled in February 2004 by TetraTech

NA - indicates insufficient or inconclusive data

NS - no sample collected

Table 5-1 Estimated IRZ Costs for a Hypothetical CAH Plume

WBS Number			DESCRIPTION	QTY	UOM	UNIT COST	COST $
33XXX			**HTRW CONSTRUCTION ACTIVITIES**				
331XX			**HTRW REMEDIAL ACTION (Capital and Operating)**				
	01		**MOBILIZATION AND PREPARATORY WORK**				
	01	01	Mobilization of Construction Equipment (Drilling Rig)	1	EA	$3,000	$3,000
	01	03	Submittals/Implementation Plans/Permits	1	EA	$30,000	$30,000
	01	--	Pilot Testing	1	EA	$75,000	$75,000
	02		**MONITORING, SAMPLING, TESTING, AND ANALYSIS**				
	02	04	Monitoring Wells - Installation	4	EA	$3,000	$12,000
	02	--	Injection Wells - Installation	25	EA	$3,000	$75,000
	02	--	Well Development	1	EA	$4,000	$4,000
	02	--	IDW Disposal (soil cuttings)	1	EA	$1,000	$1,000
	02	05	Sampling Groundwater				
	02	--	Quarterly (10 wells)	4	EA	$5,300	$21,200
	02	--	Semi-Annual (10 wells)	8	EA	$5,300	$42,400
	02	06	Sampling Soil	1	EA	$3,000	$3,000
	02	09	Laboratory Chemical Analysis	12	EA	$3,600	$43,200
	11		**BIOLOGICAL TREATMENT**				
	11	04	In-Situ Biodegradation/Bioreclamation				
	11	--	Trailer-Mounted Molasses Injection System	1	EA	$10,000	$10,000
	11	--	Monthly Molasses Injections - Labor	24	EA	$2,250	$54,000
	11	--	Bi-Monthly Molasses Injections - Labor	18	EA	$2,250	$40,500
	11	--	Field Process Monitoring - Equipment	42	EA	$200	$8,400
	11	--	Field Process Monitoring - Analytical	42	EA	$200	$8,400
	11	--	Laboratory Chemical Analysis (TOC)	100	EA	$30	$3,000
	11	--	Molasses (20 gallons per well per injection)	21000	GAL	$3	$63,000
	11	--	Water for Injection (180 gallons per well per injection)	189000	GAL	$0.0029	$548
	11	--	Well Rehabilitation	63	EA	$300	$18,900
	11	--	Progress Reporting	5	YR	$25,000	$125,000
	11	--	Completion Report	1	EA	$20,000	$20,000
	21		**DEMOBILIZATION**				
	21	--	Well Abandonment	35	EA	$500	$17,500
	--		**INDIRECT ENVIRONMENTAL ACTIVITY COSTS**				
	--	--	Environmental and Safety Training	2	FTE	$250	$500
	--	--	OSHA Ambient Environment Sampling	1	EA	$250	$250
	--	--	Waste Manifesting	1	EA	$500	$500
			TOTAL AMOUNT FOR HYPOTHETICAL SITE				$680,298

Table 5-2 Relative Costs of Various Electron Donors

Electron Donor	Bulk Price $/lb of TOC	$/lb of PCE Treated
Molasses	0.20 – 0.35	0.16
Sugar (Corn Syrup)	0.25 – 0.30	0.4
Sodium Lactate	1.25 – 1.46	NA
Whey (Powdered, Dry)	1.17	NA
Whey (Fresh)	0.05	0.04
Edible Oils	0.20 – 0.50	NA
Flour (Starch)	0.3	0.85
Cellulose	0.40 – 0.80	NA
Chitin	2.25 – 3.00	NA
Methyl Cellulose	4.00 – 5.00	NA
HRC™ (Regenesis Commercial Material)	5.00 – 6.00[2]	NA

NA - Not Analyzed
1 Harkness, 2000; DiStefano, 2000
2 Personal Communication, Leeson, 2002

Table 5-3 Cost Savings for IRZ Technology Compared to Pump and Treat Systems

Location	Description	Target COCs	Actual/Projected Savings
Rogersville, Tennessee	Parts manufacturing for trucks	PCE, TCA	$200,000
Eastern Tennessee	Fuel facility	PCE, radionuclides	$1,500,000
Chattanooga, Tennessee	Former manufacturing facility	PCE	$500,000 (50%)
Northeastern New Jersey	Pharmaceutical	PCE	$6,000,000
Williamsport, Pennsylvania	Textron/manufacturing	Cr^{+6}, TCE, DCE, VC	$2,250,000 (75%)
Reading, Pennsylvania	Textile equipment	TCE, Cr^{+6}, Pb, Cd	$700,000 (70%)
Emeryville, California	Metal plating manufacturer	TCE, DCE, Cr^{+6}	$1,600,000 (80%)
Hampton, Iowa	Metal plating	Cr^{+6}	$500,000 (66%)
Dallas, Texas	Graphics	Cr^{+6}	$1,500,000 (75%)
Pennsylvania	Lord Corporation	CAHs	$6,400,000 (74%)
East Coast	Metal plating	CAHs, Cr^{6+}	$6,000,000

Table 5-4 Economic Comparison of Probable Costs for Proposed ARCADIS CAH Site in South Carolina

Economic Category		Natural Attenuation	Vacuum-Enhanced Recovery	In-Situ Air Sparging	Iron Reactive Wall	IRZ
Capital						
	Best	$25,000	$350,000	$200,000	$600,000	$150,000
	Worst	$30,000	$500,000	$250,000	$700,000	$160,000
Annual O & M						
	Best	$25,000	$60,000	$45,000	$25,000	$30,000
	Worst	$35,000	$75,000	$60,000	$35,000	$40,000
Present Worth of Total						
	n (years) =	30	20	20	30	15
	Best	$429,000	$1,135,000	$789,000	$1,004,000	$477,000
	Worst	$595,000	$1,481,000	$1,035,000	$1,265,000	$596,000
Total Opinion of Probable Costs						
	Best Case	$400,000	$1,200,000	$750,000	$900,000	$500,000
	Worst Case	$600,000	$1,500,000	$1,100,000	$1,300,000	$800,000

Table 5-5 Results of DuPont Technology Evaluation

Metric	Pump and Treat	Zero-Valent Iron PRB	Substrate Enhanced Biobarrier	Recirculating Source Zone	Natural Attenuation
Present Cost, ($1000s)	$9,800	$3,900	$3,100	$1,300	$890
$/1,000 gallons treated	$8.90	$5.30	$4.20	$1.80	$1.20
$/lb PCE Removed	$1,600	$640	$520	$220	$150

Table 5-6 Summary of IRZ Technology Application Costs

Site	Estimated Capital Costs	Estimated Annual O&M Costs	Actual or Predicted Costs to Closure	Initial Concentration	Dimensions
Industrial Laundry/Dry Cleaning Facility, Eastern PA	$75,000	$45,000	$250,000	46,000 ug/l PCE	10,000 ft^2 x 20 ft deep
Uranium Processing Facility, Eastern US	$480,000	$65,000	$760,000	5 - 14,000 ug/l PCE (plus U)	19.3 acres or 1200 x 700 ft
Former Metal Pating Site, Western US[1]	$100,000	$150,000	$250,000	24,000 ug/l TCE (plus Cr)	< 2 acres or <87,000 ft^2 x 10 feet deep
Industrial Manufacturing Site, South Carolina	$1,400,000	$75,000	$2,000,000	800 ug/l CT, chloroform, TCE	3.25 acres or 141,600 ft^2 x 10 ft deep
Industrial Site, Northeastern US	$150,000	$80,000	$750,000	120 ug/L PCE	3000 ft long in bedrock - depth varies
Former Dry Cleaner, Wisconsin[2]	$200,000	$100,000	$400,000	1,500-4,000 ug/L PCE	30,000 ft^2 x 5 ft deep
Former Automotive Manufacturing Site, Midwestern, US	$75,000	$60,000	$375,000	800 ug/l TCE	1000 x 400 ft x 20 ft deep
AOC 50, Ft. Devens, Ayer, Massachusetts	$150,000	$150,000	NA[3]	4,000 ug/L PCE	3000 x 400 ft x 40 ft deep

Note:

All costs presented in current dollars.

1 - Site has received regulatory closure.

2 - Site has received regulatory closure.

3 - No Predicted Costs to Closure Available. Pilot study ongoing.

Appendix A-1

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IRZ/ERD Bibliography

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Appendix A-2

Validation Memos

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MEMO

To:
Chris Lutes

Copies:
Copies

From:
Libby Beach

Date:
7 May 2002

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 11/16/2000

Nine samples were collected on November 16 and 17, 2000 at Vandenberg AFB, Lampoe, California. These samples were submitted on November 18, 2000 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group DOK180141

VAN-GW-35MW12-1
VAN-GW-35MW13-1
VAN-GW-35MW16-1
VAN-GW-35MW18-1
VAN-GW-35MW17-1
VAN-GW-35MW7-1
VAN-GW-35MW7-1DUP
VAN-GW-FB-1
Trip Blank

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CL)) National Functional Guidelines for Organic Data Review”, revised in June 2001.

Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that sample coolers were within the 4 °C ± 2 °C acceptance criteria. pH of samples as received was < 2.0. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

For all of the compounds of interest, response factors were above the criteria limit of 0.05 in the initial calibration performed on October 9, 2000. The six-point calibration range was from 1 to 60 ug/L on column. Relative Standard Deviations (RSDs) were below the 30 % for all target compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for the compounds of interest. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines.

V. Blanks

Low concentrations (<0.2 ug/L) of methylene chloride, naphthalene, and chloroform were found in the trip blank, field blank and method blank. None of these compounds were identified in field samples.

VI. Deuterated Monitoring Compounds (DMCs)

All internal standard recoveries were within acceptable limits. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD was run with this batch of samples (VAN-GM-35MW7-1). MS/MSD recovery of trichlorethene was slightly below acceptance criteria at 76% and 63% respsectively. All other compounds were within acceptable limits and transcribed correctly. RPD's between the MS and MSD were all within the established acceptance criteria.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All compounds were correctly identified and met retention time criteria.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Quantitation also reflected sample dilutions. Sample volume purge was reduced from 20 mL used with standards to 0.3-2.5 mL for field samples to bring amounts of trichloroethene on-column within calibration range. This resulted in on-column concentrations of 1,2-dichloroethene to be lower than the lowest calibration standard for all field samples. No repeat analyses were performed.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Since analysis of the samples in this data set precede the April 3, 2001 ARCADIS memorandum instructing the laboratory to repeat analysis at a minimum dilution to achieve low detection limits for other chlorinated compounds falling below calibration range in diluted samples, no action can be taken for the laboratory not performing repeat analyses. Data quality is sufficient for its intended use.

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Chris Lutes

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From:
Libby Beach

Date:
7 May 2002

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 11/15/2000

Five samples were collected on November 14 and 15, 2000 at Vandenberg AFB, Lampoe, California. These samples were submitted on November 16, 2000 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group DOK160165

VAN-GW-35MW19A-1
VAN-GW-35MW14-1
VAN-GW-35MW20-1
VAN-GW-35MW11-1
VAN-GW-35MW15-1

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CL)) National Functional Guidelines for Organic Data Review”, revised in June 2001. Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Data Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that one of the sample coolers was not within the 4 °C ± 2 °C acceptance criteria with a temperature of 9.8 °C. The laboratory notified ARCADIS at the time of receipt and was authorized to continue processing the samples. pH of as-received samples was <2.0. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

For all of the compounds of interest, response factors were above the criteria limit of 0.05 in the initial calibration performed on October 1, 2000. The six-point calibration range was from 1 to 60 ug/L on column. Relative Standard Deviations (RSDs) were below the 30 % for all compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for the compounds of interest. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines.

V. Blanks

Non-detects were reported for all compounds of interest in the system blank.

VI. Deuterated Monitoring Compounds (DMCs)

All internal standard recoveries were within acceptable limits. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Results from one MS/MSD sample were included with this package. MS/MSD recoveries and RPD's were all within the established acceptance criteria. The sample used for MS/MSD was from a different SDG (DOK160354) so it could not be determined if matrices were comparable.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All compounds were correctly identified and met retention time criteria.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Quantitation also reflected sample dilutions. Sample volume purge was reduced from 20 mL used with standards to 0.2-2.0 mL for field samples to bring amounts of trichloroethene on-column within calibration range. This resulted in on-column concentrations of 1,2-dichloroethene to be lower than the lowest calibration standard for 2 of the 5 samples. No repeat analyses were performed.

Sample reports referencing a calibration performed on 10/9/2000 but date on calibration submitted with data package indicates calibration date of 10/1/2000. Even though dates do not match, by verifying quantitations, it is evident that the calibration information included in the data package is the information used to quantitate concentrations of samples.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Since analysis of the samples in this data set precede the April 3, 2001 ARCADIS memorandum instructing the laboratory to repeat analysis at a minimum dilution to achieve low detection limits for other chlorinated compounds falling below calibration range in diluted samples, no action can be taken for the laboratory not performing repeat analyses. Data quality is sufficient for its intended use.

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MEMO

To:
Chris Lutes

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From:
Libby Beach

Date:
7 May 2002

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 08/02/2001

Seven samples were collected on August 2, 2001 at Vandenberg AFB, Lampoe, California. These samples were submitted on August 4, 2001 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group D1H040148

VAN-GW-35MW14-2
VAN-GW-35MW20-2
VAN-GW-35MW11-2
VAN-GW-35MW16-2
VAN-GW-35MW7-2
VAN-GW-35MWFB-2
VAN-GW-35MWTB-1

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CL)) National Functional Guidelines for Organic Data Review”, revised in June 2001.

Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that sample coolers were within the 4 °C ± 2 °C acceptance criteria. pH of samples as received was < 2.0. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

For all of the compounds of interest, response factors were above the criteria limit of 0.05 in the initial calibration performed on July 31, 2001. The six-point calibration range was from 1 to 60 ug/L on column. Relative Standard Deviations (RSDs) were below the 30 % for all target compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for the compounds of interest. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines.

V. Blanks

Low concentrations (<0.2 ug/L) of methylene chloride were reported in the method blank. The field blank had 6.3 ug/L acetone which is below the laboratory’s reporting limit. Low concentrations of several other compounds were detected in the field blank, but they were not compounds of interest. Non-detects were reported for all compounds in the trip blank but no raw data was included for this sample so non-detects could not be verified.

VI. Deuterated Monitoring Compounds (DMCs)

All internal standard recoveries were within acceptable limits. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD results reported are within acceptable limits. Raw data for the MS/MSD could not be located with this data package, so the reported results could not be verified.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All compounds were correctly identified and met retention time criteria. It should be noted that there were several compounds present in significant quantities identified in the raw data report but not reported in the analytical report. These compounds included ethanol, ethyl acetate, n-butanol, tetrahydrofuran and isobutanol.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standards, quantitation ions, and RRFs were used to quantitate compounds. Quantitation also reflected sample dilutions. Multiple analyses were performed for samples with high concentrations of TCE. One analysis was performed at a dilution to quantitate target anaytes within the calibration range of the instrument and the sample was also analyzed undiluted or at a lesser dilution in order to achieve lower reporting limits.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The reported data meets all acceptance criteria established in the functional guidelines and associated methods and plans. It is not clear why MS/MSD and trip blank raw data was not included with the data package. Nonetheless, data quality is sufficient for its intended use.

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To:
Chris Lutes

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Copies

From:
Libby Beach

Date:
7 May 2002

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 10/24/2001

Eight samples were collected on October 24, 2001 at Vandenberg AFB, Lampoe, California. These samples were submitted on October 26, 2001 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group D1J270184

VAN-GW-35MW15-2
VAN-GW-35MW13-2
VAN-GW-35MW16-3
VAN-GW-35MW7-3
VAN-GW-35MW11-3
VAN-GW-35MW20-3
VAN-GW-35MWFB-3
VAN-GW-35MWTB-2

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CL)) National Functional Guidelines for Organic Data Review”, revised in June 2001.

Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that sample coolers were recorded to be 1.4 °C upon arrival, which is lower than the 4 °C ± 2 °C acceptance criteria. This is not significant. pH of samples as received was recorded on GC sample log as < 2.0. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

For all of the compounds of interest, response factors were above the criteria limit of 0.05 in the initial calibration performed on September 4, 2001. The six-point calibration range was from 1 to 60 ug/L on column. Relative Standard Deviations (RSDs) were below the 30 % for all target compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for the compounds of interest. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines

V. Blanks

Low concentrations (<0.85 ug/L) of methylene chloride were reported in the method blank. The field blank had large concentrations of ethanol and n - butanol, above the highest calibration standard (3424 ug/L and 511 ug/L respectively) .Low concentrations of methylene chloride, chloroform and trichloroethene were also detected. Trichloroethene is the only compound of interest in the blank and was reported at a concentration of 0.16 ug/L. Non-detects were reported for all compounds except ethanol in the trip blank.

Concentration of ethanol was reported at 60 ug/L. Two field samples also contained large concentrations of ethanol and n-butanol (VAN-GW-35MW16-3 and VAN-GW-35MW20-3). It is not clear at what point this contamination originated in the field but does not seem to effect the quantitation of the compounds of interest.

VI. Deuterated Monitoring Compounds (DMCs)

All internal standard recoveries were within acceptable limits. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Analytical report indicates that MS/MSD results were within acceptable limits. Raw data for the MS/MSD could not be located with this data package, so the reported results could not be verified.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All compounds were correctly identified and met retention time criteria. It should be noted that there were several compounds present in significant quantities identified in the raw data report but not reported in the analytical report. These compounds included ethanol, ethyl acetate, n-butanol, and isobutanol.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standards, quantitation ions, and RRFs were used to quantitate compounds. Quantitation also reflected sample dilutions. Multiple analyses were performed for samples with high concentrations of TCE. One analysis was performed at a dilution to quantitate target anaytes within the calibration range of the instrument and the sample was also analyzed undiluted or at a lesser dilution in order to achieve lower reporting limits.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The reported data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Data quality is sufficient for its intended use.

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From:
Libby Beach

Date:
15 May 2002

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 01/24/2002

Six samples were collected on January 24, 2002 at Vandenberg AFB, Lampoe, California. These samples were submitted on January 25, 2002 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots and additional samples were submitted and analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group D2A250181

VAN-GW-35MW7-4
VAN-GW-35MW11-4
VAN-GW-35MW13-3
VAN-GW-35MW15-3
VAN-GW-35MW16-4
VAN-GW-35MWFB-4

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CL)) National Functional Guidelines for Organic Data Review”, revised in June 2001. Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that the cooler temperature was –0.1 C. This is not within the 4 °C ± 2 °C acceptance criteria but should not affect data quality. pH of samples as received was < 2.0. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times. It was noted that the field blank sample vial was broken in the cooler but there was some sample left in the vial that was analyzed. Non-detects were reported for all target compounds in the field blank, so the broken sample is not an issue.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

For all of the compounds of interest, response factors were above the criteria limit of 0.05 in the initial calibration performed on July 31, 2001. The six-point calibration range was from 1 to 60 ug/L on column. Relative Standard Deviations (RSDs) were below the 30 % for all target compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for the compounds of interest. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines.

V. Blanks

Non-detects were reported in the method blank. Low concentration of chloroform was detected in the field blank, but this is not a compound of interest. Non-detects were reported for all compounds except acetone (4.7 ug/L) in the trip blank. All samples had reported levels of acetone, so this should be taken in to account when reviewing sample concentrations.

VI. Deuterated Monitoring Compounds (DMCs)

All internal standard recoveries were within acceptable limits. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD was performed on sample VAN-GW-35-MW15-3 and results reported are within acceptable limits for all compounds except tricholorethene (TCE). TCE recovery for the MS/MSD was 78 and 76%, respectively. RPD's for the MS/MSD were within acceptance criteria. Note: A significant quantity of 1,4-dioxane was detected in the original analysis of the sample but not found in the MS or MSD.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All compounds were correctly identified and met retention time criteria

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standards, quantitation ions, and RRFs were used to quantitate compounds. Quantitation also reflected sample dilutions. Multiple analyses were performed for samples with high concentrations of TCE. Several analyses were performed at a dilution to quantitate target anaytes within the calibration range of the instrument and the samples were also analyzed undiluted or at a lesser dilution in order to achieve lower reporting limits. The 10 mL purge volume data for sample VAN-GW-35-MW15-3 is shown in the GC run log as file number Z4558, but is missing from the raw data. Reported values from this run could not be verified.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The reported data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Data quality of target compounds is sufficient for its intended use.

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From:
Libby Beach

Date:
4 June 2003

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 4/16/2002

Eleven samples were collected on April 16 and April 17, 2002 at Vandenberg AFB, Lampoe, California. These samples were submitted on April 18, 2002 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. Samples were analyzed on April 24, 2002. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group D2D180135

VAN-GW-35MW-7
VAN-GW-35MW-7DUP
VAN-GW-35MW-11
VAN-GW-35MW-12
VAN-GW-35MW-13
VAN-GW-35MW-14
VAN-GW-35MW-15
VAN-GW-35MW-16
VAN-GW-35MW-17
VAN-GW-35MW-18
VAN-GW-35MWTB-1

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the "USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Organic Data Review", revised in October 1999. Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that samples met the < 4 °C acceptance criteria. pH of samples as received was neutral and samples were acidified upon receipt. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

Initial calibration was performed on April 4, 2002. The six-point calibration range was from 1 to 60 ug/L on column. Response factors were above the criteria limit of 0.05 in the initial calibration performed on April 4, 2002 for all reported compounds with the exception of acetone. According to the functional guidelines, any acetone identified in these samples should be qualified as estimated "J" and non-detects should be qualified as unusable, "R". Relative Standard Deviations (RSDs) were below the 30% for all target compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run on April 24, 2002 in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for all reported compounds. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines for all reported compounds.

V. Blanks

Low concentrations of methylene chloride (0.4J ug/L) were reported in the method blank. A trip blank was also submitted with this sample set (VAN-GW-35-TB). There were low levels of methylene chloride in the trip blank as well as most of the samples. Any methylene chloride levels <10X the level found in the blank should be qualified as non-detects, “U”.

VI. System Monitoring Compounds (SMCs)

All internal standard recoveries were within acceptable limits for diluted runs. Undiluted or lesser diluted runs for samples VAN-GW-35MW-7, VAN-GW-35MW-7DUP, VAN-GW-35MW-11, VAN-GW-35MW-12, and VAN-GW-35MW13 had one or more internal standard area counts below method specified acceptance criteria due to matrix interference. The laboratory was instructed to only report DCE, TCE, and vinyl chloride from the more concentration runs in order to attain lower reporting limits. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Sample VAN-GW-35-MW-17 was used as the MS/MSD. Recoveries reported were within acceptable limits of 80-120% for all compounds except trichloroethene (71%/74%). According to the functional guidelines, concentrations of trichloroethene reported in samples should be qualified as estimated, “J”, and non-detects should be qualified with “UJ”.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All reported compounds were correctly identified and met retention time criteria.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standards, quantitation ions, and RRFs were used to quantitate compounds.

Quantitation also reflected sample dilutions. Multiple analyses were performed for samples with high concentrations of TCE. One analysis was performed at a dilution to quantitate target anaytes within the calibration range of the instrument and the sample was also analyzed undiluted or at a lesser dilution in order to achieve lower reporting limits.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The reported data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Data quality is sufficient for its intended use.

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From:
Libby Beach

Date:
6 June 2003

ARCADIS Project No.:
RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 10/24/2002

Eight samples were collected on October 24, 2002 at Vandenberg AFB, Lampoe, California. These samples were submitted on October 29, 2002 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. Samples were analyzed on November 6 and 7, 2002. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group D2J290294:

VAN-GW-35MW-7
VAN-GW-35MW-11
VAN-GW-35MW-15
VAN-GW-35MW-16
VAN-GW-35MW-18
VAN-GW-35MW-20
VAN-GW-35MW-FB
VAN-GW-35MW-TB

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Organic Data Review”, revised in October 1999. Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that samples met the < 4 °C acceptance criteria. pH of samples as received was not documented. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

Initial calibration was performed on October 27, 2002. The six-point calibration range was from 1 to 60 ug/L on column. Response factors were above the criteria limit of 0.05 in the initial calibration performed on October 27, 2002 for all reported compounds. Relative Standard Deviations (RSDs) were below the 30% for all target compounds.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run on November 6, 2002 in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for all reported compounds. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines for all reported compounds.

V. Blanks

Three blanks were associated with the sample set: a method blank, a field blank and a trip blank. Low concentrations of methylene chloride (0.3J ug/L) were reported in the method blank. The following compounds were reported in the field blank: acetone (3.0J ug/L), methylene chloride (0.3J ug/L), trichloroethylene (0.1J ug/L) and toluene (0.1J ug/L). There were low levels of acetone (3J ug/L) and methylene chloride (0.2J ug/L) in the trip blank. Any methylene chloride, acetone and toluene levels reported for samples that are <10 times the concentration in these blanks should be qualified as non-detects, “U”. Any reported levels of trichloroethylene that are <5 times the level in the blank should be qualified as non-detect, “U”.

VI. System Monitoring Compounds (SMCs)

All internal standard recoveries were within acceptable limits for diluted and undiluted or lesser diluted runs. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

No MS/MSD sample was processed with this batch of samples. A laboratory control spike and control spike duplicate (LCS/LCSD) were processed internally by the lab. Recoveries and %D were all within acceptable criteria.

VIII. Regional QA/QC

Not Applicable.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All reported compounds were correctly identified and met retention time criteria. It was noted that the original laboratory reports for sample VAN-GW-MW35-20 had significant levels of ethanol (44,575 ug/L), 2-butanone (790 ug/L), isobutanol (1568 ug/L), n-butanol (16,212 ug/L), 2-propanol (5,674 ug/L), acetonitrile (58 ug/L) and ethylacetate (325 ug/L) that were not reported in the summary reports.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standards, quantitation ions, and RRFs were used to quantitate compounds. Quantitation also reflected sample dilutions. Multiple analyses were performed for samples with high concentrations of TCE. One analysis was performed at a dilution to quantitate target anaytes within the calibration range of the instrument and the sample was also analyzed undiluted or at a lesser dilution in order to achieve lower reporting limits.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The reported data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Data quality is sufficient for its intended use.

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To: Chris Lutes	Copies: Copies

From:
Libby Nessley

Date: 18 June 2003	ARCADIS Project No.: RN009900.0017.00001

Subject:
Validation of Water Samples Collected at Vandenberg AFB 05/01/2003

Five samples and a trip blank were collected on May 1, 2003 at Vandenberg AFB, Lampoe, California. These samples were submitted on May 2, 2003 to Severn Trent Laboratories/Denver (STL) in Arvada, Colorado. Samples were analyzed on May 13, 2003. This validation covers the samples submitted for volatile organics by USEPA Method SW-846 8260B. Other aliquots were analyzed for other parameters that will not be discussed in this report.

Sample Delivery Group D3E020220

VAN-GW-35-MW-13
VAN-GW-35-MW-15
VAN-GW-35-MW-18
VAN-GW-35-MW-19A
VAN-GW-35-FB-1
VAN-GW-35-TB-1

Validation of this data was performed following the quality assurance/quality control (QA/QC) criteria set forth in the “USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Organic Data Review”, revised in October 1999. Method 8260B has slightly different criteria for some parameters than the Functional Guidelines. In these cases, the more stringent criteria were used.

Volatile Organic Review

I. Preservation

The samples arrived at the laboratory promptly. The Case Narrative indicates that samples met the < 4 °C acceptance criteria. Chain-of-custody documentation was in order and all samples were processed within the established extraction and analytical hold times. Sample identifications were not included on the original laboratory reports for the majority of samples. The reviewer was able to correctly identify sample reports using work order numbers.

II. GC/MS Instrument Performance Checks

BFB tune was performed on the same day samples were analyzed. All ion abundance criteria were met and all samples were analyzed within the 12-hour time period.

III. Initial Calibration

Initial calibration for the main instrument was performed on May 8, 2003. The six-point calibration range was from 1 to 60 ug/L on column. Response factors were above the criteria limit of 0.05 in the initial calibration performed on April 4, 2002 for all reported compounds with the exception of acetone. Because acetone concentrations reported in the samples were <5 times the concentration found in the blanks, values are qualified as non-detects, “U”, no further qualification is necessary.

IV. Continuing Calibration

The Continuing Calibration Check (CCC) was run on May 13, 2003 in the 12-hour analysis window, prior to the analysis of the samples. The CCC had RFs above 0.05 for all reported compounds except acetone. The Relative Percent Deviations (RPDs) from the IC were less than the 30% criteria established in the functional guidelines for all reported compounds.

V. Blanks

Three blanks were associated with this data set, a method blank, a field blank and a trip blank. Low concentrations of methylene chloride (0.6J ugl/L) were reported in all the blanks. The trip blank and/or the field blank also had low levels of acetone (6J ug/L), toluene (0.3J ug/L) and carbon disulfide (0.3J ug/L). In addition, the method blank had significant levels of 2-propanone (29 ug/L). Levels of these compounds identified in samples that are <5X the levels found in the blank should be qualified as non-detects, “U”. This includes concentration data for the following: VAN-GW-35-MW-13, methylene chloride reported at 1.3JB ug/L; VAN-GW-35-MW-15, methylene chloride reported at 2.2JB ug/L; VAN-GW-35-MW-18, methylene chloride reported at 2.5JB ug/L; and VAN-GW-35-MW-19A, acetone reported at 12J ug/L and methylene chloride reported at 1.3JB ug/L. Each of these compounds should be qualified as "U", non-detected.

VI. System Monitoring Compounds (SMCs)

All internal standard recoveries were within acceptable limits for all samples. No transcription errors were noted.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Sample VAN-GW-35-MW-19A was used as the MS/MSD. Recoveries reported were within acceptable limits of 81-121% for all compounds except the matrix spike for trichloroethene (80%), which fell slightly below the acceptance criteria. All RPD values were within the ±20% control limits.

VIII. Laboratory Control Sample

An LCS/LCSD was run on May 13, 2003 using the same compounds spiked for the MS/MSD. All recoveries and RPD's were within the laboratory established control limits.

IX. Internal Standards

All retention times and area counts were within criteria limits.

X. Target Compound Identification

All reported compounds were correctly identified and met retention time criteria.

XI. Compound Quantitation and Reported CRQLs

Quantitations were verified and no discrepancies were found. The correct internal standards, quantitation ions, and RRFs were used to quantitate compounds. Quantitation also reflected sample dilutions. Multiple analyses were performed for samples with high concentrations of TCE. One analysis was performed at a dilution to quantitate target anaytes within the calibration range of the instrument and the sample was also analyzed undiluted or at a lesser dilution in order to achieve lower reporting limits.

XII. Tentatively Identified Compounds (TICs)

Not applicable.

XIII. System Performance Checks

Not applicable.

XIV. Overall Assessment of Data

The reported data meets all acceptance criteria established in the functional guidelines and associated methods and plans. Data quality is sufficient for its intended use.

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Appendix A-3

Microbial Characterization Reports

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Microbial Analysis Report

Client:	Chris Lutes Arcadis 4915 Prospectus Dr., Suite F Durham, NC 27713	Phone: Fax:	919.544.4535 919.544.5690

MI Identifier: 10 agm Date Rec.: 5/8/03 Report Date: 6/17/03

Analysis Requested: PLFA, VFA, DGGE, and Dhc

Project: Vanderbery AFB/ Suite 35

Comments:

All samples within this data package were analyzed under U.S. EPA Good Laboratory Practice Standards: Toxic Substances Control Act (40 CFR part 790). All samples were processed according to standard operating procedures. Test results submitted in this data package meet the quality assurance requirements established by Microbial Insights, Inc.

Reported by: **Reviewed by:**

microbial insights

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Microbial Analysis Report

Executive Summary

The microbial communities from three groundwater samples were characterized according to their phospholipid fatty acid composition (PLFA analysis), their denaturing gradient gel electrophoresis profiles (DGGE), concentrations of volatile fatty acids (VFA), and the presence of *Dehalococcoides.* Results from this study revealed the following key observations:

- The three samples submitted for analysis were significantly different from each other by every parameter measured.
- Sample MW-14 was typical of shallow subsurface microbial communities. It had low biomass, a community structure dominated by Proteobacteria with biomarkers for Actinobacteria and Eukaryotes. The single organism detected by DGGE in this sample was a common soil aerobe, *Microbacterium*.
- Sample MW-20 showed signs of high anaerobic metabolic activity. It had a relatively high biomass, its community structure was dominated by terminally branched fatty acids, it showed evidence of starvation, and the bacteria detected were all close relatives of the anaerobe *Bacteroides*. This is also the only sample to have detectable amounts of VFA. The characteristics of this sample are consistent with an addition of available carbon to the subsurface, leading to increased biomass and anaerobic conditions.
- Sample MW-7 is yet again different, and somewhat more unusual. By PLFA and VFA analysis, it was similar to MW-14. However, five sequences were detected by DGGE, all of them closely related to *Sulfuricurvum*. This organism was isolated from subsurface petroleum reservoirs. It is an anaerobe to microaerophile, oxidizing sulfur, sulfide, and probably organo-sulfur compounds for its energy.

Overview of Approach

Phospholipid Fatty Acid Analysis

Determination of the phospholipid fatty acids (PLFA) in environmental samples is an effective tool for monitoring microbial responses to their environment. They are essential components of the membranes of all cells (except for the Archea, a minor component of most environments), so their sum includes all important actors of most microbial communities. There are four different types of information in PLFA profiles – biomass, community structure, diversity, and physiological status.

Biomass: PLFA analysis is the most reliable and accurate method available for the determination of viable microbial biomass. Since phospholipids break down rapidly upon cell death (21, 23), the PLFA biomass does not contain 'fossil' lipids of dead cells. The sum of the PLFA, expressed as picomoles (1 picomole = 1×10^{-12} mole), is proportional to the number of cells. The proportion used in this report, 20,000 cells/pmole, is taken from cells grown in laboratory media, and varies somewhat with type of organism and environmental conditions. Starving bacterial cells have the lowest cells/pmol, and healthy eukaryote cells have the highest.

Community Structure:. The PLFA in an environmental sample is the sum of the microbial community's PLFA, and reflects the proportions of different organisms in the sample. PLFA profiles are routinely used to classify bacteria and fungi (19) and are one of the characteristics used to describe new bacterial species (25). Broad phylogenic groups of microbes have different fatty acid profiles, making it possible to distinguish between them (4, 5, 22, 24). Table 1 describes the six major structural groups employed in this report.

Table 1. Description of PLFA structural groups.

PLFA Structural Group	General classification
Monoenoic (Monos)	Abundant in Proteobacteria (Gram negative bacteria), typically fast growing, utilize many carbon sources, and adapt quickly to a variety of environments.
Terminally Branched Saturated (TerBrSats)	Characteristic of Firmicutes (Low G+C Gram-positive bacteria), and also found in Bacteriodes, and some Gram-negative bacteria.
Branched Monoenoic (BrMonos)	Found in the cell membranes of micro-aerophiles and anaerobes, such as sulfate- or iron-reducing bacteria
Mid-Chain Branched Saturated (MidBrSats)	Common in Actinobacteria (High G+C Gram-positive bacteria), and some sulfate-reducing bacteria.
Normal Saturated (Nsats)	Found in all organisms.
Polyenoic	Found in Eukaryotes such as fungi, protozoa, algae, higher plants, and animals.

Diversity: The diversity of a microbial community is a measure of the number of different organisms and the evenness of their distribution. Natural communities in an undisturbed environment tend to have high diversity. Contamination with toxic compounds will reduce the diversity by killing all but the resistant organisms. The addition of a large amount of a food source will initially reduce the diversity as the opportunists (usually Proteobacteria) over-grow organisms less able to reproduce rapidly. The formulas used to calculate microbial community diversity from PLFA profiles have been adapted from those applied to communities of macro-organisms (8).

Physiological status: The membrane of a microbe must adapt to the changing conditions of its environment, and these changes are reflected in the PLFA. Toxic compounds or environmental conditions that disrupt the membrane cause some bacteria to make trans fatty acids from the usual cis fatty acids (7). Many Proteobacteria and others respond to starvation or highly toxic conditions by making cyclopropyl (7) or mid-chain branched fatty acids (20). The physiological status biomarkers for

Toxic Stress and Starvation/Toxicity are formed by dividing the amount of the stress-induced fatty acid by the amount of its biosynthetic precursor.

PLFA were analyzed by extraction of the total lipid (21) and then separation of the polar lipids by column chromatography (6). The polar lipid fatty acids were derivatized to fatty acid methyl esters, which were quantified using gas chromatography (15). Fatty acid structures were verified by chromatography/mass spectrometry and equivalent chain length analysis.

Volatile Fatty Acids

The volatile fatty acids (VFA) pyruvate, lactate, formate, acetate, propionate, and butyrate are used as biomarkers of anaerobic metabolism. Anaerobic bacteria produce these compounds by fermentation, while under aerobic conditions these compounds are rapidly oxidized for carbon and energy by aerobic bacteria. The VFA are analyzed by ion chromatography.

Denaturing gradient gel electrophoresis (DGGE)

Denaturing gradient gel electrophoresis (DGGE) is a powerful tool for detection and identification of organisms from environmental samples (1, 18, 12). In this method, sample microbial DNA is first isolated and purified. The DNA sequence for the Bacterial 16S ribosomal RNA (rDNA) is then amplified (many copies are made) using the polymerase chain reaction. The 16S rDNA gene is used for bacterial identification since it is common to all bacteria, and there are large databases of sequences available for comparison. The amplified sequences are separated into bands using a denaturing gradient gel. Numerically dominant members of the microbial community (>1 to 2% of the community) can be detected, so the bacterial identifications reported are examples of abundant members of the microbial community. For each sequenced DNA band, the closest described relative of each is reported. Phylogenetic affiliations are determined by comparing the rDNA sequences from samples to known bacterial sequences in the National Center for Biotechnology Information database (GenBank) (13). Recent progress in classifying Bacteria has caused many of the names used for bacteria and groups of bacteria to be changed. This can be a source of confusion since most scientists and engineers were trained when the earlier nomenclature was used. Table 2 shows the current names used in this report, and the corresponding traditional terminology.

Table 2. Names for bacteria and bacterial groups used in this report and the corresponding traditional forms.

Current Names	Traditional Names
Phylogenic Groups	
Actinobacteria	High G+C Gram positive bacteria such as Actinomycetes, Mycobacterium, Rhodococcus
Eukaryotes	Fungi, protozoa, algae, flowering plants, and animals
Firmicutes	Low G+C Gram positive bacteria such as *Bacillus* and *Clostridium*
Proteobacteria	Gram-negative bacteria

Targeted Gene Detection:

Specific primers directed to a conserved region of the 16S rRNA gene of Dehalococcoides were used to determine its presence. Based upon Loffler *et al*. (2) the sensitivity of these primers is ~10^3 cells/mL or g of sample. Cloned *Dehalococcoides* 16S rDNA was used as a positive control to verify test results.

Results and Discussion

Phospholipid Fatty Acid Analysis

Biomass estimates, as determined by the total concentration of PLFA, were highest in sample MW-20. Overall, biomass concentrations ranged from ~10^4 to ~10^6 cells/mL..

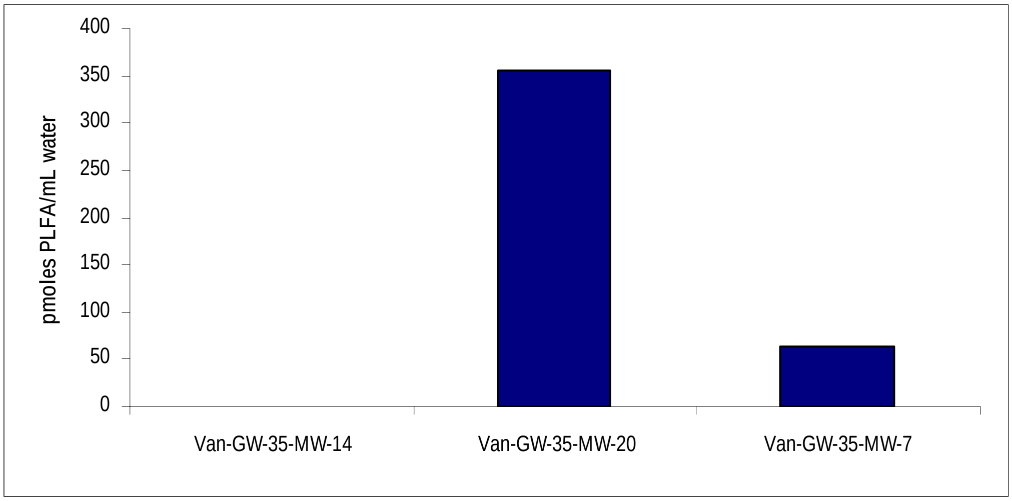

Figure 1. Biomass content is presented as the total amount of phospholipid fatty acids (PLFA) extracted from a given sample. Total biomass is calculated based upon PLFA attributed to bacteria and eukaryotic biomass (associated with higher organisms).

The PLFA profiles showed that samples MW-14 and MW-7 were primarily composed of Gram negative proteobacteria (indicated by the percentage of monoenoic PLFA). Proteobacteria are particular interest in contaminated environments due to their ability to utilize a wide range of carbon sources and adapt quickly to changes in their environment.

Sample MW-20 was dominated by terminally branched saturated PLFA (50.0%). Terminally branched saturates are most commonly due to Firmicutes and other groups such as *Bacteroides*. Increased proportions of terminally branched PLFA are often seen in environmental transects from aerobic to more anaerobic conditions.

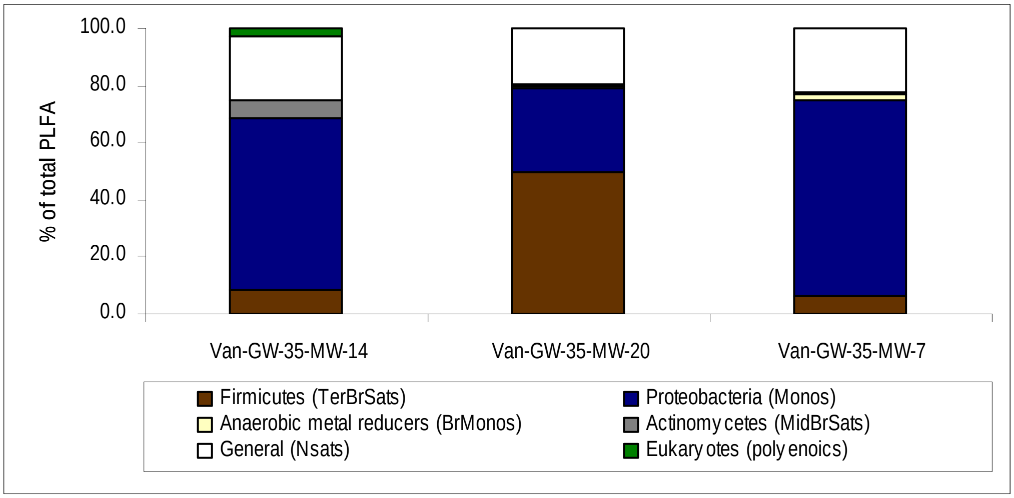

Figure 2. Relative percentages of total PLFA structural groups in the samples analyzed. Structural groups are assigned according to PLFA chemical structure, which is related to fatty acid biosynthesis. See Table 1 for detailed descriptions of structural groups.

Physiological status biomarkers indicated that sample MW-20 was notably more starved than either of the other samples, and was the only sample responding to environmentally induced stress.

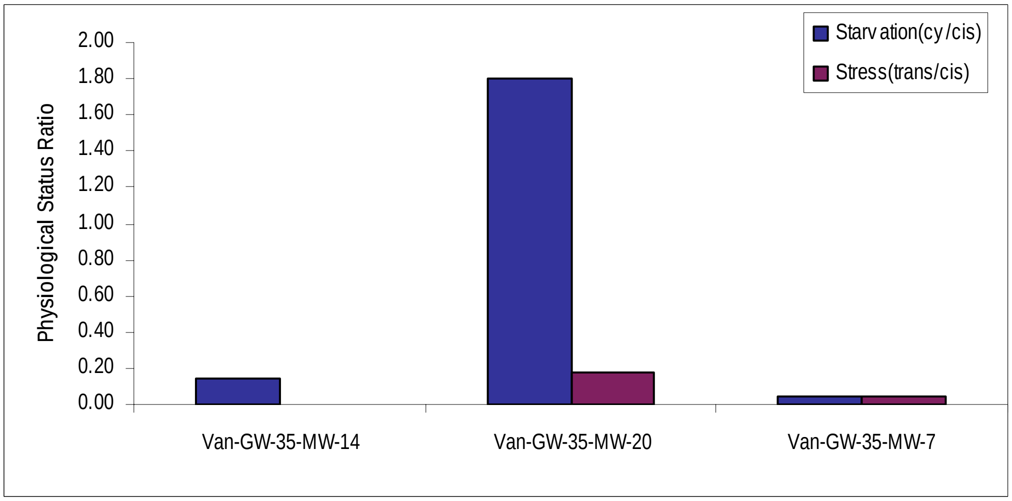

Figure 3. Microbial physiological stress markers. Starvation biomarker for the Gram-negative bacterial community is assessed by the ratio of cyclopropyl fatty acids to their metabolic precursor. Adaptation of the Gram-negative community to toxic stress is determined by the ratio of ω7t/ω7c fatty acids. Gram-negative bacteria generate *trans* fatty acids to minimize the permeability of their cellular membranes as an adaptation to a less favorable environment. Ratios (16:1ω7t/16:1ω7c and 18:1ω7t/18:1ω7c) greater than 0.1 have been shown to indicate an adaptation to a toxic or stressful environment, resulting in decreased membrane permeability.

Table 3. Values below are: viable microbial biomass expressed as picomoles of PLFA per mL of sample and as cells per mL of sample, fatty acid structural groups as percent of total PLFA, and physiological status biomarkers as mole ratio. "-" indicates data not available.

Samples		Biomass		Community Structure (% of total PLFA)						Physiological Status	
Sample Name	Sample Date	pmol/mL	cells/mL	Firmicutes (TerBrSats)	Proteobacteria (Monos)	Anaerobic metal reducers (BrMonos)	Actinomycetes/ SRB (MidBrSats)	General (Nsats)	Eukaryotes (polyenoics)	Starved cy/cis	Membrane Stress, trans/cis
Van-GW-35-MW-14	5/5/03	1	2.03E+04	8.1	60.7	0.0	6.3	21.9	3.0	0.14	0.00
Van-GW-35-MW-20	5/5/03	356	7.11E+06	50.0	29.0	0.8	0.6	19.5	0.1	1.80	0.18
Van-GW-35-MW-7	5/5/03	63	1.26E+06	6.5	68.5	1.7	1.3	21.8	0.3	0.05	0.05

Volatile Fatty Acids

MW-20 was the only sample containing metabolic acids present in detectable levels.

Table 4. Detection of Volatile fatty acids.

		Metabolic Acids (mg/L)					
Sample Name	Sample Date	Pyruvic	Lactic	Formic	Acetic	Proprionic	Butyric
MW-14	5/5/03	<4	<1	<1	<1	<1	<1
MW-20	5/5/03	<4	<1	<1	1407	493.6	516.8
MW-7	5/5/03	<4	<1	<1	2.1	<1	<1

Denaturing gradient gel electrophoresis (DGGE)

The DGGE profile (representing the bacterial composition of each sample) showed notable differences between each sample (Figure 4). MW-14 exhibited a very faint profile with few prominent bands, due to the low biomass in this sample. Band A was found to be a novel sequence with no close relatives. Band B was closely related to the genus *Microbacterium*. The genus *Microbacterium* has been reclassified and now only contains those organisms containing predominantly mid-chain branched fatty acids. Members of this genus are saprophytic, phytopathogenic and their metabolism is entirely (or primarily) aerobic.

Sample MW-20 contained several prominent bands (labeled C through G) the majority of which were associated with the genus *Bacteriodes.* Members of the genus *Bacteroides* are obligate anaerobic Gram negative bacteria, which produce high levels of acetate and succinate as metabolic end products. Members of *Bacteroides* have recently been identified as organic pollutant degraders, but falling outside of the bacterial groups typically isolated for biodegradation. The presence of Bacteroidetes is also reflected in the high proportions of terminally branched saturates in the PLFA results.

MW-7 contained five bands which produced usable sequence information all of which matched the same sequence recovered as a sulfur-oxidizing chemolithotroph growing on crude oil under anaerobic conditions and falling in the genus *Sulfurospirillum*.

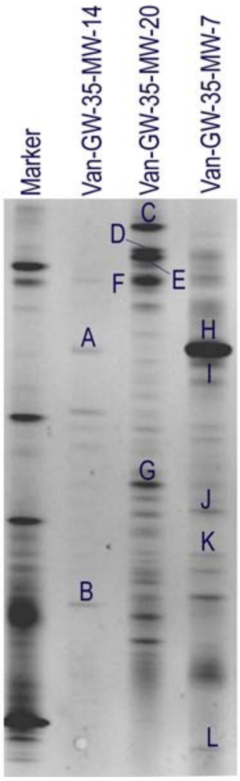

Figure 4. DGGE gel image of genes copied from a portion of the bacterial domain which provides phylogenetic information. Banding patterns and relative intensities of the recovered bands provide a measure of change in the community. Bacteria must constitute at least 1-2% of the total bacterial community to form a visible band. Labeled bands were excised and sequenced. Results from sequencing can be found in the following table.

Table 5. Sequence results from bands excised from Figure above. Identifications are based on DNA sequences in the Ribosomal Database Project (RDP). Similarity indecies above .900 are considered excellent, .700-.800 are good and below .600 are considered to be unique sequences.

Band	Closest Match	Match	Phylogenetic Affiliation	GenBank Accession Number	Ref.
A	Novel	-	-	-	-
B	*Microbacterium sp.*	0.721	Actinobacteria	AF263564	
C	*Bacteroidales str.*	0.901	Bacteroidetes	AB078832	
D	Bacteriodes sp.	0.737	Bacteroidetes	AB021157	-
E	*Bacteroidales str.*	0.965	Bacteroidetes	AB078832	
F	*Bacteroidales str.*	0.958	Bacteroidetes	AB078832	
G	unsequencable	-	-	-	-
H	*Sulfuricurvum sp.*	1.000	Proteobacteria	AB080644	
I	*Sulfuricurvum sp.*	0.899	Proteobacteria	AB080644	
J	*Sulfuricurvum sp.*	0.944	Proteobacteria	AB080644	
K	*Sulfuricurvum sp.*	0.884	Proteobacteria	AB080644	
L	*Sulfuricurvum sp.*	0.953	Proteobacteria	AB080644	

Targeted Gene Detection

None of the samples submitted for analysis were positive for the presence of *Dehalococcoides.*

Table 6. Results from DNA amplification using primers specific for *Dehalococcoides ethenogenes*. Specific primers directed to a conserved region of the 16S rRNA gene of *Dehalococcoides ethenogenes* were used to determine its presence. The sensitivity of these primers is ~10^3 cells/mL or g of sample. Presence is noted with a plus sign, and the relative abundance is presented by the number of plus signs.

Sample	Dehalococcoides ethenogenes
MW-14	-
MW-20	-
MW-7	-
Dehalococcoides etheneogenes positive control	+++
E.coli negative control	-

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Microbial Insights. Inc.

Client: Chris Lutes/Arcadis
Project: Vandenberg AFB Site 35
Date Received: 5/8/2003

Sample Name	Van-GW-35-MW-14	Van-GW-35-MW-20	Van-GW-35-MW-7
Sample Date	5/5/2003	5/5/2003	5/5/2003
Amount of Water Filtered ml	1,054	1,040	1,038
MI Identifier	10agm1	10agm2	10agm3
Total Picomoles of PLFA[1]	1,070	369,970	65,459

Analytical Report

PLFA Profile (% of total PLFA)

	Equivalent Chain Length			
Terminally Branched Saturates (TerBrSats)				
i14:0	13.58	0.0	2.6	0.2
i15:0	14.61	1.5	2.7	2.4
a15:0	14.69	1.7	26.5	1.9
i16:0	15.62	1.4	7.2	0.8
i17:0	16.63	1.2	0.4	0.4
a17:0	16.72	2.4	10.4	0.8
i19:0	18.63	0.0	0.1	0.0
		8.1	50.0	6.5
Monoenoics (Monos)				
15:1w6c	14.77	0.0	0.2	0.2
16:1w9c	15.69	1.4	1.0	0.4
16:1w7c	15.75	15.6	2.5	43.6
16:1w7t	15.78	0.0	0.3	1.4
16:1w5c	15.83	1.1	0.4	3.0
17:1w6c	16.79	0.0	1.1	0.7
cy17:0	16.81	0.0	4.4	1.2
18:1w9c	17.68	10.5	0.8	0.7
18:1w8c	17.72	6.6	0.0	0.0
18:1w7c	17.75	22.3	13.7	16.7
18:1w7t	17.79	0.0	1.0	0.2
18:1w6c	17.82	0.0	0.4	0.0
18:1w5c	17.84	0.0	0.1	0.2
19:1a	18.68	0.0	0.1	0.0
19:1w6c	18.81	0.0	2.3	0.1
cy19:0	18.85	3.1	0.7	0.3
		60.7	29.0	68.5
Branched Monoenoics (BrMonos)				
i16:1a	15.41	0.0	0.1	0.2
i17:1w7c	16.37	0.0	0.4	1.4
br19:1a	18.05	0.0	0.1	0.1
br19:1b	18.08	0.0	0.3	0.0
		0.0	0.8	1.7

Mid-Chain Branched Saturates (MidBrSats)				
br16:0	16.06	5.2	0.0	0.2
10me16:0	16.44	1.0	0.2	0.9
12me16:0	16.51	0.0	0.1	0.0
br17:0a	17.04	0.0	0.1	0.0
10me17:0	17.41	0.0	0.1	0.1
11me17:0	17.46	0.0	0.1	0.1
		6.3	0.6	1.3
Normal Saturates (NSats)				
14:0	13.98	0.0	3.6	1.6
15:0	14.99	0.0	2.0	0.4
16:0	15.99	16.0	13.0	19.0
17:0	16.99	0.0	0.4	0.3
18:0	17.99	5.9	0.5	0.4
		21.9	19.5	21.8
Eukaryotes				
18:2w6	17.59	1.9	0.0	0.2
20:4w6	19.20	1.1	0.0	0.0
20:1w11c	19.66	0.0	0.1	0.0
20:1w7c	19.73	0.0	0.1	0.1
		3.0	0.1	0.3

Data Summary Sheet

Biomass:			
pmols PLFA/ml filtered	1	356	63
Cells/ml filtered	2.03E+04	7.11E+06	1.26E+06
picomoles prokaryote PLFA/ml	1	355	63
picomoles eukaryote PLFA/ml	0.0	0.5	0.2
ratio prokaryote:eukaryote	33	713	384
Metabolic Status: (Ratio)			
Starvation			
group A (cy17:0/16:1w7c)	0.00	1.75	0.03
group B (cy19:0/18:1w7c)	0.14	0.05	0.02
Total	0.14	1.80	0.05
Membrane Stress[2]			
group A (16:1w7t/16:1w7c)	0.00	0.11	0.03
group B (18:1w7t/18:1w7c)	0.00	0.07	0.01
Total	0.00	0.18	0.05
Community Structure: (% of Total PLFA)			
Firmicutes (TerBrSats)	8.1	50.0	6.5
Proteobacteria (Monos)	60.7	29.0	68.5
Anaerobic metal reducers (BrMonos)	0.0	0.8	1.7
Actinomycetes (MidBrSats)	6.3	0.6	1.3
General (Nsats)	21.9	19.5	21.8
Eukaryotes (polyenoics)	3.0	0.1	0.3

[1] method Modified Bligh & Dyer: Detection limit 7 pmoles total PLFA

[2] ratios > 0.1 adapting to environmentally induced stress

NA: Not Analyzed NC: Not Calculated ND: Not Detected

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Appendix A-4

Data Archiving and Demonstration Plans

Appendix A-4. Data Archiving and Demonstration Plans:

1.0 Data Formats

There are four broad classes of data that were collected in this project.

1. The field measurements of groundwater parameters (generally for biogeochemical conditions) and other field observations
2. Laboratory measurements of soil and groundwater parameters, both contaminants and indicators of biogeochemical conditions
3. Engineering data on the design and operation of treatment systems
4. Economic data on the treatment systems.

1.1 Class I Data. Class I data was recorded on standardized field forms, including groundwater sampling form, photograph log, daily log, well construction log, sample/core log, water sampling log, reagent injection log, chain of custody record, Hach analytical log, and soil core/sampling log as found in Appendix D of the demonstration plan.

Chain-of-custody procedures were followed as described in Sections 5.4.3.3 and 6.1 of the demonstration plan. A field log may also be used to supplement the forms with notes and drawings describing the location, field conditions, and method of sample collection and identification.

1.2 Class II Data. Class II data will generally be received in the form of formal reports from the analytical laboratories. Note however, ARCADIS also received almost all of the analytical data on concentrations in the form of electronic deliverables.

1.3 Class III Data. Class III data is of two types. Engineering designs were documented in AutoCAD files and printouts. Field operating data such as reagent doses, flow rates, and concentrations will be documented on standard forms in a manner similar to Class I data.

1.4 Class IV Data. Procedures for collection of class IV data are discussed in Section 7 of the demonstration plan.

2.0 Data Storage and Archiving Procedures

2.1 Class I Data Storage. Class I data form originals will be retained in the office local to the site (the Fullerton office near Los Angeles CA). The field note originals will be maintained at the location of Fullerton, office. Copies of these documents are maintained in the file storage warehouse associated with the Durham, North Carolina, office.

2.2 Class II Data Storage. Class II data, as discussed above, were received and stored in both paper and electronic formats, initially at a central project archive to be maintained in the Durham, North Carolina, office of ARCADIS. It is also anticipated that the analytical laboratories involved will maintain their own copies of this data set for a period of years. However, this cannot be relied upon since firms in the analytical laboratory business have a history of rapid change.

2.3 Class III Data Storage. Class III engineering design data will be archived to the central project file following preparation. Copies will also be maintained in any office preparing engineering designs. Field operating data will be handled in the same manner as class I data.

2.4 Class IV Data Storage. Class IV data will be collected as discussed in Section 7 of the demonstration plan and archived to the central project file in the Durham, North Carolina, office of ARCADIS.

2.5 Archiving Procedures. The central hardcopy project archives at the Durham, North Carolina, office of ARCADIS will be maintained largely on site until the final reports are finalized for this project. This archive will include all data, documentation, records, protocols, reports, and correspondence. The archive will be transferred off-site at the completion of the project and stored for at least five years in a commercial file storage warehouse operated by Iron Mountain, Inc., 130 Nova Drive, Morrisville, North Carolina. The masonry and steel construction of this facility protects from most natural and human threat. Iron Mountain is the sole tenant of the facility, thus eliminating any conflicts associated with a multi-tenant facility. The facility can only be accessed by card key entry. Only those on the authorized list have access to the facility. The facility is monitored 24 hours a day, 365 days a year, by Sonitrol Security Systems. They employ the following type of security measures: motion, sound, smoke and heat detectors, as well as laser-trigger alarms. The facility is protected against fire by an Early Suppression Fast Response (ESFR) 6 ln. CSC Central sprinkler system. Their current operating system for records management is Total Recall by DHS Associates, Inc., of Orange Park, Florida. A back up tape for the Iron Mountain Facilities records is created daily and sent off site to a secure vault location to ensure that the data is protected and can be restored in the event of an emergency. The property the facility is on has been determined by FEMA, as of March 3, 1992, to be located in the 500-year flood plain, Zone X on map number 37183CO284E, community number 370242 and 550 feet from the 100-year flood plain.

The central electronic project archive will also be maintained in the Durham, North Carolina, office of ARCADIS on the central office server. The directory that will be used is accessible only to the project manager, system administrator, and a small group of his direct reports. This server is backed up to tape daily by the system administrator; these tapes are maintained for at least three weeks. The server is backed up to tape monthly and these tapes are permanently retained. Tape storage takes place in an on site fire proof cabinet. At the completion of this project ARCADIS anticipates placing the primary data tables on CD for ease of storage and access.

2.6 Data Availability Following Key Personnel Changes. In order to ensure data availability following key personnel changes, the project manager will be notified of any change in the employment status of that employee either by the employee or their direct supervisor (such as an office manager). The project manager will immediately take action as appropriate in conjunction with operations management to ensure the integrity and readability of all data. Should the transition affect the project manager himself for some unanticipated reason, the principal investigator and quality assurance officer would work together to ensure the integrity and readability of all data.

3.0 Demonstration Plan Availability

These are available as needed from Chris Lutes, the ARCADIS Project Manager, whose contact information is in Appendix A.

Appendix C-1

Quality Assurance Project Plan
(Chapter 9 of Technology Demonstration Plan)

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Technology Demonstration Plan
Vandenberg Air Force Base

TECHNOLOGY DEMONSTRATION *IN-SITU* SUBSTRATE ADDITION TO CREATE REACTIVE ZONES FOR TREATMENT OF CHLORINATED ALPHATIC HYDROCARBONS

Prepared by:

ARCADIS Geraghty & Miller, Inc.
P.O. Box 13109
Research Triangle Park, NC 27709

April 11, 2000

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9. Quality Assurance Plan

9.1 Purpose and Scope of the Plan

This QA Plan delineates our approach for monitoring the demonstration to ensure that the facilities, equipment, personnel, methods, practices, records, and controls are in conformance with ESTCP-approved data quality objectives. In addition to preparing this QAPP, ARCADIS Geraghty & Miller's Research Triangle Park Office, the lead office for this project, operates under a quality system that is described in an office Quality Management Plan written according to ANSI/ASQC E4-1994 *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs.*

9.2 Quality Assurance Responsibilities

The ARCADIS Geraghty & Miller Program Manager/Principal Investigator has the following QA responsibilities:

- Review Demonstration QA Project Plan, Sampling Plans, Test Plans, etc.
- Serve as the project's liaison with senior corporate management to ensure the assignment of adequate resources
- Review decisions about major corrective actions
- Review Final Report and Cost & Performance Report
- Serve as the primary quality assurance reviewer and authority for engineering design and geologic matters. Will be assisted in this regard by personnel licensed in states where Mr. Palmer is not licensed

The ARCADIS Geraghty & Miller Project Manager has the following QA responsibilities:

- Coordinate preparation of Demonstration QA Project Plan, Sampling Plans, Test Plans, etc.
- Ensure personnel assigned to project are adequately trained
- Ensure activities are carried out as planned and deviations are documented
- Ensure equipment and instrumentation is calibrated and in good working condition
- Initiate corrective action procedures
- Communicate any problems or deviations from plan to the QA Officer
- Coordinate preparation of Final Report and Cost & Performance Report

The ARCADIS Geraghty & Miller QA Officer for this demonstration has the following responsibilities:

- Review and approve Demonstration QA Project Plan, Sampling Plans, Test Plans, etc.
- Perform periodic audits to ensure demonstration is conducted as planned and any deviations from plan or standard methods are adequately documented
- Report any audit findings or problems to the Project Manager
- Review laboratory data and ensure it is supported by appropriate QA/QC information
- Review Final Report and Cost & Performance Report to ensure that is accurately describes the methods and standard operating procedures, and that the reported results are supported by raw data

It is the responsibility of the Project Manager and Deputy Project Manager to ensure that required QA/QC documentation is in place before any demonstration activity is begun and that documented QA/QC activities are carried out in all phases of the demonstration. Christopher Lutes is the Project Manger and Don Kidd is the Deputy Project Manager for this demonstration. Project Management is responsible for ensuring that staff members are adequately trained to perform assigned duties.

Ms. Laura Beach is the Data Quality Assurance Officer for the IRZ demonstration. Ms. Beach is the QA Manager for ARCADIS Geraghty & Miller’s Technology Services Division. She has more than 10 years of experience in providing QA support to government contracts (for example, USEPA-APPCD, USEPA Environmental Technology Verification Program, NFESC Innovative Technology Project and USAF Environics Directorate Support) and is very familiar with the QA/QC activities required to support them. The Data Quality Assurance Officer will assume responsibility for, or assign an on-site QA representative to perform QA support activities during the demonstration. Any designated QA representative will report regularly to Ms. Beach and will be jointly responsible for ensuring that QA tasks meet contractual requirements as well as the requirements that are established in the ARCADIS Geraghty & Miller Raleigh RTP Office Quality Management Plan referenced earlier. The Data Quality Assurance Officer’s responsibilities include support in the preparation and review of this work plan, conducting internal systems and/or performance audits, QA/QC reporting, and involvement in the correction of any issues leading to data quality concerns.

As Project Managers, Mr. Lutes and Mr. Kidd will openly communicate with both Ms. Beach and the senior project advisors. The assigned Engineering and Biogeochemical Assessment Team Leaders for the IRZ demonstration are Mike Hansen and Jeffrey Burdick respectively. Project personnel including both Team Leaders, other technical staff, and field technicians are expected to work closely with the Data Quality Assurance Officer to ensure that QA/QC activities are adequate and that any problems are identified and corrected. Corrective actions are initiated by the Team Leader Project Manager and reported to both the Principal Investigator and the Data Quality Assurance Officer.

It is the intention of ARCADIS Geraghty & Miller that communications about data quality flow freely both up and down the organizational chart during the demonstration. Past experience in ARCADIS Geraghty & Miller suggests that it is imperative to include field level personnel in communications pertinent to data quality. This open communication to and from field staff will aid in ascertaining the quality of the data generated during the effort.

9.3 Data Quality Parameters

Table 5 contains goals for the data quality parameters accuracy, precision, and completeness for the analytical measurement process. The table incorporates data quality goals for field analysis (temperature, ORP, pH, and dissolved oxygen) and for fixed laboratory based analysis. Thus, this table has been compiled with input from ARCADIS Geraghty & Miller as well as from the two analytical laboratories that will conduct laboratory based analyses for analytes stable enough to be shipped.

ARCADIS Geraghty & Miller and its subcontract analytical laboratories will rely primarily on timely servicing and appropriate calibration of analytical instruments to attain the accuracy goals listed in Table 5. With the possible exception of hydrogen analysis, the analyte list contains parameters that have been chemically quantified for many years in environmental media. As a result, correctly performed analysis of these parameters is capable of generating the accuracy needed to guarantee the success of this demonstration.

It is important to attain the accuracy goals contained in Table 5 for the listed analytes so as to facilitate inter-comparison of analytical results from multiple collection points at individual demonstration sites. The IRZ technology is expected to affect/generate trends in the groundwater analytes listed in Table 3 within each reactive zone. The trends generated by molasses injection are important in determining the size and bacterial community characteristics of the reactive zone over time.

ARCADIS Geraghty & Miller routinely checks the precision of its analytical field instruments as a course of collecting data during low flow well sampling activities. The procedure universally utilized is to purge the well being sampled and then begin pumping the groundwater through a low-flow, flow-through sample cell where it comes into contact with probes that are calibrated for the parameters of interest. The groundwater is pumped through the sample cell until the readings for the parameters of interest stabilize with the precision guidelines found in Table 5. Thus, precision is determined at the completion of the period required for the parameter readings to stabilize. Likewise, the contract analytical laboratories chosen for this project are accustomed to goals similar to those shown in Table 5. Accuracy, Precision, and Completeness Measures for Analytical Parameters are routinely determined in keeping with their commitment to quality control.

Representativeness of groundwater samples is assured by careful well placement and through purging of each well prior to sample collection. ARCADIS Geraghty & Miller's assessment of site geology and hydrogeology is essential to verification of appropriate well placement. ARCADIS Geraghty & Miller has commenced this assessment using available data from individual site characterization efforts and will complete the effort in the course of establishing initial site conditions during the first round of biogeochemical analyses. The purging of groundwater wells is a part of the sampling procedures to be utilized at the demonstration sites. Purging of the wells insures that the chemical properties of the groundwater collected for analysis has not altered as a function of residence time within the well casing itself.

The use of identical analytical methodologies during the conduct of work at four demonstration sites will support the comparability of the data gathered during this project. This standardization of analytical methods is important so that the economics of IRZ implementation at the four sites can be delineated and reported to ESTCP/AFCEE.

9.4 Calibration Procedures, Quality Control Checks, and Corrective Action

Calibration procedures for the standard EPA and ASTM methods are covered fully in those methods. Copies of the methods are available upon request.

9.4.1 Dissolved Gas Methods - Fixed Facilities. The dissolved gas methods referred to above are provided in full in Appendix B. In short the light hydrocarbon method calls for a three point external calibration with calibration standards prepared from commercial certified gas standards traceable to the National Institute of Standards of Technology standards. The carbon dioxide method uses triplicate external calibration points with calibration standards prepared from commercially available certified gas standards traceable to National Institute of Standards of Technology standards. The hydrogen method uses a 7 point external calibration with calibration standards prepared from commercial certified gas standards. The laboratory data package provided by VaporTech includes initial calibration, continuing calibration check results (control limit is +/-20%), case narrative, chain of custody and laboratory blank results. There are no established holding times for these analyses. Vapor Tech uses the 7 day VOA unpreserved holding time for the light hydrocarbons and carbon dioxide, and has demonstrated the adequacy of a 28 day holding times for hydrogen. Since the calibration is performed with gas standards, and analyses from liquid samples, it is generally not possible for Vapor Tech to report laboratory control spikes or matrix spikes. Vapor Tech will provide Excel compatible electronic deliverables which can be directly used by ARCADIS Geraghty & Miller to prepare final data tables following validation.

9.4.2 Chemical Fixed Facility Measurements. Quanterra's QC protocols include the following:

- Minimum of one method blank is analyzed per 20 samples to detect contamination during preparation and/or analysis
- Laboratory Control Sample (LCS) consisting of target analytes spiked into a inert matrix is analyzed every 20 or fewer investigative samples. The LCS is used to monitor the laboratory's day to day as well as ongoing performance of the applicable analytical methods
- Matrix spikes and matrix spike duplicates (MS/SD) for organic analyses and matrix spikes and matrix duplicates (MS/DU) or MS/SD's for inorganic analyses will be analyzed every 20 or fewer samples to determine the effect of the matrix on the method performed. Due to the potential variability of the matrix, the MS/SD results may have bearing on the specific sample spiked and not all samples in the batch
- Internal and surrogate standards will be added where appropriate to quantitate results, determine recoveries and to account for sample-to-sample variation

Calibration of instrumentation will be determined according to the appropriate EPA methods.

The Quanterra data reports will contain the following items:

1. Case Narrative
    a. Date of issuance
    b. Laboratory analysis performed
    c. Any deviations from intended analytical strategy
    d. Laboratory batch number
    e. Numbers of samples and respective matrices
    f. Quality control procedures utilized and references to the acceptance criteria
    g. Laboratory report contents
    h. Project name and number
    i. Condition of samples received
    j. Discussion of whether or not sample holding times were met
    k. Discussion of technical problems
    l. Signature of Laboratory Project Manager

2. Chemistry Data Package
    a. Case narrative for each analyzed batch of samples
    b. Cross reference of laboratory sample to project sample identification numbers
    c. Sample results with sample preparation and analysis dates
    d. Raw data for sample results and laboratory quality control samples
    e. Initial and continuing calibration checks, GC/MS tunes
    f. Matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, calibration check compounds, system performance check compounds
    g. Labeled and dated chromatograms and spectra of sample results and laboratory quality control checks

The data package will include a full CLP-like deliverable package without CLP forms.

Quanterra will provide an ASCII comma delimited electronic deliverable.

9.4.3 Geotechnical Fixed Facility Measurement. Calibration procedures for the ASTM particle size methods are included in the method. Essentially the only required calibration is on a balance. The balance calibration will be reported with that data set. The sieve screens are ‘calibrated’ by the manufacturer and inspected by the laboratory for tears before use.

9.4.4 Field Measurements. Calibration procedures for field instruments are included in Appendix F ARCADIS Geraghty & Miller Field Instrument Standard Operating Procedures Manual.

9.4.5 Data Validation.

Formal validation will be performed on measurements of the contaminants but only a rapid review of data quality indicators will be performed for the other biogeochemical parameters. Site by site final reports and a cost and performance report will be prepared in accordance with ESTCP formats. It is anticipated that these reports will include both tabular and graphical depictions of the data collected.

9.5 Demonstration Procedures

9.5.1 Start-up. Start-up activities for the demonstration will be limited. Initiation of the demonstration will begin with the collection of the baseline groundwater monitoring data (as outlined in Section 5.4). This will be followed by the initial reagent solution injection in the injection well network. Upon completion of the baseline data collection and initial reagent injection the demonstration will move into the technology maintenance phase.

9.5.2 Technology Maintenance. Please see section 5.3.9.

9.5.3 Corrective Actions. Corrective action with regard to analytical measurements has been discussed in section 6.1. Corrective action with regard to system operation is covered in section 5.3.8.

9.6 Calculation of Data Quality Indicators

Calculation of Data Quality Indicators

Accuracy

Accuracy can be expressed as percent bias from a known standard or percent recovery based upon known spiked amounts. Percent bias is calculated using the following equation:

%Bias =[known value – obtained value)/known value] * 100

Percent recovery is calculated by:

%Recovery = [measured value/spiked amount] * 100

Precision

Precision, expressed as relative standard deviation (RSD) between replicate measurements can be determined using the formula:

%RSD = standard deviation of replicate measurements/average *100

Completeness

Completeness is defined as the number of acceptable measurements compared to the number of total measurements taken expressed as percent. Acceptable measurements are defined as measurements that fall within data quality indicator goals for accuracy and precision.

Comparability and Representativeness

Comparability is defined as the degree to which different methods, data sets, and/or decisions agree or can be represented as similar. The methods used to obtain data and the manner in which data is presented will be consistent throughout this program to ensure comparability between data sets.

Representativeness is defined as the degree to which data accurately and precisely represent the frequency distribution of a specific variable in the population. A great deal of thought will be spent by the Principal Investigators at each site to ensure that the data obtained is representative. Issues that will be assessed are the number and location of wells with regard to the plume at each site, the number of samples taken, and the analytes present at each site.

9.7 Performance and System Audits

Performance and Systems Audits. The ARCADIS Geraghty & Miller QA Officer, or her designee, routinely performs audits to ensure that projects are performed according to plan and that acquired environmental data is of a known and defensible quality. Audits performed by ARCADIS Geraghty & Miller on ARCADIS Geraghty & Miller projects are considered internal audits. Audits performed by a third party or by EPA are considered external audits.

An internal technical systems audit (TSA) for at least one site will be performed during the early stages of this demonstration. The QA Officer will use this QA Project Plan as a basis for the TSA checklist, in addition to the standard methods used for sampling and analysis. The purpose of the technical systems audit is to ensure that the project is carried out as planned and that any deviations from the methods or plan are adequately documented. To reduce costs, the QA Officer may assign a Deputy QA Officer from an office located in close proximity to the sampling site to perform the field audit of sampling procedures. This Deputy QA Officer will be independent of the project and technically qualified to carry out this duty.

Analytical activities may be audited by providing the subcontracted laboratories with a performance evaluation audit (PEA) sample. The laboratories that are being used are routinely audited under EPA’s contract laboratory program and through ARCADIS Geraghty & Miller’s internal laboratory approval program. The date and results from the last audit performed at each laboratory will be requested. If they have not been audited within the last year, by EPA or ARCADIS Geraghty & Miller, analysis of PEA samples supplied blind by the ARCADIS Geraghty & Miller QA Officer will be required.

Contingency Laboratory. During the competitive bidding process discussed above contingency laboratories were identified. STL and IES can serve as contingency labs in case Quanterra is unable to perform. Microseeps can serve as a contingency laboratory in case vapor Tech is unable to perform. ARCADIS Geraghty & Miller can perform the particle size analysis in its own facility if WEA is unable to perform.

9.8 Quality Assurance Reports

Quality related problems will be addressed in monthly progress reports prepared by the Project Manager if data quality is compromised. Reports will detail any limitations on the data and any corrective actions that were implemented to resolve the problem.

Any findings, problems, or observations found through internal audits by the QA Officer will be reported directly to the Project Manager. Major concerns will be expressed on the day of the audit if immediate corrective actions are necessary. The QA Officer will submit an audit report to the Project Manager within 15 days of completion of any internal audit.

The final report for each site will contain a QA section which will specify the QA activities that were conducted at the site and the quality of data achieved. It will provide sufficient information to enable users to have confidence in the data. If the data have limitations, the QA section will detail those limitations. The QA section of the final report will also relate data to the established data quality objectives and data quality indicator goals and explain any significant differences.

It is anticipated that significant quality assurance issues will be discussed in monthly status reports and quarterly performance and cost reports as well as annual presentations. Therefore interested parties will be aware of these issues if any arise before completion of the final report.

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Appendix C-2

Addendum to Technology Demonstration Plan

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Ms Catherine Vogel, ESTCP
c/o HydroGeoLogic Inc.
Attn Susan Walsh
1155 Herndon Blvd, Suite 900
Herndon, VA
20170

TECHNOLOGY EVALUATION

Subject:
Amendment of Demonstration Plan dated April 10, 2000
For *In-situ* Substrate Addition to Create Reactive Zone for Treatment of Chlorinated Aliphatic Hydrocarbons: Vandenberg AFB, ESTCP Project #199920

Research Triangle Park,
10 July 2000

Contact:
Chris Lutes

Extension:
919-544-4535

Dear Ms. Vogel:

We were pleased to have the opportunity to sit down and discuss this project with you and your staff. We have outlined the response to these issues that you requested in your letter of May 6th and that we discussed on June 1st and July 7th. As we discussed, the general aim of these questions and responses is to provide a higher level of certainty for the evaluation of the technology at this site. Your major comments have been listed below in *italics* with our responses and discussion following in plain text.

Responses to ESTCP's Written Comments:

There are several substantive concerns with the work plan:

- *Comments made relative to other plans regarding the criteria to be used for success also apply here. That is, achieving closure via MNA status is not an appropriate criterion for this ESTCP technology demonstration project.*

Amend the relevant language in section 1.3 (page 5) and section 5.1 (pages 24 and 25) to read as follows:

"Specifically quantitative goals for effectiveness depend on the starting concentration of the contaminants at each site.

At sites with relatively high concentrations, i.e., > 200 ppb total CAHs
ARCADIS Geraghty & Miller seeks to achieve 80% removal of the contaminants in a one year treatment time-frame. This goal can be further specified as follows. If a

desorption induced spike occurs, then an 80% removal from the initial baseline concentration is also sought.

At sites with relatively low concentrations, i.e., < 200 ppb total CAHs
Implementation of the IRZ on lower concentration plumes may take one to five years. Thus, between 200 and 50 ppb, we seek to achieve 75% reduction in a one-year treatment time frame, and below 50 ppb, we seek to achieve 50% reduction in a one-year treatment time frame. Furthermore, ARCADIS Geraghty & Miller must show evidence that degradation of CAHs is not 'dead-ending' at undesirable end products such as vinyl chloride."

- *A specific statement is needed that describes the conditions at Vandenberg that differ from other test sites being used, and how those conditions impact the demonstration design and operation. All of the tests use different injection designs, but there is no discussion of the rationale for the designs used at different sites.*

We recommend that the discussion of this topic at the end of section 5.4.3.1 (pages 53-55) be amended to read as follows:

"Essentially for a pilot test the combination of injection and monitoring wells must be sufficient to create a reactive zone that is:

a) of sufficient size for a realistic field test

b) certain to include the locations of more than one monitoring well, preferably with the monitoring wells being located at different positions downgradient of the injection point so that the width and length of the reactive zone created can be estimated.

This objective can be achieved with different combinations of monitoring and injection wells. In general, since groundwater flow paths and dispersion can never be exactly predicted *a priori*, the larger the number of monitoring wells employed, the more likely it is that the effect of a single injection well will be accurately delineated. Conversely, the larger the number of injection wells employed, the more certain it is that a given number of optimally located monitoring wells will lie within the created reactive zone. Site-specific factors may influence this decision as well. At shallow sites with low permeability or gradient we have been successful using a large number of drive points or other low cost injection points (up to several hundred in some cases) to disperse the reagent rather than primarily relying on groundwater flow for this purpose.

In assessing the effectiveness of any *in-situ* technology, a similar trade off exists between the number of wells monitored and the frequency of that monitoring. Where large well networks exist or can be economically installed, one can achieve both statistical certainty about the effectiveness of the technology and information about the extent of the zone treated by using a substantial number of wells and close to the minimum number of observations required to demonstrate a concentration trend. Where lesser well networks exist and the cost of each well installation is very high (i.e. great depth, difficult geology), it can be reasonable to use a somewhat lesser number of wells but more frequent observations at each well. Thus, the concentration trends in each well can be established with greater statistical certainty, and it may be possible to discern something about the reaction rate and how it may be changing over time.

Finally, in designing an injection system, it can be advantageous to plan on frequent, low dose reagent injections, which can give the engineer the opportunity to carefully control the dosing on the basis of feedback from field parameters. However, it can also be argued that less frequent, higher dose injections can provide important economic advantages at some sites.

Thus, the designs outlined in Table 1 and in the figures provided in each work plan represent differing design solutions to the three tradeoffs discussed above in the context of site-specific factors. Although they undoubtedly reflect the hand of differing designers, we submitted them in the belief that

a) there can be a range of appropriate solutions to a single design problem, and
b) it is beneficial in this demonstration program to further explore some variations in implementation protocol.

Then, we will synthesize the wisdom gained from exploring some of these variations both at DoD sites and the numerous commercial sites listed in Table 2 before writing the draft protocol (scheduled in our proposal to begin approximately a year from now). In this context, the proposed design solution for Hanscom represents a fairly typical “baseline” design, which relies on a large number of monitoring wells to discern the impact of a single injection well with frequent injection. The system proposed at Badger is similar except that two injection wells and slightly fewer monitoring wells are used. Finally, Vandenberg AFB Site 9 was characterized by great depth, rough topography, limited roads, and sensitive biological and cultural resources that greatly limit the available well placements. Therefore, we chose to use an increased frequency of monitoring events in a lesser number of wells. However, site 35 has less sensitive biological and cultural resources and somewhat less difficult topography. Site 35, judging by the shape of the CAH plume, as currently known, seems to have a ratio of lateral vs. transverse dispersivity that may result in a relatively long, narrow reactive zone from any given well. Since the fine scale groundwater flow direction may be influenced by preferential flow paths, we have used three injection wells to create a reactive zone of reasonable width.

The test program design outlined in the April 10th work plan used four downgradient and one upgradient wells sampled on 7 occasions to attempt to define both the length and the width of the reactive zone formed. It attempted to economize on drilling and sampling costs be skewing the well network to the south, thus defining only the southern half of the anticipated reactive zone. As we have since discussed, we outline later in this document a recommendation for increasing the number of wells in this monitoring program."

- *The text describes a desorption flush that typically occurs, presumably because the molasses has surfactant-like properties, and/or it causes production of biosurfactants. Please discuss this phenomenon. How do we assure ourselves and others that the effects of molasses are not largely a "soil washing" effect? A mass balance approach seems essential. Please discuss this general concern, and consider the monitoring plan in light of this concern.*

The presence of an abundant source of easily degradable organic carbon, such as the carbohydrate substrate, typically results in a rapid and large increase in the population of microorganisms in the treatment zone. As in any microbiological system, this large population increase will also result in an increase in the production of natural biosurfactants by the microorganisms. These natural biosurfactants can in turn result in desorption of VOCs adsorbed to the aquifer media as the existing equilibrium conditions are disrupted and altered.

Although it may be considered that this surfactant effect is only "washing" the VOCs out of the impacted area, the VOCs will still ultimately be degraded within the reactive zone. In fact, the increased desorption of target constituents will actually allow for greater access to typically "untreatable" constituent mass – a benefit over conventional remedial techniques that treat only the dissolved phase. Thus, we want to "wash" the aquifer solids to remove material that otherwise would form a continuing source of groundwater contamination. Monitoring trends in concentrations of product species (such as DCE , VC, CA and ethene) vs. a tracer, is one way to attempt to separately quantify the degradation and the washing effects.

From a purely "closure-minded" perspective, what is typically required by regulatory agencies is that 1) concentrations downgradient ultimately go down long term and 2) any interim spike does not measurably increase risk at a sentinel well near the receptor. However, from a scientific/demonstration perspective, it is important to attempt to semi-quantify the fate of the treated material and to understand the mechanism by which the technology acts. To that end, we recommend additional wells and monitoring to address this concern and concerns regarding spreading, as described below.

A true mass balance seems cost prohibitive in a large pilot test. It would require several dozen solid phase samples (soil) before and after treatment to attempt to accurately estimate the change in the solid phase concentration. Indirect evidence of residual contaminant removal, derived from dissolved concentration is thus favored.

- *Information from all of the IRZ sites is summarized in an attached table. There are several data gaps identified that seem significant relative to the design of the demonstration project. Notably, the amounts of molasses and water to be added, the injection pressures, planned radius of influence, and volume influence are not defined. Please discuss and provide more information.*

The injection design information regarding Vandenberg is summarized below and should be considered an addition to plan section 5.2.2. Similar information about the other sites is being provided in separate letters. We intend to finalize this design after the biogeochemical assessment and will provide any further details you may need at that time.

<u>Vandenberg – Injection/Demonstration Details</u>

Molasses & Water Amount – Based on the anticipated horizontal groundwater flow velocity (50 feet/year), as well as the target TOC concentrations (50 mg/L in the monitoring wells), it has been determined that the initial reagent loading for the demonstration will require injection of between 40-80 pounds of organic carbon per injection well in the demonstration zone every week or 120-240 pounds total (three injection wells). Based on the assumed reagent to water dilution ratio of 10:1 (water:reagent), as well as the available organic carbon content of the molasses reagent (50 – 60 % by weight), this corresponds to a total injection of between 260 and 530 gallons of the reagent solution every week. Given the relatively low groundwater velocity, it is expected that the actual injections will be closer to the lower end of the volume estimate.

Injection Pressure – Based on the geologic information and conceptual site model, it is assumed that groundwater flow occurs predominantly in the layers of sand and gravel present in the Orcutt formation. Given this fairly coarse geologic material for which the reagent injection is targeted, required reagent injection pressures are expected to be low (similar to Badger AAP – see discussion in companion letter). The smaller saturated thickness of some of these sand and gravel layers may necessitate slightly higher injection pressures. Therefore, on the basis of our experience at other similar sites, the design basis for injection pressure was selected to be between 5 to 10 pounds per square inch gauge (psig). This level of injection pressure will require pumping for the injection system as proposed.

Planned Radius of Influence – As outlined, the dispersion of the reagent will be dictated by both the initial lateral spreading during injection and by migration downgradient with groundwater flow, as well as transverse dispersion during that migration.

At the Vandenberg demonstration site, we anticipate that the overall area to be influenced by the reagent injection will extend between 60 and 70 feet downgradient of the injection area, and will extend laterally approximately 10 feet from each of the three injection wells, or an area approximately 60 feet wide by 60-70 feet long. This expected influence is based on experience we have had at sites with similar geologic conditions and groundwater velocities.

Volume of Influence – Given the expected area influenced by the reactive zone, the expected volume of influence can be estimated using the depth and thickness of the injection zone as determined by the injection wells. At the Vandenberg site, each injection well will be screened over 10 feet of aquifer thickness, thus the expected volume of influence will be roughly 42,000 cubic feet (total volume), or roughly 90,000 to 100,000 gallons of groundwater in the pore spaces.

- *The number of monitoring wells seems low, the screened interval(s) are not defined, and the rationale for the well placement is not provided. In general, the level of spatial coverage seems inadequate for a quantitative field demonstration. Please discuss and revise accordingly.*

While we believe that the well layout proposed in the April 10th plan, as discussed previously, would be able to meet the performance objectives outlined in the plan, we agree that additional wells are desirable to better define the reactive zone. Thus, this response supplements demonstration plan section 3.2. The revised Figure 4, attached, includes provisions for 5 additional groundwater monitoring wells for the demonstration program. It is advisable to defer the installation of these wells until completion of the pump test, described below, such that their precise locations may be optimized with respect to the findings of the pump test. This also implies that their locations as currently shown may change based on the outcome of the pump test. These additional wells have been designated as 35-MW-15 through 35-MW-20. One additional upgradient well (35-MW-15), located approximately 15 feet upgradient from injection well I-1, has been included to better establish upgradient groundwater conditions, to permit monitoring of potential upgradient influence from the injection activities. Additionally, three wells added to a line of wells orthogonal to groundwater flow (35-MW-16 through 35-MW-18) are included to provide more thorough spatial coverage downgradient from the injection array in order to permit assessment of transverse dispersion and better monitor the width of the treatment zone. One additional downgradient well has been included, positioned 120 feet downgradient from the injection array. This well provides for monitoring the downgradient extent of changes to the treatment zone, and may serve as a backup well, along with well 35-MW-13, if, despite findings from the pump test, groundwater velocities are found to be greater than predicted. Finally, an additional well 35-MW-20 is to be located approximately 8 feet downgradient of injection well I-2. This well plus well 35-MW-11, 15 feet downgradient will serve as early indicators of the effect of the reactive zone in decreasing redox potential in the aquifer and thus allow the molasses quantity injected to be carefully controlled. These closely spaced wells will also provide backup if groundwater velocities are found to be less than predicted. We have assumed that these new wells will be sampled in the full sampling rounds for the full parameter list, but not sampled at all in the abbreviated sampling rounds.

In practice it may be advisable to develop a more refined list of what wells are sampled on what occasions after preliminary results are received from early monitoring rounds. For example if the zone is observed to move rapidly, it would be wise to reduce the number of monitoring events at close-in wells and add events at distant wells.

Proposed injection well screen intervals are given as 10-foot screen lengths for all wells (nominally 31-41 feet below grade) on page 20 and 21 of the work plan. The well placements shown in Figure 4 are based on assumed aquifer conditions and are subject to change upon acquisition of additional site data. Specifically, the locations may be modified should a significantly different hydraulic conductivity value, and hence calculated groundwater velocity, be evident upon completion of the aquifer pump test (see response to Comment #4 below).

Specific comments are provided below.

1. *(Section 3.2, Pre-Demonstration Sampling and Analysis) The well spacing indicates that monitoring wells will be spaced out up to 60 feet from the injection points, based on an assumed doubling of the natural groundwater velocity. Also, one well is offset by 15 feet to measure the IRZ ROI influence in the lateral direction. What, if any, preliminary modeling or experience supports the assumed doubling of velocity or indicates the IRZ will extend laterally this distance? Please provide more rationale for the monitoring plan, and discuss the spacing relative to current and future groundwater flow regimes. Would using piezometers to actually measure mounding and ROI make more sense, with a contingency plan to install other monitoring wells once the ROI is established?*

As stated in the work plan, ARCADIS has utilized a conservative hydraulic conductivity value of 1 foot/day, which was based on aquifer test results from well 35-MW-7, located within the proposed demonstration area at Site 35. The value of 1 foot/day, which when used in Darcy's Law with a site derived hydraulic gradient of 0.041 feet/feet, and a total porosity value of 0.35, yields a groundwater velocity of approximately 0.12 feet/day. We restate that this is a conservative value, recognizing that a higher value was used in the Conceptual Site Model (CSM) presented in the RI Report (Tetra Tech, 1999). In development of the CSM, the USGS MODFLOW model was used to derive the "calibrated" hydraulic conductivity value of 2 feet/day for the Orcutt formation sands at Sites 32/35. However, to arrive at this value of 2 feet/day, several simplifying assumptions were made during the modeling exercise, including the provision of a constant discharge rate and a constant head boundary at the downgradient boundary of Site 35, both of which are known to be variable. Since these assumptions essentially control the "rate of drainage of water" from the modeled aquifer, iteratively changing the hydraulic conductivity to match expected or measured groundwater head values is a rather straightforward process, but leads to the incorporation of uncertainties in the model results.

Using the hydraulic parameters input into the MODFLOW model: a hydraulic conductivity value of 2 feet/day, a gradient of 0.05 feet/feet, and an effective porosity value of 0.226 (Tetra Tech, 1999); a calculated groundwater velocity is 0.44 feet/day, which is nearly four times greater than that assumed in the work plan. Our previously stated assumption of a doubled hydraulic gradient, which might result locally and temporarily from groundwater mounding during injection, doubles the estimated groundwater velocity from 0.12 to 0.24 feet/day, which remains well below the groundwater velocity of 0.44 feet/day used in the CSM. It is also important to note that the well-field design proposed in the work plan contained provisions for downgradient monitoring in the event that the actual groundwater velocity exceeded the conservative estimates used in the work plan. For instance, if the actual groundwater velocity is closer to the value of 0.44 feet/day developed in the CSM (Tetra Tech, 1999), downgradient monitoring well 35-MW-13, positioned 60 feet from the injection array, would be expected to first encounter the injection solution after approximately 136 days (60 feet / 0.44 feet/day), well within the timeframe of the demonstration program. If an increase in hydraulic gradient is observed beyond 0.05 feet/foot, then this timeframe will be reduced accordingly. In short, the proposed well array is designed to enable monitoring of the program over a range of potential groundwater velocities.

Regardless of which value is used, hydraulic conductivity values calculated from either single well slug tests or derived from the MODFLOW model will invariably result in incorporating greater uncertainty than that afforded from an aquifer pump test conducted within the treatment area. To address this issue, ARCADIS is recommending the inclusion of an aquifer pump test utilizing multiple monitoring wells in the area of the proposed demonstration program. The aquifer pump test is designed to provide a more robust hydraulic conductivity value in the area of the proposed demonstration, and to provide insights into sustainable pumping rates from the treatment area. These data can be subsequently used to refine well spacings, as necessary, and to target appropriate injection rates during the program. The pump test is further described in our response to specific comment #4.

The temporary existence of a small mound at the point of injection may also increase lateral spreading radially away from the mound, resulting in a temporal increase in transverse reagent dispersion. The proposed well-field discussed in the work plan included provisions for measuring the extent of transverse reagent dispersion, although the locations proposed are preliminary and subject to change upon completion of the pump test program

The expected radius of influence is discussed above in our answer to your fourth general comment. Based on this discussion the 60' long line of wells perpendicular to the direction of flow should lie mostly or entirely within the created reactive zone. The placement of these wells should allow for an evaluation of the uniformity and width of the zone if the actual small-scale direction of flow follows that inferred from currently available data. This line should also provide some protection for a contingency in which the small-scale direction of flow differs somewhat from what is currently expected.

The suggested use of piezometers to measure mounding during the injection is appropriate. ARCADIS has designed the proposed monitoring well array with a dual functional use in mind; for use as piezometers to monitoring groundwater mounding and as conventional wells for sampling and *in-situ* monitoring. In addition, as we discussed, we are adding an arc of three well piezometers located directly downgradient and side gradient to injection well I-2 (see Figure 4). These piezometers will be located as follows:

- P1 – 5 ft downgradient from I-2 on a 45-degree angle to the line of flow
- P2 – 10-15' downgradient from I-2 on a 45-degree angle to the line of flow
- P3 – 3-5' sidegradient from I-2

The exact locations will be finalized after the pump test.

We intend to monitor water level and temperature at least hourly for a period of a few days, as well as TOC and bromide on two occasions. The TOC and bromide from these piezometers will be sampled with peristaltic pumps. This data will help address the question of how much mounding or spreading occurs after injection. Clearly, this increase in the number of monitoring wells/piezometers will permit greater ability to observe and delineate the areal extent of mounding, as well as changes in groundwater chemistry. If ESTCP would like to gain an even more quantitative understanding of this issue we could use a pressure logger installed below the water table in several adjacent monitoring wells (in addition to the monitoring of the piezometers) to provide frequent readings of water level during the first few injection events at one site to evaluate these effects. This data could be used to supplement the tracer data in gaining an understanding of how the injection event affects the saturated zone.

1. *(Section 5.2.1.1, Equipment Set-Up) The bromide tracer helps in evaluating migration. However, the monitoring network may be insufficient to accurately measure any contaminant spreading in lateral, vertical or upgradient directions. This is a major objection raised for any technology relying on injections under pressure without capture. Please discuss and revise as appropriate.*

From the discussion of injection volume and volume of influence presented above it is reasonable to expect that the injected volume will be equal to approximately 10% of the flow through the demonstration zone during the demonstration project. Thus only moderate mounding would be expected under these conditions. Volumetric displacement would be unlikely to cause significant lateral, vertical, or upgradient contaminant migration. Given the existence of a confining layer below the demonstration zone, vertical displacement is especially unlikely. As with the soil washing concern, the formation of products (such as DCE, VC, CA and ethene) can help differentiate decreases in contaminant concentration that are attributed to dispersion from those due to induced biodegradation. The absence of increased TOC and tracer in upgradient wells can be used to verify the assumption of little upgradient dispersion.

Thus we would anticipate that any dispersion that did occur would be horizontal. Unlike the situation at Badger AAP, this plume may be relatively narrow - a width of <300’ upgradient of the likely demonstration zone can be inferred from the fact that the line of wells (35-MW-4, 35-MW-6, 35-MW-1 and 35-MW-3), which should lie between the source area and 35-MW-7, show only low concentrations of CAHs. On the other hand, a minimum width for the plume can be inferred from the concentrations observed at 35-P-7 and 35-MW-8 downgradient of the likely demonstration zone (see figures 3.8-6 and 3.8-8 in Appendix B). These data suggests a 200 – 400’ wide 100 ppm TCE plume at the intersection with El Rancho Oeste Road. Further insight into the likely shape of the plume and reactive zone can be drawn from the Groundwater Modeling input parameters used for this site (longitudinal dispersivity 50’, transverse dispersivity 1/8 of longitudinal, and vertical dispersivity 1/160 of longitudinal). The uncertain delineation of the plume leaves two possible cases:

Case 1: If the plume is truly fairly wide (>200’) it seems unlikely that a small horizontal dispersion effect induced in this 60’ demonstration zone would be observed. However, mounding in the immediate vicinity of the injection wells could be observed as discussed above. Under these circumstances it seems likely that any dispersion induced by the injection would cause little net change in the concentration in any given well. Furthermore since the plume would be much larger than the demonstration zone, any expansion of the plume caused by dispersion at this site would be small in percentage terms and therefore difficult to detect even with additional wells.

Case 2: If, however, the high concentration portion of the plume is quite narrow at the location of the demonstration zone (perhaps 100’), then it might be possible for some horizontal dispersion to be observed. Thus, the addition of wells as discussed above may be of value in determining if this is occurring

At this site, an injection pressure of between 5 and 10 psig is proposed as discussed above. Any pressure effect during injection would be exerted on only a small volume and for a short period. Since water is an incompressible fluid, the effect of the pressure would be increased head (mounding) at the point of injection. It is thus apparent that the magnitude of such an effect would be transient and diminish rapidly as the pressure effect propagated radially away from the well. Any flow induced in the aquifer by a pressure effect would thus not be expected to materially affect the size of the plume, beyond the effect of the injected volume, discussed above.

3) *(Section 5.2.1.1, Equipment Set-Up) The injection pressures need to be defined, to the extent currently possible, and the basis for determining injection pressures should be detailed. Some discussion of the design basis for the injection volumes, pressures, and frequency must be provided.*

This information is provided above in the answer to the fourth general question.

4) *(Section 5.3.3, Factors Affecting Technology Performance) Preliminary groundwater modeling would provide more robust analysis of the injection and monitoring details. Are there plans to do this? If not, provide more detail on the rationale for the monitoring plans.*

We have provided additional details above on the rationale for the injection and monitoring plans. As discussed above, the greatest uncertainty in these plans stems from the high variability in previously measured hydraulic parameters at this site. Thus, ARCADIS recommends the completion of an aquifer pump test in the area of the demonstration program as an alternative to completion of a groundwater model in order to make the injection and monitoring plans more robust. A step-drawdown test is proposed such that at least three different pumping rates can be imposed on the well, permitting a robust determination of aquifer hydraulic conductivity. It is proposed that pumping be conducted at injection well I-2, with drawdown monitoring to be conducted at a minimum of three wells positioned proximal to well I-2. These four wells can be installed within an initial phase of drilling. Based on results from the pump test, the calculated hydraulic conductivity value can then be used to refine the calculated travel times of the injection solution, and thus refine the locations of the remaining monitoring wells, as necessary, proposed in this program. Results of the pump test can also be used to determine the cones of depression resulting from selected pumping rates, which should closely resemble the expected groundwater mounding resulting from equivalent injection rates, in accordance with hydraulic theory.

Step Drawdown Pump Test Procedures

To permit calculation of the aquifer hydraulic conductivity and transmissivity, and to assist with identifying appropriate injection rates during the demonstration program, a step drawdown test will be conducted by pumping from injection well I-2 (later to be used for molasses injection). Groundwater level data will be collected prior to the aquifer test in order to establish a baseline trend in water levels in the pumping and observation wells. This baseline water level data will be used, if needed, to adjust drawdown data collected during the pumping test. Following baseline data collection, the well I-2 will be pumped using an electrical submersible pump placed at a depth adjacent to the screened zone of the well. The pump will be powered by a generator if AC power is otherwise not available. The test will be conducted by pumping the well at an initial constant rate until the hydraulic head in the well stabilizes. Following stabilization after the first pumping rate, the process will be repeated at two additional steps of successively increasing flow rates of at least one-hour duration each.

Based on review of existing purge logs for well 35-MW-7, located nearest the proposed future pump test, pumping at an average rate of approximately 0.9 gallons per minute (gpm) for about 120 minutes (100 gallons of water purged total) yielded 4.89 feet of drawdown in the well. Although it is unclear as to whether or not the pump was stopped to permit its lowering during the purge cycle, and although no nearby monitoring wells were gauged during this purging effort, the observation that the water level returned to near static conditions within 10 minutes after termination of purging indicates that water flows into the well at a reasonable rate. Based on these limited data, targeted pumping rates are preliminarily set for 0.7 gpm, 2 gpm, and 5 gpm, if achievable. These targeted rates are subject to change based on conditions encountered in the field during the pump test.

The flow rate from the pumping well will be recorded at each step and drawdown in the pumping well will be recorded using a pressure transducer connected to an electronic data logger. The pump flow rate will be measured with an in-line flowmeter or from a discharge line into a bucket or 55-gallon drum. Drawdown in at least three proximal groundwater monitoring wells, including well 35-MW-20 (located approximately 8 feet downgradient from I-2), 35-MW-11 (15 feet from I-2), and 35-MW-14 (located approximately 20 feet upgradient from I-2) will also be measured. Existing well 35-MW-7, located approximately 30 feet downgradient from I-2, may be utilized for monitoring of drawdown, if it is determined during the test that the radius of drawdown during pumping may intersect this well. Each drawdown monitoring well will be fitted with a pressure transducer connected to a datalogger, similar to the pumping well configuration.

Records will be collected at one-minute intervals providing a robust dataset for subsequent analysis. Both temperature and water level (pressure) will be recorded during the test. Additional field data (date, time, initial depth to water measurements, flow rate, weather conditions, etc.) will be recorded on field data sheets. As noted above, the test will be conducted at a minimum of three pumping rates with each successive step maintained for at least one hour. The actual total duration of each test will depend on the observed hydraulic response in the pumping well and observation wells. Before ending the test, the flow rate will be increased to estimate the maximum short-term well yield.

A recovery test will be conducted immediately following the termination of the pumping test by measuring the recovery of groundwater levels in the extraction well at the same frequency as the drawdown measurements. The test will be conducted until at least 90% of the initial static water level is recovered. This recovery data will be evaluated and compared to the drawdown data.

Groundwater generated during the tests will be stored on-site pending characterization and identification of appropriate disposal options.

Pump Test Data Analysis

Step drawdown test and recovery test data will be downloaded from the data logger, plotted, and analyzed using appropriate aquifer test analysis methods. The analysis methods will be used to calculate aquifer hydraulic parameters and well information including hydraulic conductivity, radius of influence, and targeted injection rates for the subsequent molasses injection program.

Although departures from ideal behavior may result from partial penetration of the screened interval with respect to the total aquifer thickness, and dewatering of the upper portion of the unconfined aquifer, both of which may result in underestimating the overall aquifer conductivity, the analysis will be useful in predicting the performance of the same well, I-2, when used as an injection well.

5) *(Section 7.4, Life-Cycle Costs) What cost methodology will be applied in calculating the life cycle costs for this project (e.g., present worth method, annual cost)?*

All costs will be reported using the present worth method. Any projected costs for future periods will be discounted back to present value.

6) *(Table 3) Some biological characterization seems essential to verify that dechlorinators are present and active. Please discuss and revise.*

It has now been shown that a wide variety of organisms, including both methanogens and sulfate reducers (Zwiernik et. al. ES&T, 1998, 32, 3360-3365), can participate in anaerobic dechlorination processes. These include both organisms that degrade chlorinated aliphatics cometabolically and those that utilize dehalorespiration. It has not been conclusively shown that any of these organisms, individually, are ubiquitous. However, it has been our experience at a large number of sites that when the proper geochemical conditions are induced (as discussed in section 2.1), populations of dechlorinating organisms develop in the absence of any obvious cause of toxicity. This process requires time – see the discussion of terminal electron accepting process (TEAP) shifts in Section 3 of the draft RABITT protocol (Morse et al., ESTCP, Feb 23, 1998). Thus, it may be difficult to detect these organisms in an initial biogeochemical characterization of a site, since the nucleus of these populations may be present only as spores or in microzones within the geologic matrix with lower redox potentials. The progress of TEAP shifts can be followed with the results of the biogeochemical analyses already included in the plan.

However, to gain more certainty regarding dechlorinating microbial populations, we plan to add a brief 3-4 month microcosm study, based broadly on Section 5 of the RABITT draft protocol (ESTCP, 1998, http://www.estcp.org/projects/cleanup/Rabbitt_Protocol.pdf), in which we examine only one substrate in one composite sample from one site (with appropriate subsamples and controls). The objectives of this microcosm study, which would be conducted prior to the field demonstration test, include:

- a yes/no answer as to whether dechlorinating activity can be induced at this location within this site with this substrate
- to provide an additional line of evidence to aid in interpreting the field demonstration results for this site. Specifically, it may aid in separating the effects of desorption "soil washing" or dilution from the desired biodegradation.

As part of the first round of new well installation at this site, we will collect a sample of unpreserved site groundwater and core samples to be used in the microcosm study. Relatively undisturbed soil core samples will be collected using a California-modified split-spoon sampler fitted with 2.5-inch diameter by 20-inch length brass rings driven to targeted depth ahead of the lead auger flight. Since heaving sands are anticipated to be encountered during borehole advancement into the saturated zone, potable water will be added to the auger flights, as necessary, to equalize the pressure differential between the atmosphere and aquifer sands at depth. O-rings will be fitted on auger flight joints to create a watertight seal and enhance the water holding capacity of the drill string. The amount of water added to each borehole to equalize pressure will be recorded during the sampling activity. Upon attaining the targeted sampling depth, the sampler will be removed from the borehole using the drill rig wire line. The sampler will then be disassembled, with the middle ring retained for treatability testing, while the upper ring will be used for lithologic classification using the Unified Soil Classification System (USCS). Each retained soil core sample will be fitted with Telfon^{TM} sheets placed over the core ends and kept in place by snug-fitting plastic end caps. The caps will then be sealed to preserve the aerobic/anaerobic nature of the samples and the samples will be kept cool. Boring logs will include the boring designation, a complete soil description, and blow counts.

We anticipate using techniques such as Denaturing Gradient Gel Electropherisis of DNA (DGGE) and Phospholipid Fatty Acid analysis (PLFA) to determine if the changes in microbial consortium induced in the lab are induced in similar ways in the field. We intend to subcontract analysis by DGGE and PLFA of at least one sample each of unamended site groundwater, the treated microcosm sample, and later site groundwater after full scale treatment. We have been told by Microbial Insights (www.microbe.com) that although the normal full scale sample size is 1 L, chilled, unpreserved per analysis (2 L for both DGGE and PLFA), they can perform these analyses on reduced 100 ml sample sizes for microcosm work. We intend to ensure that the sample from the microcosm supernatant water is as similar to a purged well sample in the field as possible, by shaking the microcosm 24 hours before withdrawing the DGGE/PLFA samples and then allowing it to settle for 24 hours. SOPs for these analyses are appended.

The microcosm study report will include:

- methods – detailed either in the text or by citation documented to a level sufficient that someone knowledgeable in the field could replicate the work
- results – in appropriate summary tables, these will include primarily results of measurements of chlorinated hydrocarbon concentrations, methane, hydrogen, electron donor as TOC for actual test sample (molasses added), biotic control, and abiotic control. Gas generation as measured from pressure and headspace volume should also be reported. PLFA and DGGE results as discussed below should also be reported. Quantitation of volatile fatty acids is desirable but not required.
- Conclusions

Additional Demonstration Plan Changes

We had orally discussed that an additional sampling event may be desirable to look at rebound effects, roughly 1 year after the conclusion of the demonstration program. We intend to conduct such a sampling event for the full parameter list in 10 wells and provide a brief follow-up letter report.

The following minor changes in the work plan are also needed, which are not directly a result of your comments:

Recently, the base installed in seven of ten Site 35 wells (wells 35-MW-6, -9, and -10 remain unmodified) **dedicated** QED Micropurge pumps, allowing us to "hook up" to existing pumps at the site using a controller and flow cell. What this may entail for us is to equip new wells proposed in our programs with Micropurge pumps so that data amongst monitored wells will be comparable. A cost-benefit analysis was completed to assess the fiscal impact associated with purchasing dedicated QED Micropurge pumps in the ten proposed site wells, versus utilizing rented submersible pumps and adhering to the previous 3-well purge protocol used at the site. Actual well purge logs from previous site work were consulted for this study to aid in estimating labor hours and materials used. Eight monitoring events were assumed for purposes of completing the analysis. The outcome of this cost-benefit analysis was that the cost of capital expenditure for new dedicated QED pumps in 10 site wells would be more than made up (by a factor of two), primarily in significantly reduced field labor associated with well purge duration, with additional cost savings provided by an order of magnitude decrease in purge water generated, and elimination of equipment blanks/cross-contamination potential, tubing costs, etc.

Originally, 4-inch diameter Schedule 40 PVC casing was specified for all proposed monitoring wells at Site 9. 4-inch casing was specified due to the great depth required to reach groundwater, and the possibility that the installed casing may not be straight and true following installation. However, since Site 35 groundwater depth is about 15 feet below grade, and total well depth is about 45 feet below grade, 2-inch diameter Schedule 40 PVC well casing is regarded as an appropriate and sufficient alternative. This modification is interpreted to have no substantial effect on the monitoring program, but will result in moderate cost savings in materials cost, and substantial cost savings in purge water disposal costs.

Page 20, section 3.2, second paragraph, fourth sentence should read “30 ~~40~~ feet upgradient from existing well 35-MW-7”

Page 21 second line “using 2 -inch diameter Schedule 40”

Page 35 section 5.1.1 “At the VAFB site ~~9~~ 35 TCE groundwater plume,”

Page 37, section 5.2.1.4 “impacted portion of the ~~Carega~~ Orcutt Formation”

Bottom of Page 54 and 55 "~~Finally Vandenberg AFB is characterized by great depth as well as rough topography, limited roads and sensitive biological and cultural resources that would limit the available well placement Therfore we chose to use an increased frequency of monitoring events in a lesser number of wells as indicated in Table 1~~".

Several of these changes obviously alter the sequence of planned events in the next few months. We anticipate beginning fieldwork with initial well installation within 1 month after final approval of this memo. Then work would proceed on parallel tracks as shown in the attached figure for the pump testing, biogeochemical sampling, additional well installation, and microcosm testing. All of the tracks would come back together in late November when we would be able to make a go/nogo decision regarding the full-scale demonstration effort at this site. Please feel free to call either myself or David Springer (805-687-7559) in our Santa Barbara office to discuss any questions you may have about these matters.

Sincerely,

ARCADIS Geraghty & Miller, Inc.

Christopher C. Lutes
Project Manager

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