ESTCP
Cost and Performance Report

(ER-0224)

In Situ Bioremediation of Perchlorate in Groundwater

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ENVIRONMENTAL SECURITY
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COST & PERFORMANCE REPORT

Project: ER-0224

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
AFIT	Air Force Institute of Technology
bgs	below ground surface
bls	below land surface
CDA	Central Disposal Area
CDHS	California Department of Health Services
CDPH	California Department of Public Health
COC	contaminants of concern
COR	Contracting Officer Representative
DCE	dichloroethene
DO	dissolved oxygen
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
FBR	fluidized bed reactor
FRTR	Federal Remediation Technologies Roundtable
FS	feasibility study
GCW	groundwater circulation well
GET D	Groundwater Extraction Treatment Facility D
gpm	gallons per minute
GWET	groundwater treatment and extraction
HFTW	horizontal flow treatment well
HFTW-D	horizontal flow treatment well-downflow
HFTW-U	horizontal flow treatment well-upflow
hp	horsepower
HRC	hydrogen release compound
ID	inner diameter
ITRC	Interstate Technology & Regulatory Council
m	meter(s)
MADEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
MDL	method detection limit
msl	mean seal level
mV	millivolt(s)
NAS	National Academy of Sciences
NDMA	N-nitrosodimethylamine

NPV	net present value
O&M	operation and maintenance
ODC	other direct costs
ORP	oxidation reduction potential
P&ID	Piping and Instrumentation Diagram
PLC	programmable logic control
PQL	practical quantitation limit
PRB	perchlorate-reducing bacteria
PVC	polyvinyl chloride
RfD	reference dose
RI	remedial investigation
RL	Reporting Limit
SCADA	Supervisory Control and Data Acquisition
SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethene
TDH	total discharge head
TOC	toxic organic carbon
UCMR	Unregulated Contaminant Monitoring Regulation
UNM	University of New Mexico
USCS	Unified Soil Classification System
USEPA	United States Environmental Protection Agency
VC	vinyl chloride
VFA	volatile fatty acids
VOA	volatile organic acid
VOC	volatile organic compound
wt/vol	weight/volume

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Groundwater contamination by perchlorate is recognized as a significant environmental issue in the United States and abroad. Current remediation methods for perchlorate-contaminated groundwater generally involve extracting the water and treating it ex situ using either selective ion exchange resins to adsorb the dissolved perchlorate or biological reactor systems to destroy it. In situ remediation of perchlorate has the potential for both cost and safety benefits compared to current ex situ approaches. Extensive laboratory and field studies conducted during the past decade have revealed that perchlorate-reducing bacteria (PRB) are indigenous to most groundwater aquifers, and that these bacteria can be stimulated to degrade perchlorate through the addition of a variety of different organic electron donors, including various fatty acids, alcohols, sugars and natural oils. The PRB oxidize the electron donor and subsequently reduce perchlorate to chloride and water, two innocuous products. The main challenge for implementing in situ perchlorate bioremediation is effectively mixing an electron donor into the perchlorate-contaminated groundwater, and delivering the mixture to the indigenous PRB, without having to extract water from the subsurface. Other challenges include preventing microbial biofouling of pumping wells and minimizing the mobilization of secondary groundwater contaminants, such as manganese (Mn) and iron (Fe).

An innovative in situ bioremediation technology, known as a horizontal flow treatment well (HFTW) system, was evaluated during this demonstration for delivering electron donor, and promoting the biological reduction of perchlorate. The HFTW technology consists of two dual-screened treatment wells, one pumping contaminated groundwater from a deep aquifer region and injecting it into a shallower zone and the other pumping contaminated groundwater from the shallower aquifer region and injecting it into the deeper zone. The two wells work in tandem to establish a groundwater recirculation zone in the subsurface. The electron donor is added and mixed with contaminated groundwater at each well, creating an anaerobic, bioactive zone between and downgradient of the HFTWs during system operation. Contaminated water is never brought to the surface, as treatment occurs in the in situ bioactive zones.

1.2 OBJECTIVES OF THE DEMONSTRATION

The objectives of this project were to demonstrate the following: (1) that in situ biological perchlorate treatment is feasible in the field using electron donor addition; (2) that perchlorate can be treated to <4 micrograms per liter (μg/L); (3) that perchlorate can be treated in a drinking water aquifer without mobilizing significant quantities of Fe and Mn or bringing oxidation reduction potentials (ORP) to very low levels; (4) that the zone of influence and efficiency of the HFTW system are sufficient to make the technology a viable, cost-effective option at many sites; (4) that biofouling can be effectively controlled by measures that are easily implemented and (5) that co-contaminants, including nitrate and trichloroethene (TCE), can be treated using the same HFTW technology. As with any pilot-scale technology demonstration, a main objective of this field project was to collect and document information that is relevant to site managers and regulators who are responsible for choosing and implementing technologies.

1.3 DEMONSTRATION RESULTS

During this ESTCP project, an HFTW system was installed at Aerojet General Corporation's (Aerojet) 8500-acre site in Rancho Cordova, CA. The pair of HFTWs were installed ~34 ft apart, and screened within a shallow zone in the aquifer from 46-61 ft below land surface (bls) (upper screen) and within a deeper zone at 80-100 ft bls (lower screen). A group of 19 monitoring wells screened within the shallow and deep zones and placed at various locations upgradient and downgradient of the HFTW pumping wells were used to evaluate overall system performance. Each well was operated at a net flow rate of 6 gallons per minute (gpm), citric acid was used as the electron donor, and chlorine dioxide was periodically added to each of the HFTWs as a biofouling control agent.

The demonstration was conducted in three phases. The objectives of Phase I were to evaluate the overall groundwater mixing and capture by the system and to determine the extent of perchlorate and nitrate reduction possible without mobilizing significant quantities of Fe and Mn. Between the final background monitoring event (Day -15) and the final groundwater event in Phase I on Day 275, perchlorate concentrations in the seven shallow monitoring wells declined by an average of 95% from the starting average of 2230 µg/L to 90 µg/L. One of the downgradient wells reached <5 µg/L on Day 67, but most of the wells showed stable perchlorate concentrations ranging from ~40–160 µg/L. These concentrations remained reasonably consistent with electron donor dosages up to 2.5 times the calculated stoichiometry.

The consistent decline in perchlorate concentration throughout the entire shallow aquifer zone during Phase I showed that the HFTW system provided good mixing and electron donor delivery within this region. This observation was consistent with conservative tracer tests conducted during background testing. Moreover, a rapid and consistent reduction in perchlorate concentrations observed in a side-gradient monitoring well showed that that the region of influence of the HFTW system in the shallow zone met or exceeded initial predictions derived from a site-specific groundwater transport model. The low residual concentrations of perchlorate throughout this region during Phase I Operation may reflect a limitation in electron donor in this region (the donor was intentionally limited to prevent mobilization of Fe and Mn) or may be a function of the mixing design and flow field of the HFTW system combined with aquifer heterogeneity. In later testing (Phase III), low concentrations of residual perchlorate were detected in several downgradient wells even in the presence of excess electron donor suggesting that the latter hypothesis is more likely.

Like the shallow downgradient wells, the perchlorate concentrations in the deep downgradient monitoring wells at the site also declined significantly during Phase I operation, although the extent and consistency of the reduction was less than for the shallow wells. In the nine deep downgradient wells within the treatment zone, perchlorate concentrations declined by an average of 60% from a starting concentration of 3722 µg/L on Day 0 to 1780 µg/L on Day 275. However, in the five deep wells furthest downgradient, which are beyond the immediate influence of the upgradient water entering the system through the HFTWs, average perchlorate reductions exceeding 93% were achieved by Day 146. Thus, with increased residence time, perchlorate reduction in the deep region of the aquifer was much greater than for the wells close to the HFTWs.

One of the key variables in Phase I was to determine if perchlorate could be degraded without significant mobilization of Fe and Mn. This was accomplished by tightly controlling the addition of citric acid, based on expected concentrations of oxygen, nitrate, and perchlorate. Mobilization of both Fe and Mn was minimal during the course of Phase I operation. With the exception of two shallow wells closest to the HTFW-upflow (HFTW-U), soluble Fe concentrations throughout the plot remained well below 500 µg/L. Moreover, Fe that was dissolved and mobilized during the active phase of operation rapidly re-precipitated when the system was shut down. Dissolved Mn concentrations also generally remained low during Phase I. Concentrations reached a maximum of 1470 µg/L in one well but rapidly declined back to <50 µg/L after electron donor addition ceased at the end of Phase I. During the final sampling event in Phase I in which Mn was measured, concentrations of the metal were below 50 µg/L in 12 of the downgradient monitoring wells.

The key objective of Phase II was to treat perchlorate without promoting significant well biofouling, which was an operational issue in Phase I. The two HFTWs were redeveloped between Phase I and Phase II. The electron donor dosing regimen was switched from a daily addition (as in Phase I) to larger weekly or twice-per-week doses in order to evaluate the impact of dosing schedule on both perchlorate treatment and well fouling. In addition, chlorine dioxide was added to each well on a daily basis (four to eight times per day) as a preventative measure. The wells were operated continuously at 6 gpm during Phase II. The objective of Phase III was to assess an "active-passive" mode of operation. In this case, the HFTWs were used primarily for mixing electron donor with the perchlorate-contaminated groundwater. The pumping wells were then turned off between mixing periods. The key objective was to determine whether this mode of system operation would result in a consistent reduction in perchlorate concentrations and reduced system operation and maintenance (O&M) costs. During Phase III, the HFTW treatment wells were operated in a 15-day cycle consisting of 3 days of active pumping followed by 12 days in passive (non-pumping) mode. Citric acid was added to both HFTWs in three 12-hour pulses during the active period, and each HFTW was operated at a net flow rate of 6 gpm. The 15-day cycle was repeated six times during the 3-month test period, and three sampling events were performed.

A total of nine groundwater sampling events were performed during the Phase II and Phase III operations. These sampling events included one background event prior to each phase, four events to measure system performance in Phase II and three events to measure system performance in Phase III. As was observed in Phase I, perchlorate concentrations in all the downgradient shallow wells declined rapidly during Phase II, but they did not generally go below detection but rather ranged from ~30–110 µg/L despite increasing the electron donor addition rate to ~4 times the stoichiometric requirement in the HFTW-U through most of the Phase II. Perchlorate concentrations generally remained low in the shallow wells during the Phase III active-passive testing. Concentrations in several wells near the HFTW pumping wells were lower during Phase III than in either Phase I or Phase II testing, likely reflecting an increased residence time of water in the bioactive zone while the HFTWs were not pumping. In addition, with the system shut down during passive treatment, upgradient water (containing oxygen and nitrate as well as perchlorate) was not continually circulated throughout the plot. The increased reaction time and absence of new electron acceptor demand (particularly from oxygen and nitrate) probably resulted in the significantly lower perchlorate concentrations in this region during Phase III.

The consistent decline in perchlorate throughout the entire shallow aquifer during Phase II confirmed that, even with much more periodic dosing of electron donor (i.e., from daily dosing during Phase I to one or two times per week during Phase II), the HFTW system operated well as a treatment technology in the shallow zone. Moreover, the data from Phase III suggest that perchlorate treatment can be achieved by using the HFTW system intermittently as a vehicle to mix electron donor with the contaminated groundwater. Even in the side-gradient well, perchlorate concentrations remained <100 µg/L throughout Phase III, even though the system was not pumped continuously. This suggests that the capture zone of the system during active pumping was maintained during the active-passive phase. The ability to operate this system several days per month rather than continuously could appreciably reduce the O&M costs associated with biofouling and well redevelopment, which is the most significant issue with this design.

The perchlorate concentrations in the shallow zone on Day 801 (the final sampling event in Phase III) represent a 96+4% reduction in dissolved perchlorate from the starting concentration in each well prior to Phase I (Day -7) and an average 94+3% reduction from perchlorate concentrations prior to Phase II (Day 472). Thus, perchlorate treatment in the shallow zone was very effective. However, with the exception of one well, perchlorate concentrations of <4 µg/L were not generally achieved in the shallow zone during Phase II and Phase III. Rather, perchlorate stabilized between ~30 to 100 µg/L in most wells. Interestingly, a low residual concentration of contaminant was also observed during previous testing of an HFTW system for cometabolic treatment of TCE. The low residual contaminant was attributed primarily to competitive interactions between toluene (the co-substrate) and TCE during biodegradation by toluene-oxidizing strains. However, the occurrence of low residual contaminant concentrations in both demonstrations suggests that this may be characteristic of the HFTW system.

The perchlorate concentrations in the deep downgradient monitoring wells showed a less consistent pattern of decrease during Phase II and Phase III than did the shallow wells during the same interval. However, the overall percentage reduction in the deep zone on Day 801 was 80+39% from the starting perchlorate concentration in each well prior to Phase I (Day -7), and an average 52+29% reduction from perchlorate concentrations at the end of Phase I (Day 275). If one only considers the six deep wells furthest downgradient from the HFTWs, the total perchlorate reduction during the 801-day demonstration was 88+9%. Thus, although nondetect concentrations of perchlorate were achieved in only a few wells, reasonable perchlorate treatment occurred in the deep zone, particularly considering results from the far downgradient wells.

The persistence of low concentrations of perchlorate in the test plot likely resulted from local aquifer heterogeneity, and this effect may have been exacerbated with the HFTW system design due to the complex groundwater flow patterns of the paired pumping wells (i.e., deep water being brought up in the HFTW-U and shallow water pushed down in the HFTW-downflow (HFTW-D), with perhaps some static zones in between the wells). In some regions, electron donor may not mix with groundwater during the course of the demonstration due to low permeability, poor connectedness to the injection well, etc. As a result, little degradation of perchlorate is likely in these zones, while extensive degradation (probably to nondetect concentrations) occurs in other regions. When groundwater is sampled from a broadly screened well, zones with varying degrees of local reaction may be represented in the bulk sample. As a result, partial degradation of various electron acceptors, including perchlorate, nitrate, and sulfate, may be observed in the sample. This appears to be the case for many wells in Phase II and Phase III of this HFTW demonstration.

The treatment of TCE by the HFTW system was also evaluated during Phase II and Phase III. The electron donor concentration was increased significantly and a commercial culture containing Dehalococcoides spp. (Shaw culture SDC-9) was injected into the HFTWs during Phase II to enhance reductive dechlorination. TCE concentrations in many of the shallow wells declined significantly during Phase II and Phase III. There was a 76+23% reduction in total TCE in all the shallow wells from the beginning of Phase II (Day 472) to the end of Phase III (Day 801). If only the downgradient wells are considered, then the loss was 87+14%, with average final concentrations being 323 μg/L. Cis-1,2-dichloroethene (DCE) (the initial reductive degradation product of TCE) was detected at high concentrations (>1000 μg/L) in three of the shallow wells, while vinyl chloride (VC) was only detected during the last sampling event (Day 801) in one well. The relatively rapid and significant decline in TCE during the months after bioaugmentation with Dehalococcoides spp. in many of the shallow wells suggests that the procedure enhanced the dechlorination kinetics. The TCE concentrations in a number of the deep downgradient monitoring wells also declined significantly from the beginning of Phase II to the end of Phase III. Most notably, the TCE concentration in the far downgradient wells declined by as much as 98% from the start of the demonstration. However, as with perchlorate, the average decline in TCE concentrations in all the deep monitoring wells was appreciably less than in the shallow wells, averaging 71+23% in the four wells furthest downgradient from the beginning to the end of Phase III.

There were various mechanical issues with the chlorine dioxide system (used to prevent HFTW biofouling) during Phase II. These issues were primarily based on the design of the "demonstration scale" unit and are unlikely to be an issue for a full-scale system, as chlorine-dioxide systems are used on a large commercial scale for drinking water disinfection, among other applications. However, based on overall pressure trends observed during Phase II operation, it appears that an operational mode in which large, infrequent doses (one or two per week) of electron donor are injected, coupled with small, frequent doses (several per day) of chlorine dioxide is a more effective long-term operating condition for this type of treatment system than daily additions of both amendments. It may still be necessary to redevelop the HFTWs on a periodic basis, but this operational regimen should significantly increase the time between redevelopment events.

1.4 IMPLEMENTATION

The operational data from Phase III suggest that an active-passive approach may be the best overall operational strategy for an HFTW system in terms of both contaminant treatment and reduced O&M costs. Pressure increases also occurred in the HFTWs during Phase III, but with the short-term operation and large doses of citric acid (which assists in biofouling control through both acidification of local groundwater and chelation of precipitated metals), these increases did not affect operation during active phases. In addition, large additions of chlorine dioxide or other biofouling agents can be applied to wells during the passive phases to assist with long-term biofouling control. Thus, given that the treatment of perchlorate, as well as TCE, during this phase was equivalent to or better than that observed during the continuous-pumping phases, in which biofouling was more readily controlled, active-passive operation appears to be the most desirable operational approach for this type of in situ design.

2.0 INTRODUCTION

This ESTCP project was a collaborative effort among Shaw Environmental, Inc. (Shaw), the Air Force Institute of Technology (AFIT), the University of New Mexico (UNM), and Aerojet General Corporation (Aerojet). The objective was to demonstrate in situ bioremediation of perchlorate in a contaminated aquifer using electron donor addition to stimulate naturally occurring bacteria capable of perchlorate reduction. A groundwater recirculation system (HFTWs) was employed to distribute and mix electron donor with perchlorate in the subsurface. This system has previously undergone successful testing for application of electron donor (toluene) for cometabolic remediation of TCE at Edwards Air Force Base (AFB), CA (McCarty et al., 1998). This project represents the first application of this design for in situ perchlorate remediation.

2.1 BACKGROUND

Ammonium perchlorate (HN_4ClO_4) has been used since the 1940s in the United States as an oxidizer in solid propellants and explosives. Discharges during the manufacture of this compound, and from the periodic replacement of outdated solid fuels in military missiles and rockets, has resulted in substantial perchlorate contamination in groundwater in numerous states (ITRC, 2008; Brandhuber and Clark, 2005; Hatzinger, 2005; Urbansky, 1998; Damian and Pontius, 1999). Perchlorate is also present in commercial products, (including flares, fireworks, chlorine bleach, and chlorate herbicides) and occurs naturally in Chilean nitrate fertilizers and some soils and mineral deposits in the Southwest United States (Aziz and Hatzinger, 2008; Aziz et al., 2006; Rajagopalan et al., 2006; Dasgupta et al., 2006). It is estimated that the drinking water of more than 15 million people may be impacted by perchlorate (Wu et al., 2001).

Standard water treatment technologies such as sedimentation, air-stripping, carbon adsorption, and advanced oxidation are generally not effective at removing perchlorate from water because the compound is nonreactive and nonvolatile, its salts are highly soluble, and it cannot be reduced by common reducing agents (Urbansky, 1998; Logan, 1998; USEPA, 2001). Unlike abiotic approaches, however, biological treatment represents a promising technology for perchlorate remediation in groundwater and surface water. A wide variety of microbial strains have been isolated with the ability to degrade perchlorate by using the molecule as a terminal electron acceptor, producing chloride and water as final products. (ITRC, 2008; Coates and Achenbach, 2004; Achenbach et al., 2001; Coates et al., 1999; Rikken et al., 1996) (Figure 1).

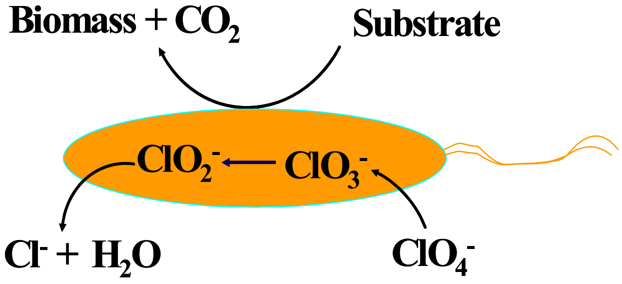

Figure 1. Schematic showing the microbial reduction of perchlorate.

Ex situ biological treatment systems have been successfully developed and implemented to treat perchlorate-contaminated groundwater (ITRC, 2008; Sutton, 2006; Hatzinger, 2005; Logan, 2001). In fact, seven full-scale reactor systems are presently treating groundwater (five) and wastewater (two) (ITRC, 2008; Sutton, 2006; Hatzinger, 2005). Electron donors, such as ethanol and acetate, are supplied to perchlorate-reducing bacteria in these reactors to promote biological reduction of the propellant. The success of ex situ biological treatment of perchlorate has prompted researchers to evaluate in situ treatment options. Current data suggest that PRB are naturally occurring in various environments, including soils, sludges, wastewater, and most groundwater aquifers (Coates et al., 1999; Wu et al., 2001; Waller et al., 2004; Tan et al., 2004). In general, the reason that these indigenous bacteria do not degrade perchlorate in groundwater environments is the absence of a suitable electron donor and unfavorable geochemical conditions (in fact, the two go hand-in-hand). Many aquifers contaminated with perchlorate are aerobic, contain substantial quantities of nitrate, and have low total organic carbon. Each of these factors serves to inhibit perchlorate biodegradation. However, in many instances, adding a suitable organic or inorganic electron donor is all that is required to promote perchlorate bioremediation. When an electron donor is added, indigenous bacteria will often rapidly consume both oxygen and nitrate, thus removing any geochemical inhibitors of perchlorate reduction. PRB will then metabolize perchlorate, producing chloride and water as degradation products.

A wide variety of different electron donors, including ethanol, acetate, benzoate, lactate, citrate, emulsified vegetable oil, molasses, and others have been shown to support biological perchlorate reduction (Hatzinger, 2005 and references therein). Since PRB are indigenous in most aquifers, the prime in situ treatment approach is biostimulation through electron donor addition. A good method for adding electron donor and mixing that donor with perchlorate-contaminated groundwater is the key for successful in situ treatment of perchlorate. The approaches for in situ perchlorate treatment include active systems that mix soluble electron donors into groundwater during continuous active pumping; semi-passive systems that mix soluble electron donors into groundwater during intermittent pumping; and passive systems that apply slow-release electron donors in trenches and wells, or by using direct-push methods, and rely on natural groundwater flow to mix electron donor with contaminated water. The pros and cons of these different possible approaches are described in a recent ESTCP monograph (Stroo and Ward, 2008).

For this demonstration, an active pumping approach based on a recirculating well technology developed at Stanford University was evaluated for electron donor addition and mixing (McCarty et al., 1998; Goltz et al., 1998; Gandhi et al., 2002a, 2002b). This HFTW technology was chosen for this application because it was anticipated to be an effective and inexpensive option for applying electron donor to deep aquifers contaminated with perchlorate. Many competing in situ technologies, such as treatment trenches and barrier walls, are applicable for perchlorate in shallow (<30 ft) isotropic aquifers, but these technologies are not feasible or cost-effective in deep groundwater. This point is important because much of the groundwater perchlorate contamination in the western United States is within deep aquifers (>100 ft bgs). Drilling to these depths particularly if many wells are required for injection of poorly dispersed substrates can be prohibitively expensive. Therefore, a system that effectively meters and mixes electron donor with a large zone of influence, such as the HFTW system, is anticipated to be the most effective in situ remediation option.

2.2 OBJECTIVES OF THE DEMONSTRATION

The objectives of this project were to demonstrate the following: (1) that in situ biological perchlorate treatment is feasible in the field using electron donor addition; (2) that perchlorate can be treated for a sustained period to <4 µg/L; (3) that perchlorate can be treated in a drinking water aquifer without mobilizing significant quantities of iron and manganese or reducing ORP to very low levels; (4) that the zone of influence and efficiency of the HFTW system are sufficient to make the technology a viable, cost-effective option at many sites; (4) that biofouling can be effectively controlled by measures that are easily implemented; and (5) that co-contaminants, including nitrate and TCE, can be treated using the same HFTW technology. As with any pilot-scale technology demonstration, a main objective of this field project was to collect and document information that is relevant to site managers and regulators who are responsible for choosing and implementing technologies.

2.3 REGULATORY DRIVERS

There is currently no federal drinking water standard (maximum contaminant level [MCL]) for perchlorate. However, perchlorate monitoring is required in drinking water by U.S. Environmental Protection Agency (USEPA) under the Safe Drinking Water Act, 1996 amendment. According to this act, USEPA must publish a list of unregulated contaminants (Unregulated Contaminant Monitoring Regulation [UCMR] List) for which monitoring is performed in anticipation of possible future regulatory action. Perchlorate is one of 36 contaminants currently on the final UCMR list published in 1999 (USEPA, 2000). In addition to the UCMR ruling, a special committee of the National Academy of Sciences (NAS) recommended a reference dose (RfD) of 0.7 micrograms (µg) perchlorate/kilogram body weight/day for perchlorate (NAS, 2005). This RfD equates to a drinking water standard of 24.5 µg/L using assumptions made previously by USEPA (USEPA, 2002). In October 2008, the USEPA decided not to promulgate a federal MCL for perchlorate based on Safe Drinking Water Act criteria. However, in December, 2008, USEPA issued an Interim Health Advisory for perchlorate in drinking water of 15 µg/L (USEPA, 2008) and, at the time of publication of this report, perchlorate regulation remains a topic of scientific and political debate.

Although there is presently no federal MCL, a number of states have set their own drinking water advisory levels, including Texas (4 µg/L), New York (5 µg/L), Arizona (14 µg/L), Nevada (18 µg/L), and Maryland (1 µg/L). In addition, in 2006, Massachusetts promulgated the first state regulatory standard for perchlorate at 2 µg/L (Massachusetts Department of Environmental Protection [MADEP], 2009). California followed suit in 2007, setting a slightly higher regulatory standard of 6 µg/L (California Department of Public Health [CDPH], 2009).

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3.0 TECHNOLOGY

This project demonstrates the combined use of two innovative technologies: (1) bioremediation of perchlorate-contaminated groundwater through electron donor addition and (2) horizontal flow treatment wells to achieve in situ mixing of the electron donor with the perchlorate-contaminated water and delivery of the mixture to indigenous perchlorate-degrading bacteria. The field demonstration of in situ perchlorate treatment using electron donor addition builds upon extensive laboratory data showing that PRB are indigenous to many natural environments, including groundwater aquifers and that they can be stimulated to biodegrade perchlorate upon addition of appropriate electron donors (Tan et al., 2004; Waller et al., 2004; Hatzinger et al., 2002; Coates et al., 1999). The HFTW system is used to distribute electron donor within the contaminated zone in the aquifer. The HFTW design combines the best features of pump-and-treat and funnel-and-gate technologies to contain and treat contaminated groundwater. As an in situ technology, contaminant destruction occurs below ground, and there is no need to pump contaminated water to the surface for treatment. On the other hand, since the HFTW system uses pumping wells, the contaminant plume is actively contained, and the limitations of funnel-and-gate systems (restricted to relatively shallow contamination depths and potential for plume to bypass the treatment system) are overcome.

3.1 TECHNOLOGY DESCRIPTION

HFTWs are designed to operate in pairs in the subsurface. The key advantage of these well pairs is that they promote significant mixing of amendments with groundwater without the necessity of pumping groundwater to the surface (i.e., the process occurs in the saturated zone). In this field demonstration, one pair of HFTWs was installed. A schematic of the two wells is provided in Figure 2, and photos of the pumps and packers being installed into one of the HFTWs are provided in Figure 3. As shown in Figure 2, each treatment well has two screens, one an injection screen, the other an extraction screen. One of the two treatment wells is operated in an upflow mode such that groundwater is extracted from the aquifer through the lower well screen, and amended with citric acid as the electron donor (HFTW-U). The electron donor-augmented groundwater is then injected back into the aquifer through the upper well screen. The second treatment well is operated in a downflow manner (HFTW-D). In this case, the groundwater is extracted from the aquifer into the upper well screen, augmented with electron donor, and then injected back into the aquifer through the lower well screen. Inflatable packers are placed within each well to prevent water exchange between the upper and lower screen intervals. A bentonite seal is placed at the location of each packer during well installation to prevent water movement/leakage from one zone to another in the filter pack of each well. With this two-well arrangement, a percentage of the groundwater is recycled between the two wells. This percentage can be modified by changing pumping rates in the two HFTWs.

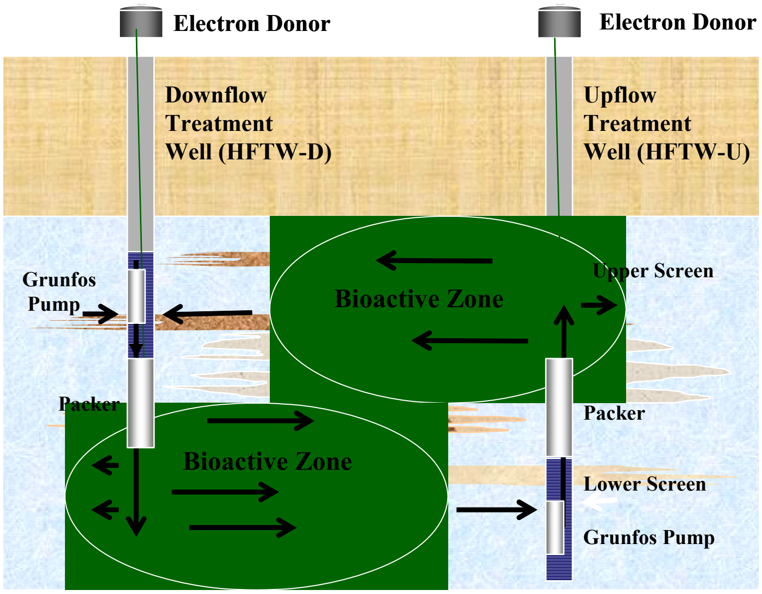

Figure 2. Schematic of HFTW design.

Figure 3. Photograph of equipment installation into the downflow HFTW at Aerojet. The packer is visible in photo A, and the wiring, tubing, and equipment present in the HFTW is seen in photo B.

Due to hydraulic conductivity anisotropy such as is typically seen in aquifers (Fetter, 1994), groundwater flow between the injection and extraction screens of a well pair is predominantly horizontal in the HFTW system. This is in contrast to conventional groundwater circulation wells (GCW) that depend on vertical flow between the injection and extraction screens of a single well. For any installation, the distance between the pair(s) of HFTWs, the screen intervals, the distance separating the two well screens, and the pumping rates of each well are key variables. Groundwater flow modeling is generally used to determine these key variables. A model specifically designed to simulate groundwater flow from HFTWs has been developed and field-tested by Dr. Mark Goltz and colleagues at the AFIT. The details of the model are provided in several publications (Parr, 2002; Knarr, 2003; Chosa, 2004; Secody, 2007).

The key design parameters for this demonstration were determined using the AFIT model. Input data for the model included detailed results from slug and pump conducted as pre-demonstration activities. In addition, complete cores were collected from two locations at the site using rotosonic drilling. A geological evaluation of these cores was performed in order to evaluate the vertical stratification in the aquifer and determine zones with the highest hydraulic conductivities. The geological evaluation combined with pump test and slug test data were used to determine the final placement of the screens in each treatment well and the distance between the wells, and to design the monitoring well network.

A generalized overhead view of the demonstration plot installed at Aerojet is provided in Figure 4 and a photograph of the site in Figure 5. This version is not to scale (see Figure 10 for a plan view to scale). The two HFTWs were placed ~34 ft apart cross-gradient to groundwater flow. A series of groundwater monitoring wells were installed to quantify concentrations of perchlorate and to evaluate geochemical conditions within and outside of the treatment zone. Many of these wells were nested installations so that the geochemistry and contaminant concentrations could be monitored throughout the vertical profile of the aquifer. The monitoring well network consisted of a total of 19 wells, with screen intervals as shown in Figure 4.

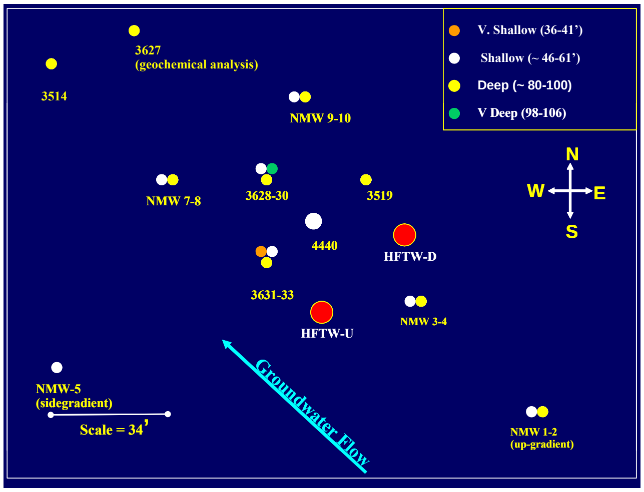

Figure 4. General layout of demonstration plot.
Distances between all monitoring wells are not to scale. The HFTWs are placed 34 ft apart, cross-gradient to the general direction of groundwater flow.

Figure 5. Photograph of the Aerojet HFTW system showing location of HFTWs and all monitoring wells.

While this project constitutes the first field test of the HFTW technology for perchlorate remediation, key components of the technology have been tested previously for remediation of volatile organic compounds (VOC). The idea of using HFTWs to mix chemicals into contaminated groundwater to stimulate bioremediation by indigenous microorganisms was first implemented to treat TCE-contaminated groundwater at Site 19, Edwards AFB (McCarty et al., 1998; Gandhi et al., 2002a, 2002b). During the demonstration at Edwards AFB, two dual-screened treatment wells were used to establish two bioactive zones, one in an upper unconfined aquifer and the other in a lower confined aquifer. Both aquifers were contaminated with about 1000 µg/L of TCE. TCE-contaminated groundwater circulating through the treatment wells was amended with an electron donor (toluene) and oxygen to stimulate aerobic cometabolic biodegradation of the TCE. Based on extensive sampling, it was estimated that TCE concentrations in the groundwater were reduced about 85% during a single pass through a bioactive zone of toluene/oxygen-amended water. However, because of the recirculation of groundwater between the two wells, overall TCE removals of 97-98% were achieved, when comparing contaminant concentrations upgradient and downgradient of the treatment system. Biofouling at the injection screens was successfully managed by adding hydrogen peroxide to the water flowing through the treatment wells. However, the peroxide treatment did not completely prevent fouling, and physical well redevelopment was required periodically to restore pumping rates in each HFTW.

The study at Edwards AFB demonstrated the efficacy of HFTWs for obtaining hydrologic control, while containing and destroying contaminants in groundwater without the need to bring contaminated groundwater to the surface. By adjusting pumping rates in each of the two treatment wells, and therefore controlling the extent of recirculation in the treatment system, desired overall contaminant destruction efficiencies could be achieved. The results of the Edwards AFB study, including details on the design, modeling, and operation of the horizontal mixing treatment well system, have been published (McCarty et al., 1998; Goltz et al., 1998;

Gandhi et al., 2002a, 2002b). The HFTW concept was further applied at Edwards AFB in two separate projects (Strategic Environmental Research and Development Program [SERDP] Project ER-1064 and ESTCP Project ER-0012). SERDP Project ER-1064, Bioenhanced In-Well Vapor Stripping to Treat TCE, which was concluded in 2002, demonstrated the efficacy of using HFTWs near a TCE source area (SERDP, 2003), while ESTCP Project ER-0012, evaluated the utilization of HFTWs to effect abiotic destruction of a TCE plume (ESTCP, 2007).

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The main advantages of this in situ destruction technology are (1) decreased risk and cost, as groundwater contaminants are destroyed below ground and not brought to the surface for treatment and disposal; (2) increased acceptability to regulators, since there is no need to reinject contaminated water or bring contaminant to the surface; and (3) small aboveground footprint, which may be crucial at Department of Defense (DoD) installations, where space is sometimes limited. Both of the main components of the technology, (1) the use of HFTWs to effect mixing and amendment of electron donor and (2) the application of electron donor to stimulate indigenous microorganisms to biodegrade perchlorate, have been successfully field tested.

One potential limitation with this and any in situ technology in which organic substrate is added to an aquifer is that the donor addition will result in zones of reduced groundwater that could potentially mobilize metals or promote hydrogen sulfide production or other changes in geochemistry that can impact groundwater quality. These issues frequently occur with the addition of high quantities of slow release substrates, such as vegetable oil, molasses, or polylactate ester (e.g., hydrogen release compound [HRC]). During this demonstration a single soluble substrate (citric acid) was metered and mixed with the contaminated groundwater in order to minimize the consequences of high excess toxic organic carbon (TOC) addition, such as sulfate reduction and methanogenesis, to the extent possible. In addition, with active mixing systems, the electron donor can be decreased in concentration or changed completely if undesirable geochemical endpoints are observed. This is not true for slow release substrates, which will persist in an aquifer for months or years after application.

A second potential concern or limitation with this technology is that microbial fouling may have a significant impact on HFTW performance and long-term operational cost. Biofouling was a significant issue during the demonstration at Edwards AFB as well as this demonstration at Aerojet. At Edwards, the problem was controlled through the addition of hydrogen peroxide to the treatment wells and periodic redevelopment. During this demonstration, chlorine dioxide was used as an anti-fouling agent; an electron donor shown to promote less significant fouling than others was chosen (i.e., citric acid) (Chopra et al., 2004); and electron donor dosing was conducted periodically rather than continuously, all in an attempt to minimize issues associated with well fouling. A third concern with the HFTW approach is short-circuiting of the pumped groundwater, resulting in primary flow between the upper and lower screens in a single HFTW rather than between the paired HFTW units. In the previous test of this technology at Edwards AFB for aerobic cometabolism of TCE, a clay aquitard was present between the upper and lower screen intervals of each individual HFTW, thus limiting any possible short circuiting (McCarty et al., 1998). This project represents the first demonstration in which a confining layer was not present between HFTW screens.

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4.0 PERFORMANCE OBJECTIVES

The performance objectives for this project are listed in Table 1. These include (1) consistent reduction in perchlorate concentrations in Phase I and Phase II treatment, (2) minimal mobilization of Fe and Mn in Phase I, (3) greater than 165 ft (~50 m) of groundwater capture by the HFTW system, (4) control of biofouling, and (5) reduction of TCE concentrations during Phase II and/or Phase III operation. Actual performance data are summarized in Table 1, and more detail is provided in Section 6 and in the project final report (Hatzinger and Diebold, 2009).

Table 1. Demonstration performance objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (metric)	Actual Performance
Quantitative	Reduction of perchlorate levels in HFTW treatment zone	Consistent reduction to <4 µg/L; >99.8%	Reduction to <100 µg/L; 96% in shallow wells and 88% in deep, downgradient wells
	Reduction of nitrate levels in HFTW treatment zone	Consistent reduction to <0.2 mg/L as N	Consistent reduction in shallow wells during Phase I and inconsistent reduction in deep wells
	Reduction of TCE levels in treatment zone in Phase II and/or Phase III of study using biostimulation +/- bioaugmentation	Reduction by >95%	Reduction by 76% in shallow wells and 71% in 4 deep downgradient wells
	Minimal mobilization of iron and manganese; reduction in background levels within 100 ft of downgradient influence of HFTW system	Minimal mobilization and reduction in background Fe and Mn values in downgradient monitoring well(s)	Minimal mobilization of Fe and Mn during Phase I; greater mobilization in Phases II & III
Qualitative	System reliability and ease of operation	Continuous operation with minimal downtime and supervision	Significant biofouling and O&M with Phase I continuous flow operation; less with active-passive operation (Phase III)
	Biofouling control using chlorine dioxide injection	Ability to maintain injection screen pressures in operable range	Chlorine dioxide slowed but did not prevent biofouling in Phase I and II; significant pressure increases observed

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5.0 SITE DESCRIPTION

Several field sites for the demonstration were evaluated during the first 3 months of the project. These sites included the Jet Propulsion Laboratory (Pasadena, CA), two locations at Edwards AFB (Edwards, CA), and two locations at Aerojet (Rancho Cordova, CA). Based on a review of relevant site data, Area D at the Aerojet facility was chosen for the demonstration.

5.1 SITE LOCATION

The Test Site is located within Aerojet's 8500-acre Sacramento, CA facility used for rocket engine development, testing, and production. Aerojet has been manufacturing and testing rocket propulsion systems at this facility continuously since the year 1951 when the facility was first occupied. Both solid rocket motors and liquid rocket engines are produced at this facility. The source of the Area D plume at Aerojet is a former propellant burn area known as the Central Disposal Area (CDA). The Test Site area is located approximately 2400 ft downgradient of CDA. A plume map with the Test Site Area demarcated is provided in Figure 6. The CDA, specifically Site 42D, is the apparent source of the perchlorate and VOCs (primarily TCE) plume that underlies the Test Site. The CDA is an area where during the 1950s, waste propellant and solvents were open burned for disposal purposes. The mixed TCE-perchlorate groundwater plume that is thought to originate from Site 42D is approximately 5800 ft long and 3000 ft wide and impacts multiple fluvial aquifer units to depths of 300 ft over its course. The plume is intercepted and treated approximately 3000 ft downgradient of the Test Site at Aerojet's 1000 gpm Groundwater Extraction Treatment Facility D (GET D).

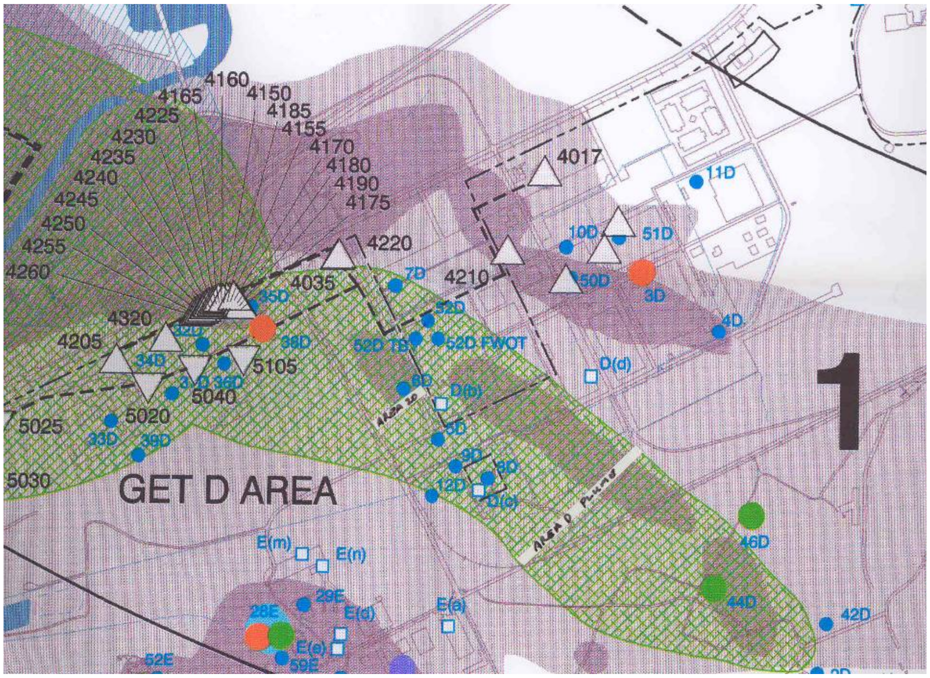

Figure 6. Location of the test site.

5.2 SITE GEOLOGY AND HYDROGEOLOGY

The Aerojet Site is located in eastern Sacramento County near the transition zone between the Great Valley and Sierra Nevada geomorphic provinces. The geology of the Great Valley, as summarized by Hackel, (1966), can be described as a large elongate northwest-trending asymmetric trough. This trough is filled with a very thick sequence (up to 60,000 ft) of sediments of primarily marine origin ranging in age from Jurassic to recent. The sediments that compose the eastern flank of the Great Valley (where the Aerojet Site is situated) thin dramatically as they approach the foothills of the Sierra Nevada and eventually thin out completely, exposing the underlying crystalline basement rocks of pre-Tertiary age igneous and metamorphic rocks that make up the Sierra Nevada Mountain Range. The Aerojet site is underlain by fluvial and marine sedimentary deposits ranging in age from Cretaceous to recent. These sedimentary deposits unconformably overlie Jurassic-aged metamorphic basement rocks that dip to the west. These sediments form a wedge, which thickens from east to west, across the Aerojet site. The easternmost sediments at the Aerojet site are about 60 ft thick while at its western boundary, (a distance of six miles) the sediments are nearly 2000 ft.

The Laguna and Mehrten Formations contain the most productive aquifers underlying the Aerojet site and serve as the principal source of water for private and public water supply wells in the area. Six individual aquifer units (A through F) have been defined beneath the Aerojet site, with A being the shallowest (unconfined) and F being the deepest. The directional trend of groundwater flow generally mimics topography. Groundwater flows in a westerly direction towards the center of the Sacramento Valley due to a decrease in topographical elevation of several hundred feet. The unconfined Aquifer A is present at a depth of about 50 ft at the eastern portion of the Aerojet facility and is found at a depth of 120 ft at Aerojet's western boundary, a distance of 6 miles. Hydraulic conductivities for the various aquifers range from 1 to 446 ft/day with an average of about 70 ft/day. Hydraulic gradients range from 0.005 ft/ft to 0.02 ft/ft. Vertical hydraulic gradients tend to be downward at the Aerojet site.

The Test Site is situated over undredged sedimentary deposits of the Merhten Formation. Ground surface elevation for the Test Site is approximately 160 ft above mean sea level (msl). Soil borings at the Test Site indicated that the underlying soil materials are composed primarily of interbedded fine sands, silty sands, and silt with occasional gravel lenses. A representative soil boring log from the Test Site is provided in Figure 7. Some of the sands and silts display moderate induration, and the first groundwater is encountered at a depth of 25 to 30 ft bls, with static groundwater at about 30 ft bls. Groundwater flow is towards the southwest with a gradient of approximately 0.017 ft/ft.

5.3 CONTAMINANT DISTRIBUTION

Prior to the demonstration, four groundwater wells were present at the Test Site. Three were screened at intervals from 30 to 105 ft bls, where perchlorate contamination is present. These wells were used for groundwater monitoring during the demonstration along with wells that were installed during the demonstration for this purpose (19 wells total). Table 2 summarizes perchlorate and VOC results from 10 of the monitoring wells at the Test Site prior to the demonstration. The groundwater sample results obtained from two sets of nested wells installed during the pre-demonstration site assessment activities (wells 3628 through 3633) indicate that perchlorate and VOC concentrations increase with depth. The groundwater sample obtained from well 3631, screened between 36 and 41 ft bls in the upper water bearing zone, indicated a perchlorate concentration of 65 µg/L, while the samples obtained from wells 3628 and 3632, each screened from 52-57 ft bls, contained perchlorate concentrations of 330 and 155 µg/L, respectively. The samples obtained from the lower water bearing zone (75 to 105 ft bls) contained perchlorate ranging from 970 µg/L up to 3920 µg/L.

Table 2. Perchlorate and VOC concentrations in monitoring wells in the demonstration area.

Well[1]	Perchlorate (µg/L)	TCE (µg/L)	Screen Interval (ft bls)
3628	330	47	52 – 57
3629	1500	600	80 – 85
3630	3140	1200	96 – 101
3631	65	14	36 – 41
3632	155	78	52 – 57
3633	3350	650	98 – 103
3627	970	1200	75 – 95
3519	2320	1700	78 – 103
3514	3920	2100	77 – 90
4440	3300	2200	75 – 93 and 98 – 106

[1] All data are from 2003 sampling except well 4440 (1995 data)

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6.0 TEST DESIGN

6.1 CONCEPTUAL EXPERIMENTAL DESIGN

The HFTW system is designed to mix electron donor into groundwater below ground surface and promote the in situ biological reduction of perchlorate. Because no water is pumped aboveground, there is neither a contaminated feed nor an effluent stream to characterize. Rather, the operational performance of the system was evaluated by measuring and comparing contaminant levels in system monitoring wells at the demonstration site. An extensive well network was installed for this purpose. Table 3 contains a list of contaminants that were measured during the demonstration. To evaluate system performance in this demonstration, concentrations of perchlorate and co-contaminants were monitored with time in a series of nested monitoring wells placed within the expected treatment zone of the HFTW system (19 wells shown in Figures 4 and 10). For experimental purposes, the concentrations of perchlorate and co-contaminants in the monitoring wells were compared to the following values: (1) baseline perchlorate and co-contaminant levels in each monitoring well prior to electron donor addition but during HFTW operation (4 baseline sampling events were performed during the initial 6 weeks); (2) contaminant levels in a nested upgradient monitoring well screened in similar zones to the HFTWs (NMW-1 and NMW-2); and (3) historical perchlorate and co-contaminant levels in monitoring wells 4440, 3514, and 3519, each of which was pre-existing at the site.

Table 3. Parameters measured during groundwater sampling.

Parameter	Method/ Procedure	Preservative	Bottle Size
Nitrate	USEPA 300.0	4°C	100 mL[1]
Sulfate	USEPA 300.0	4°C	100 mL[1]
Chloride	USEPA 300.0	4°C	100 mL[1]
Bromide	USEPA 300.0	4°C	100 mL[1]
Dissolved manganese	USEPA 200.7	0.45-µm cartridge filter; nitric acid	250 mL[2,4]
Dissolved iron	USEPA 200.7	0.45-µm cartridge filter; nitric acid	250 mL[2,4]
Volatile organic hydrocarbons	USEPA 8260	Hydrochloric acid	40 mL VOA[5]
Perchlorate	USEPA 314.0	Sterile 0.22-µm syringe filter	50 mL sterile[3]
Volatile fatty acids	USEPA 300.0m	Sterile 0.22-µm syringe filter	50 mL sterile[3]
Reduction potential (ORP)	Field meter	--	--
Dissolved oxygen	Field meter	--	--
pH	Field meter	--	--
Conductivity	Field meter	--	--

[1] The same sample bottle was used for the analyses noted.
[2] The same sample bottle was used for all analyses noted.
[3] The same sample bottle was used for all analyses noted.
[4] Performed for only selected wells and sampling events.
[5] VOA = volatile organic acid

A coupled groundwater transport-biodegradation technology model was employed to predict perchlorate concentrations (as well as electron donor and competing electron acceptor concentrations) throughout the demonstration site as a function of time. This technology model was used to help design the HFTW treatment system (determine treatment well location, pumping rates, and the electron donor injection schedule) in order to achieve desired downgradient perchlorate concentrations. The results of the demonstration are compared to model predictions by Secody (2007). The HFTW model simulates transport of the electron donor, perchlorate, and competing electron acceptors (oxygen and nitrate) in the groundwater flow field induced by operation of the HFTW well pair. The rate of perchlorate reduction is modeled using Monod kinetics, with the rate dependent on both perchlorate and electron donor concentrations. Kinetic parameters for the model were estimated based on laboratory batch studies (Farhan and Hatzinger, 2009).

The operational period of the HFTW system consisted of initial background and tracer testing, followed by three operational phases over a period of approximately 2 years from September 2004 until December 2006. Sampling events are provided in Table 4. A summary of the experimental goals of each phase of testing is provided below:

1. Background sampling and tracer testing: All wells were sampled five times after the HFTW operation commenced on August 12, 2004 but prior to the initial injection of electron donor on October 28, 2008 (See Table 4). The objective of this phase was to quantify baseline levels of key contaminants (perchlorate, nitrate, VOCs) in each monitoring well. A dual tracer test was also performed during this period (beginning on August 30, 2004) to evaluate and verify local hydrogeological characteristics. Select wells near the HFTWs were sampled for the two tracer salts (bromide and chloride) twice during the initial week after injection, then all wells were sampled for these salts during the reminder of the background testing phase (five more sampling events).

2. Phase I of system operation occurred from October 28, 2004, until August 1, 2005 (~275 days). The objectives of Phase I were as follows: (1) to evaluate groundwater mixing/flow, (2) to determine the extent of perchlorate and nitrate bioreduction that was possible without mobilizing significant quantities of iron and manganese as secondary groundwater contaminants, and (3) to evaluate biofouling control and treatment. Only a slight excess of the citric acid electron donor was applied during this period of testing. A total of nine groundwater sampling events were performed during Phase I, seven of which occurred during active system operation, and two of which were performed after citric acid addition was stopped on April 24, 2005 (Table 4).

3. Electron donor was not injected from the end of Phase I until the beginning of Phase II operation. This period was used to evaluate biofouling treatment approaches for the HFTWs and to allow rebound of contaminants for Phase II testing. Each of the HFTWs was redeveloped via chemical and physical methods prior to the commencement of Phase II on February 28, 2006. The key objective of Phase II was to treat perchlorate without promoting significant well biofouling. This objective is critical to the long-term viability of HFTWs for perchlorate treatment. The electron donor dosing regimen was switched from a daily addition (as in Phase I) to larger weekly or twice-per-week doses in order to evaluate the impact of dosing schedule on both perchlorate treatment and well fouling. In

addition, chlorine dioxide was added to each well on a daily basis (four to eight times per day) from February 15 to April 12, 2006, then reduced to one dose only after citric acid injection from April 12 to June 20, 2006.

4. Phase III of system operation was implemented from September 11 to December 11, 2006. The objective of Phase III was to assess an active-passive mode of operation. In this case, the HFTW wells were used primarily for mixing electron donor with the perchlorate-contaminated groundwater. The pumping system was then turned off between mixing periods. The key objective was to determine whether this mode of system operation would result in a consistent reduction in perchlorate concentrations and reduced system O&M costs. During Phase III, the HFTW treatment wells were operated in a 15-day cycle consisting of 3 days of active pumping followed by 12 days in passive (non-pumping) mode. Citric acid was added to both HFTWs in three 12-hour pulses during the active period resulting in the addition of approximately 60 L of electron donor per 12-hour cycle and 180 L per operating time. Each HFTW was operated at a net flow rate of 6 gpm. The 15-day cycle was repeated six times during the 3-month test period, and three sampling events were performed. An initial sampling round was conducted prior to beginning the active-passive operation (September 6, 2006) to provide a baseline, and a final round was performed on January 15, 2007.

Table 4. Phases of operation and dates of groundwater sampling.

Phase	Date	Days
Bkgd & Tracer	8/12/2004	Initiate flow
	8/30/04	Begin tracer tests
	8/31/04	-58 (Br[1] and Cl[2] only)
	9/02/04	-56 (Br and Cl only)
	9/7/2004	-51
	9/15/2004	-43
	9/22/2004	-36
	9/30/2004	-28
	10/13/2004	-15
Phase I	10/28/2004	Begin citric acid injection (Day 0)
	11/3/2004	7
	11/17/2004	20
	12/1/2004	34
	12/20/07	53
	1/3/2005	67
	2/3/2005	98
	3/21/2005	146
	4/24/2005	End Phase I citric acid addition
	5/5/2005	188
	8/1/2005	275
Phase II	2/14/2006	472
	2/15/2006	Begin Phase II citric acid injection
	4/3/2006	520
	5/8/2006	555
	7/5/2006	614

Table 4. Phases of operation and dates of groundwater sampling (continued).

Phase	Date	Days
Phase III	9/6/2006	677
	10/11/2006	712
	11/28/2006	760
	1/8/2007	801

[1] BR = bromine
[2] Cl = chlorine

6.2 BASELINE CHARACTERIZATION

Baseline characterization consisted of (1) collection of sample cores via rotosonic drilling to characterize site lithology, (2) slug and pump testing to quantify hydraulic conductivity, and (3) baseline sampling of contaminant concentrations. These data were incorporated into the site model and used to finalize system design.

6.2.1 Soil Borings

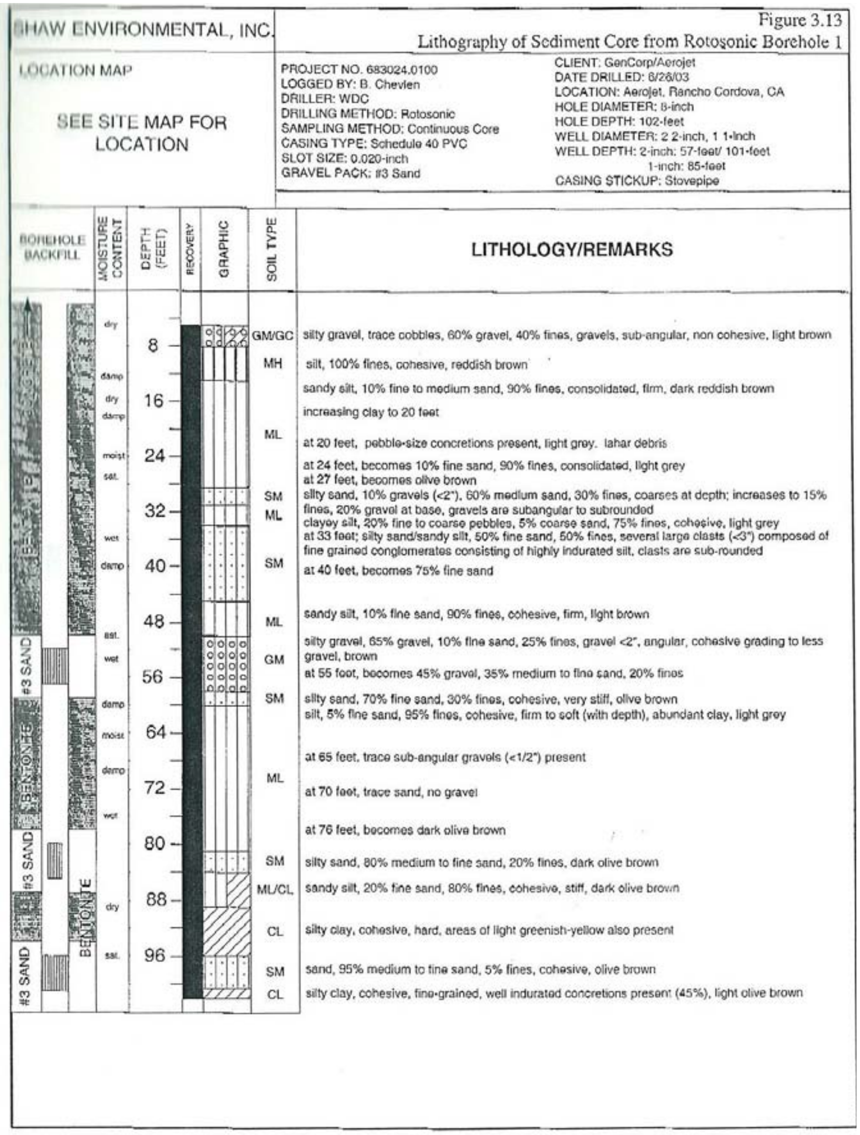
Rotary-vibratory drilling, also known as rotosonic drilling, was used to advance soil borings, and to collect two continuous soil core samples. Field personnel characterized the soil samples in 2-ft intervals using the Unified Soil Classification System (USCS). The final screen completion depths were determined in the field based on the lithology observed within the soil cores collected during borehole advancement. In the first borehole, water-bearing zones containing sands and/or gravels were observed from 27–36 ft, 50–57 ft, 81–85 ft, and 96–101 ft bls (Figure 7). Based on this field observation, piezometers (used for demonstration sampling) were installed in this boring and screened from 52–57 ft, 80–85 ft, and 96–101 ft bls. The second boring was performed to determine the continuity of the different layers observed in the first sonic borehole as well as from historical well logs for the area. As with the previous borehole, saturated zones were again observed in the vicinity of 80 ft bls and again from approximately 96–105 ft bls. Based on the lithography reported, the piezometers in this boring were screened at 36–41 ft, 52–57 ft, and 98–103 ft bls. The screen intervals chosen for both borings provide a good vertical representation of the geochemistry within the B aquifer at the Test Site.

6.2.2 Groundwater Sample Collection

Groundwater samples were collected from newly installed piezometers in July 2003 after the development of each well. Collected samples were analyzed for the following geochemical and contaminant parameters: perchlorate, nitrate, sulfate, and VOCs. The concentrations of perchlorate and TCE (the primary VOC at the site) for all wells within the demonstration area prior to completion of the demonstration monitoring well network are presented in Table 3. These baseline samples better established the vertical distribution of perchlorate and co-contaminants in the demonstration area and aid in the selection of proper screen intervals for the HFTWs. Several additional rounds of groundwater sampling were conducted between August and October 2004 as shown in Table 4.

6.2.3 Aquifer Pump and Slug Testing

Additional aquifer testing was performed to better define the horizontal and vertical hydraulic conductivity of the saturated intervals encountered between 25 and 105 ft bls and the degree of hydraulic separation between these intervals. Well 4440 was used for pump testing. A stepped pumping method was used during this test. Draw-down measurements were obtained using electronic data-loggers (trolls) from wells 3629, 3630, 3632, 3633, and historical wells 3514, 3627, and 3519 during the pump test. Measurements were made by hand using water level meters for the 1-inch piezometers (wells 3628 and 3631). Slug testing was also performed on the newly installed 2-inch inner diameter (ID) wells. The rate of water level decrease or increase was measured for both falling head and rising head tests, respectively. The data were then analyzed by the Bouwer and Rice slug test solution using commercially available computer software. The pump and slug test data obtained from this additional aquifer testing were utilized to refine the flow model and establish the final screen intervals and well spacings for the HFTWs.



SHAW ENVIRONMENTAL, INC.

Figure 3.13
Lithography of Sediment Core from Rotosonic Borehole 1

LOCATION MAP

SEE SITE MAP FOR LOCATION

PROJECT NO. 683024.0100
LOGGED BY: B. Chevien
DRILLER: WDC
DRILLING METHOD: Rotosonic
SAMPLING METHOD: Continuous Core
CASING TYPE: Schedule 40 PVC
SLOT SIZE: 0.020-inch
GRAVEL PACK: #3 Sand

CLIENT: GenCorp/Aerojet
DATE DRILLED: 6/26/03
LOCATION: Aerojet, Rancho Cordova, CA
HOLE DIAMETER: 8-inch
HOLE DEPTH: 102-feet
WELL DIAMETER: 2 2-inch, 1 1-inch
WELL DEPTH: 2-inch: 57-feet/ 101-feet
1-inch: 85-feet
CASING STICKUP: Stovepipe

SOIL TYPE	LITHOLOGY/REMARKS
GM/GC	silty gravel, trace cobbles, 60% gravel, 40% fines, gravels, sub-angular, non cohesive, light brown
MH	silt, 100% fines, cohesive, reddish brown
ML	sandy silt, 10% fine to medium sand, 90% fines, consolidated, firm, dark reddish brown increasing clay to 20 feet at 20 feet, pebble-size concretions present, light grey. lahar debris at 24 feet, becomes 10% fine sand, 90% fines, consolidated, light grey at 27 feet, becomes olive brown
SM	silty sand, 10% gravels (<2"), 60% medium sand, 30% fines, coarses at depth; increases to 15% fines, 20% gravel at base, gravels are subangular to subrounded
ML	clayey silt, 20% fine to coarse pebbles, 5% coarse sand, 75% fines, cohesive, light grey
SM	at 33 feet; silty sand/sandy silt, 50% fine sand, 50% fines, several large clasts (<3") composed of fine grained conglomerates consisting of highly indurated silt, clasts are sub-rounded at 40 feet, becomes 75% fine sand
ML	sandy silt, 10% fine sand, 90% fines, cohesive, firm, light brown
GM	silty gravel, 65% gravel, 10% fine sand, 25% fines, gravel <2", angular, cohesive grading to less gravel, brown at 55 foot, becomes 45% gravel, 35% medium to fine sand, 20% fines
SM	silty sand, 70% fine sand, 30% fines, cohesive, very stiff, olive brown
ML	silt, 5% fine sand, 95% fines, cohesive, firm to soft (with depth), abundant clay, light grey at 65 feet, trace sub-angular gravels (<1/2") present at 70 feet, trace sand, no gravel at 76 feet, becomes dark olive brown
SM	silty sand, 80% medium to fine sand, 20% fines, dark olive brown
ML/CL	sandy silt, 20% fine sand, 80% fines, cohesive, stiff, dark olive brown
CL	silty clay, cohesive, hard, areas of light greenish-yellow also present
SM	sand, 95% medium to fine sand, 5% fines, cohesive, olive brown
CL	silty clay, cohesive, fine-grained, well indurated concretions present (45%), light olive brown

Figure 7. Lithography of sediment core from Borehole #1.

6.2.4 Modeling Support for Final System Design

Based on the geologic and contaminant results, as well as slug and pump test results, several system configurations were considered and simulated using flow and transport models. All simulations focused on establishing horizontal flow and electron donor addition within the saturated deposits between 46 and 105 ft bls, which correlates to the areas with higher perchlorate concentrations. The initial process involved developing a conceptual geologic layering pattern. Using results from the pump test, flow modeling (using MODFLOW) and optimization techniques were used to estimate layer hydraulic conductivities that provided a best fit of model-simulated draw-downs to measured draw-down data. Initially, a 14-layer site model was developed. Based on initial simulations, this model was subsequently modified to a 15-layer, four-zone model. Layer depths and conductivities for the 15-layer site model are shown in Figure 8. Using calibrated conductivities, the model was successfully validated by comparing model-simulated and measured draw-downs at a monitoring well (well 3633) that was not used for calibration.

After completing the model calibration and validation, the multilayer flow model was used to simulate the flow regime created by the pair of HFTWs, Additional details concerning the modeled flow for the system are provided in the Final Report.

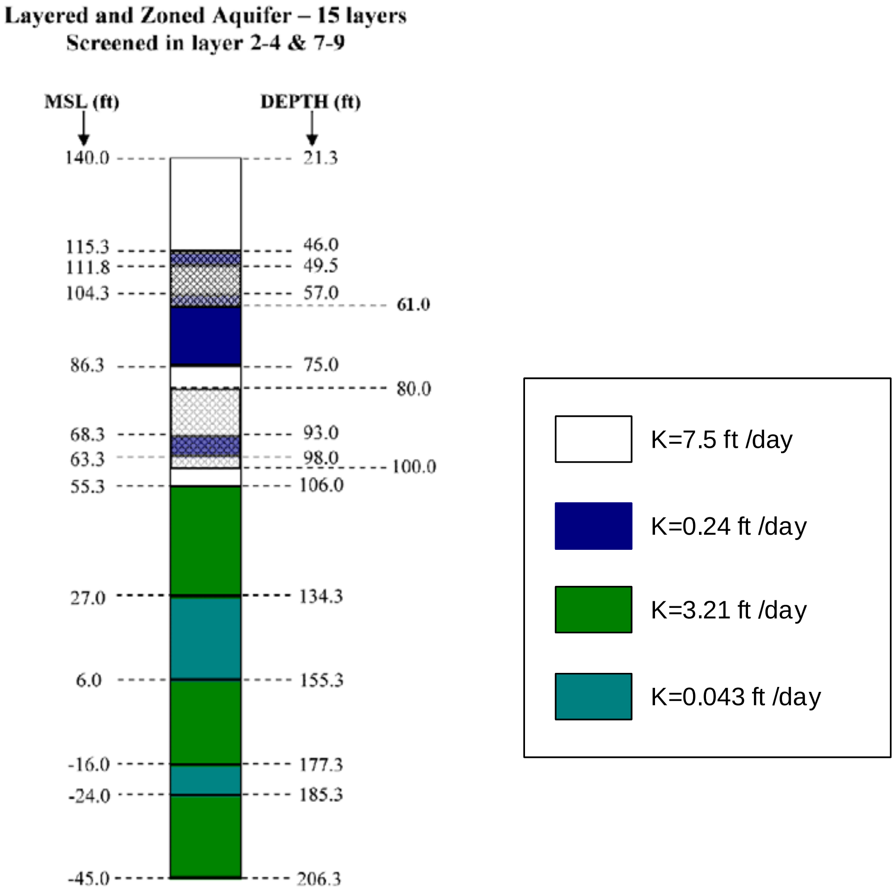


Figure 8. Conceptual model of demonstration site aquifer based on rotosonic logs and pump tests.

6.3 TREATABILITY STUDY RESULTS

Site-specific microcosm studies were conducted to evaluate the most effective electron donors for biological reduction of perchlorate and nitrate in the Area D location. The degradation of the TCE was also evaluated in these studies. Aquifer solids from the installation of well 3627 (from 40-42 ft, 50-52 ft, 60-62 ft, 80-82 ft, and 90-92 ft) were homogenized combined in 160-mL serum bottles with groundwater collected from well 3519, then quadruplicate samples were amended with 3 mM of ethanol, citrate, or lactate as electron donors. Killed controls (one set formaldehyde-treated and one set acid-treated) were prepared as were unamended live controls. The bottles were filled so that no headspace remained.

Nitrate concentrations in microcosms declined from approximately 16.8 mg/L (3.8 mg/L as N) to below detection within 5 days in all microcosms receiving electron donors. Perchlorate levels declined in the same samples to below detection after approximately 15 days of incubation. Interestingly, nitrate and perchlorate were also consistently degraded in microcosms that did not receive an amendment of electron donor (i.e., unamended controls), although not in the formaldehyde-killed controls. It is likely that a natural electron donor was present in the site aquifer solids (probably organic matter) and that the bioavailability of this material was increased during sample collection and homogenization. This "released" electron donor was then able to support nitrate and perchlorate reduction.

In order to evaluate the ability of the added electron donors to support perchlorate reduction, each set of microcosms was re-spiked with additional perchlorate to 5 mg/L. Within 10 days, perchlorate concentrations in bottles with citrate, acetate, and lactate were below detection. Perchlorate concentrations in bottles with no electron donor and those receiving formaldehyde to inhibit microbial activity remained near 4-6 mg/L (Figure 9). Thus, based on these results, any of the three electron donors tested are likely to support perchlorate reduction at the test site.

After 88 days of incubation, there was no appreciable difference in TCE concentrations in any of the active treatments (amended with electron donor) compared to the unamended or killed controls. This was true, even though in bottles receiving lactate, acetate was detected at the 60-day sampling point, suggesting that fermentation of lactate was occurring. An additional microcosm study was set up to look specifically at TCE degradation over a longer period of time. In this study, 16 g of homogenized Aerojet aquifer solids and 55 mL of site water from well 3519 were placed into 50-mL serum vials so that the bottles were filled. The electron donor amendment, incubation, and sampling conditions were otherwise as described previously. As with the previous study, although there was some decline in TCE concentrations during the incubation time (due to sampling and increasing headspace volume), degradation of TCE was not apparent after nearly 3 months of incubation. Common daughter products of TCE dechlorination such as cis-DCE or VC were not observed. The two microcosm studies suggest that anaerobic dechlorination in the demonstration site location is likely to be either minimal or very slow. As a result, bioaugmentation of aquifer samples with dechlorespiring enrichment cultures was tested in microcosm samples. Two separate cultures, one isolated from North Island Naval Air Station in CA, and one isolated from Pinellas, FL, were tested for activity in the Aerojet samples. Each of these cultures contains multiple bacterial species, and each consortium is capable of degrading TCE all the way to ethene in liquid culture. The two cultures were then added separately to duplicate bottles from the previous study. To ensure that carbon was in excess, each bottle also received 1 mM lactate as a carbon source and 0.025% yeast extract as a vitamin source. Replicate bottles received the lactate and yeast extract only to ensure that any TCE dechlorination could be attributed to the augmented cultures. After 5 days of incubation, the TCE in each bottle was converted to cis-DCE. The cis-DCE slowly declined during the next several weeks (data not shown). These data suggested that bioaugmentation may be a viable strategy to reduce TCE concentrations in the demonstration plot.

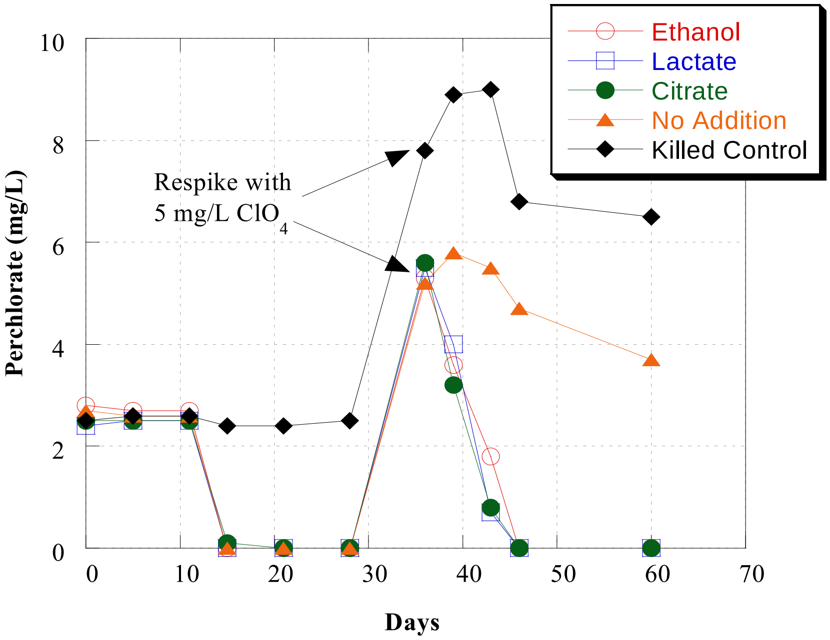


Figure 9. Effectiveness of different electron donors for stimulating biological perchlorate reduction in aquifer samples from the demonstration area.

6.4 FIELD TESTING

6.4.1 Demonstration Plot Design and Installation

The AFIT transport model was used to establish the final layout of the two HFTWs and nine final monitoring wells in the demonstration site area (19 wells total). Figure 10 provides a generalized plan view of the wells, and Figure 11 provides a representative cross-section demarcating well screen intervals and interpreted geologic units. As shown on Figure 10, the HFTWs were located approximately 15 ft upgradient of the existing monitor wells 3519, 4440 (originally installed as an extraction well) and nested monitor wells 3631-3633. The installation details of the HFTWs and the additional monitoring wells are provided in the final report (Hatzinger and Diebold, 2009). Two sets of monitor wells (NMW-1&2 and NMW-3&4 on Figure 10) were installed upgradient of the HFTWs, and each include nested completions (dual 2-inch-diameter wells) with screen intervals transecting the upper and lower treatment zones (46–61 ft bls and 80–100 ft bls, respectively). The NMW-1&2 nest is located approximately 60 ft upgradient of the HFTWs, to provide continuous monitoring of the groundwater chemistry in both the upper and lower aquifer layers before it enters the treatment zone.

The NMW-3&4 nest is located approximately 10 ft upgradient of the HFTWs, to allow for monitoring of the changes in groundwater chemistry and the early stages of the biodegradation process as the natural groundwater flow begins to mix with the electron donor enriched water re-circulating between the HFTWs. Two monitor well locations (NMW-7&8 and NMW-9&10) were placed approximately 45 ft downgradient of each HFTW, and each completion was a nested well consisting of a pair of 2-inch-diameter monitoring wells screened from 46–61 ft bls and 80–100 ft bls, respectively. These locations were chosen to monitor the reaction process and changes in groundwater geochemistry after the water and electron donor mixture have been reacting for a period of approximately 20 to 60 days based on tracer breakthrough curves obtained from model simulations. One individual shallow monitoring well (MW-5; 46–61 ft bls) was placed downgradient and ~60 ft side gradient of the upflow HFTW. This location will be used to assess the actual width of the treatment zone within the upper layer as predicted by the flow and transport model.

Existing wells 3514 and 3627, which are located 70 ft downgradient of the HFTWs and screened from 77 to 90 ft and 75 to 95 ft bls, respectively, allow for monitoring of the completion of the reaction process and recovery of various groundwater geochemical and contaminant parameters such as dissolved iron and manganese within the formation after 2 to 3 months of groundwater travel time. Figure 11 provides a representative cross-section depicting the interpreted geologic units (as used in the flow model simulations) and the basic well construction details. Variations in layer depths and thicknesses can be seen when comparing the graphic logs to the geologic layer interpretations used for the model simulations.

6.4.2 System Design

A Piping and Instrumentation Diagram (P&ID) diagram showing the design of the two treatment wells and the associated equipment is provided in Figure 12. Submersible variable-speed pumps were used to extract the contaminated groundwater from the aquifer through the well screens (P-107 & P-110). These pumps had a 30 gpm maximum flow at 125 ft of hydraulic head. In the upflow treatment well (HFTW-U), the groundwater was extracted from the lower screen, passed through a custom packer, amended with electron donor and/or biofouling control agent, and then released near the top screen of the HFTW. The supply piping was bent at a 180° angle to push water downward upon release and to enhance mixing of water with amendments. In the downflow well (HFTW-D), the process was reversed. Citric acid was added as an electron donor to each well from a tank at the surface. The citric acid (50% solution weight/volume [wt/vol] which equates to a 609 g citric acid/L) was injected directly into the recirculation water piping (prior to the piping bend) within the well to blend the chemicals into the extracted groundwater.

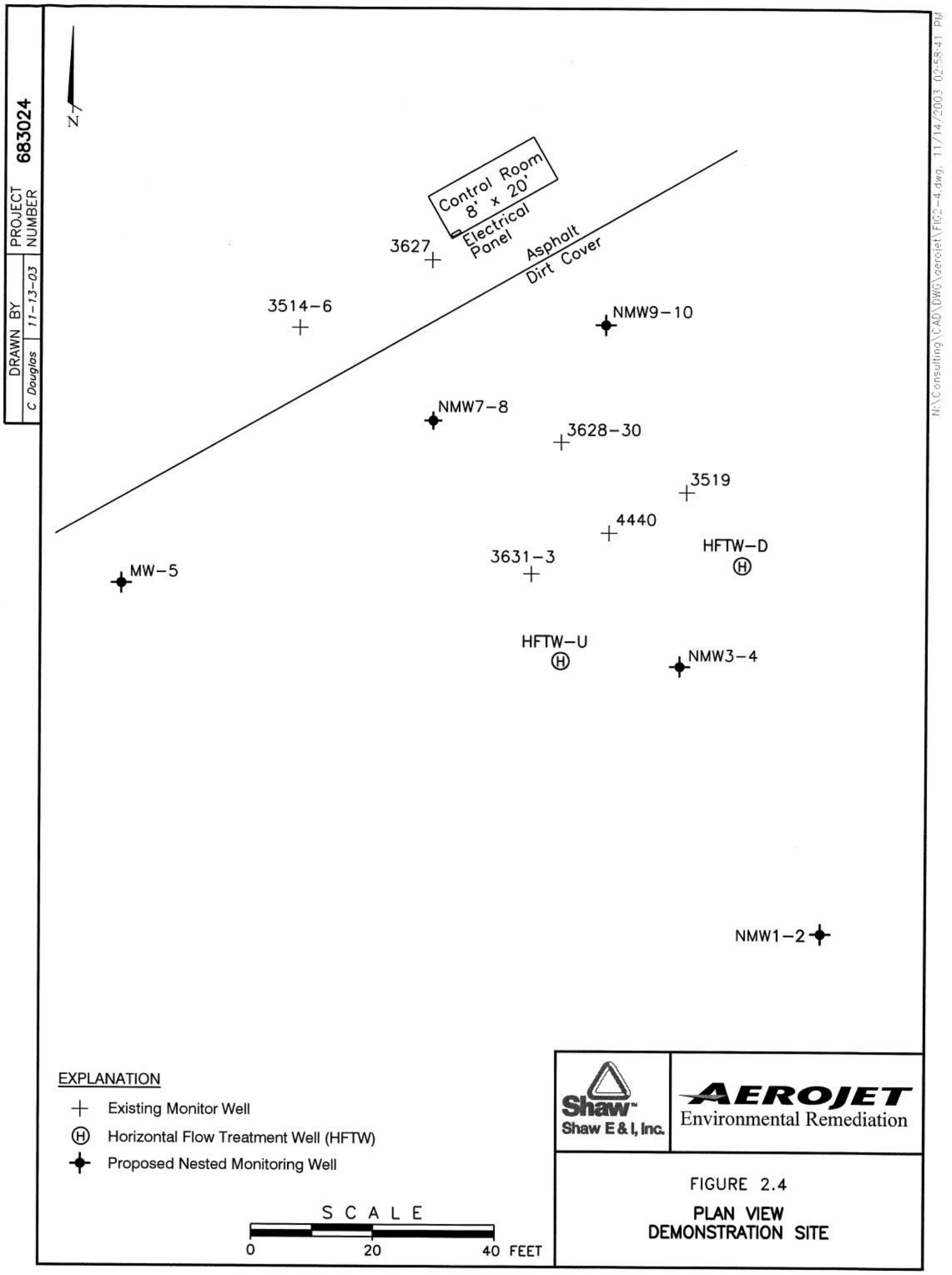


Figure 10. Plan view of wells in test plot.

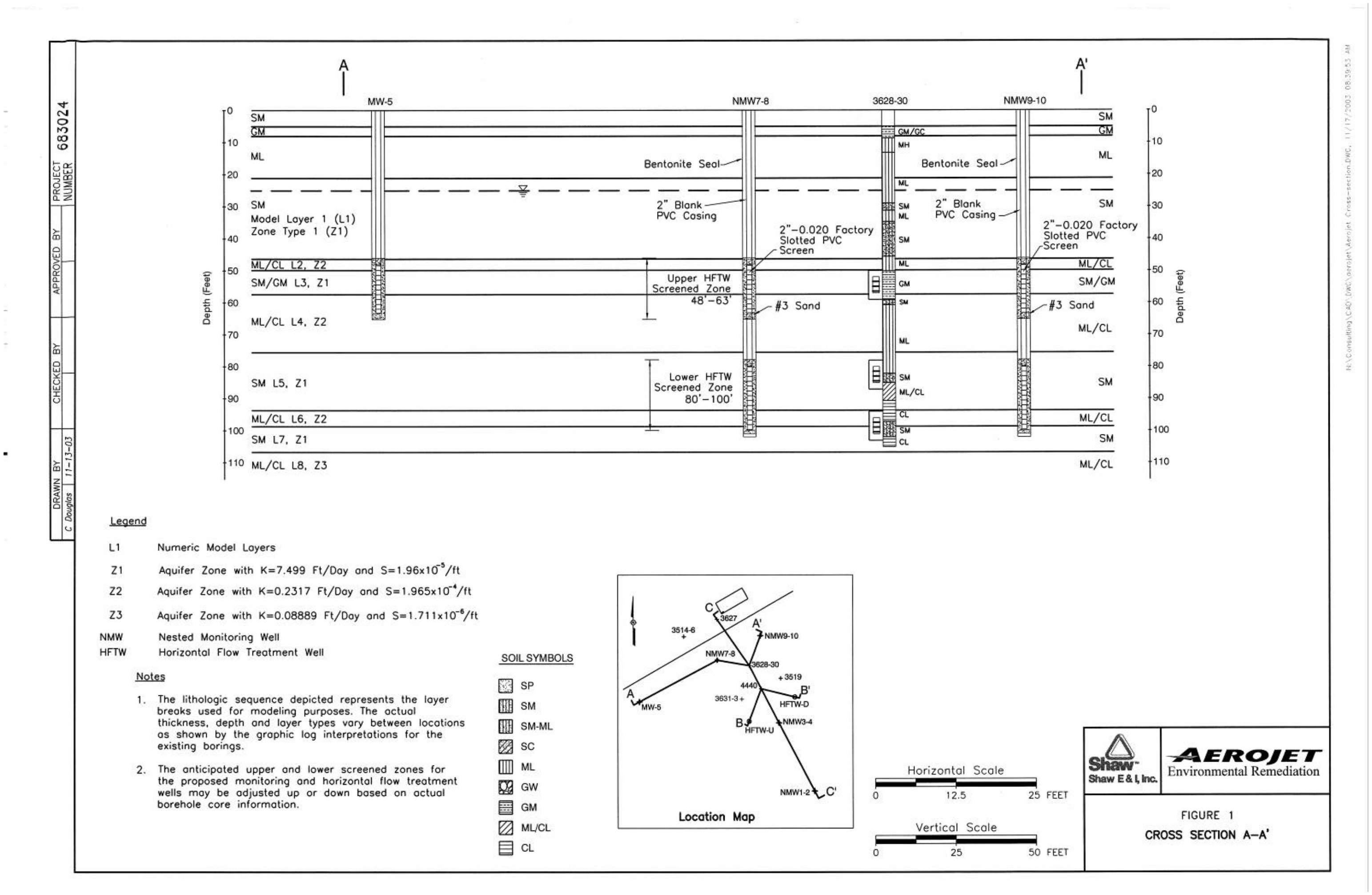


Figure 11. Cross-sectional view (A-A') of test plot wells detailing screen intervals and interpreted geologic units.

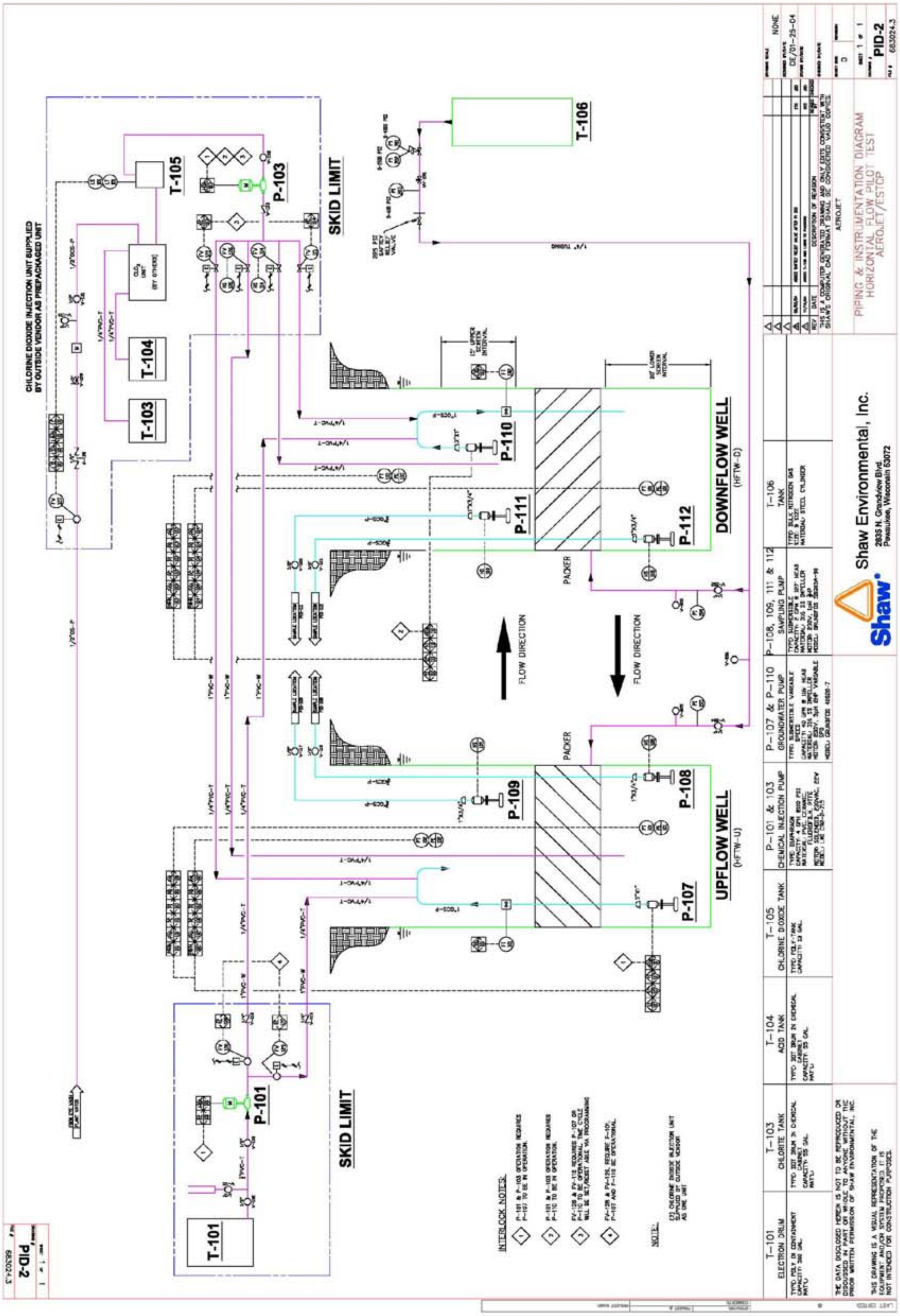


Figure 12. P&ID of the HFTW system.

A metering pump was used to supply citric acid to each well from the surface (P-103 A/B in Figure 12). Each HFTW was also fitted with two sampling pumps, one in the vicinity of each well screen (P-108/P-109 for HFTW-U and P-111/P-112 for HFTW-D) and two pressure transducers to measure the hydraulic head near each screen (PT-101/PT-102 for HFTW-U and PT-103/PT-104 for HFTW-D). In-line flow meters were used to measure instantaneous and cumulative flow within the piping of each well (note that no water is pumped to the surface so all equipment is within each HFTW).

A custom inflatable packer was used in each HFTW to prevent ejected groundwater flow from circulating back to the influent screen (See Figure 2). An annular bentonite seal was placed at the location of each packer during well construction to prevent any flow around the packer (i.e., leakage in the annular space of the well). The treatment system was operated through a Supervisory Control and Data Acquisition (SCADA) system, which allowed remote monitoring and control of the system through a computer with a modem connection. Control features included remote system start-up and shut-down, control of groundwater pumping rates in each well, and control of dosage rates and timing for all amendments. The system could also be operated manually on-site. Parameters measured during system operation included metering pump run times, recirculation pump cycles and flow rates, changes in hydrostatic pressure within the upper and lower screened intervals of each HFTW, and fluid levels within the liquid amendment storage vessels.

A utility trailer provided by Aerojet was located near the HFTWs. The trailer was used to house the programmable logic control (PLC) panel, 3-phase/240V/200 amp power service, and phone line. The PLC and phone line allowed for remote monitoring and control of the system operating conditions. Electrical conduits were run from the main power supply to each HFTW. As previously noted, a solution of 50% citric acid (wt/vol), equivalent to 609 g/L citric acid, was used as the electron donor and also as an activator for the chlorine dioxide system. The citric acid was delivered premixed in a small tank truck and was placed in a 1000-gallon storage tank placed next to the Conex box. A metering pump was placed on top of the storage tank, and a line and foot valve was run to the bottom of the tank to supply citric acid to each of the HFTWs. The storage tank was equipped with secondary containment.

A liquid chlorine dioxide solution was used as a biofouling control agent. The chlorine dioxide was produced as a stabilized solution by mixing aqueous sodium chlorite (sold as Oxine solution) with small amounts of citric acid to produce a solution containing ~2% chlorite (ClO_2) (Bio-Cide International, Norman, OK). The Bio-Cide AANE ClO_2 generation system was installed in a chemical cabinet placed next to the utility trailer used to house the system computer and equipment. The AANE system utilizes water pressure (rather than an electric pump) to mix appropriate amounts of Oxine system and citric acid in a 5-gal holding tank. A secondary metering pump was then utilized to supply the appropriate volume of the active solution (i.e., liquid with ClO_2) to each of the HFTWs. The quantities of solution added and the timing of addition could be varied using the PLC.

6.4.3 Period of Operation

The HFTW system was operated for slightly more than 2 years from September 2004 (beginning with the 6-week tracer test) until December 2006. The three phases of system operation are provided on a Gantt chart (Table 5). Phase I of system operation occurred from October 28, 2004 until August 1, 2005 (~275 days). The objectives of Phase I were as follows: (1) to evaluate the overall performance of the HFTW system as a mixing and capture system; (2) to determine whether perchlorate reduction was possible without mobilizing significant quantities of iron and manganese as secondary groundwater contaminants; and (3) to evaluate biofouling control and treatment strategies. The evaluation of perchlorate treatment at moderate electron donor dosing is important for assessing the influence of in situ remediation on water quality in drinking water aquifer. During the initial phase of operation, the HFTW system was run in a continuous pumping mode at a net flow rate of 6 gpm in each treatment well. The actual pumping rate in the downflow HFTW was set at 9.3 gpm to account for leakage in the filter pack. This setting achieved the desired net flow based on water table elevations in nearby monitoring wells. Electron donor addition was initiated on October 28, 2004 after tracer testing was complete.

The HFTW was operated with a moderate excess of electron donor in Phase I to evaluate levels of perchlorate bioreduction that were possible without major impacts to groundwater geochemistry. The electron donor dosage was initially set at 1.25X the stoichiometric requirement based on average levels of oxygen, nitrate, and perchlorate entering the plot. The quantity of electron donor required for complete biological destruction of these electron acceptors was calculated to be 23 mg/L (i.e., 1X stoichiometry). The equations and assumptions are provided in the project final report (Hatzinger and Diebold, 2009). Initially, an electron donor dosage of 1.5 L of 50% (wt/vol) citric acid (609 g/L citric acid) was added to both the upflow and the downflow HFTW as a daily pulse to achieve the desired 1.25X stoichiometric dosage of citric acid (~29 mg/L). Based on initial monitoring well data, the citric acid quantity was increased to 2.5X stoichiometry on December 4, 2004 (i.e., 3.0 L/well/day or 58 mg/L). The dosing in the downflow HFTW was increased further to 4X stoichiometry on February 11, 2005 (i.e., 6 L/HFTW-D/day or 115 mg/L). The system was shut down on April 24, 2005, due to biofouling of the upflow well. The system was operated intermittently from this time until the end of Phase I (August 1, 2005—275 Days) while various biofouling treatment strategies were tested (See Section 3.5.3 of the Final Report). Thirteen groundwater sampling events were performed during the 9 months of Phase I operation (October 28, 2004, through August 1, 2005).

No electron donor injections were conducted from the end of Phase I until the beginning of Phase II operation. The initial phase of this period was used to evaluate biofouling treatment approaches for the HFTWs (enzyme treatment, citric acid treatment, and physical rehabilitation). At the conclusion of these tests, each HFTW was redeveloped via chemical and physical methods. All equipment was removed from each HFTW at this time. This period was also utilized to allow perchlorate levels to rebound prior to commencing Phase II Operation. Phase II operation began on February 28, 2006, after a period of shutdown for well redevelopment. During the shutdown period, (in the absence of citric acid addition), the perchlorate levels in many of the monitoring wells rebounded as expected. The electron donor dosing and the biofouling control regimen were modified during Phase II to determine if long-term perchlorate treatment was feasible without significant well fouling. Electron donor dosing during Phase II was changed from daily addition (Phase I operation) to larger weekly or twice-per-week doses in order to evaluate the impact of dosing schedule on well fouling. On February 15–17, 2006, 45 L of citric acid was injected into each well. A volume of 15 L citric acid was added to each well on a weekly basis from this time through April 12, 2006, then this dosing was doubled between April 17, 2006 to June 20, 2006, by adding 15 L to each HFTW two times per week. Chlorine dioxide was added to each well on a daily basis (four to eight times per day) from February 15 – April 12, 2006, then reduced to one dose only after citric acid injection from April 12 – June 20, 2006.

A final mode of HFTW system operation (Phase III) was implemented from September 11, 2006 – December 11, 2006. The objective of this phase was to determine whether the system could be effectively operated in an active-passive mode, whereby the HFTW treatment wells are used primarily for mixing electron donor and the system is turned off between mixing times. We were interested in understanding whether this mode of system operation would result in consistent reduction in perchlorate levels to <4 µg/L and the potential for reduced system O&M costs and better long-term operation due to minimal pumping times. During this phase, the HFTW treatment wells were operated in a 15-day cycle consisting of 3 days of active pumping followed by 12 days in passive (non-pumping) mode. During the active period, citric acid was added to both HFTWs as an electron donor in three 12-hour pulses (followed by chlorine dioxide as a biocide), resulting in the addition of approximately 60 L of electron donor per 12-hour cycle and 180-L per operating time. Each HFTW was operated at a net flow rate of 6 gpm. The 15-day cycle was repeated 6 times during the 3-month test period, and three sampling events were performed. An initial sampling round was conducted prior to beginning the active-passive operation (September 6, 2006) to provide a baseline, and a final round was performed on January 15, 2007. The system was shut down at the end of December 2006 after the final round of citric acid injection.

Table 5. Gantt chart of system operation.

Testing Phases	2004		2005						2006					
	S/O	N/D	J/F	M/A	M/J	J/A	S/O	N/D	J/F	M/A	M/J	J/A	S/O	N/D
1) Tracer testing	■													
2) Phase I operation		■	■	■	■	▌								
3) Biofouling control tests					■	■								
4) Rebound period							■	■	■					
5) Well develop/system mod.							■	■						
6) Phase II testing										■	■	■		
7) Phase III testing													■	■

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7.0 PERFORMANCE ASSESSMENT

7.1 PERFORMANCE CRITERIA

See Table 1 for relevant performance criteria and associated metrics and Table 6 for performance confirmation methods.

Table 6. Performance confirmation methods.

Performance Criteria	Expected Performance Metric	Performance Confirmation Method
PRIMARY CRITERIA (Performance Objectives) (Quantitative)		
Perchlorate	Reduce perchlorate to <4 µg/L	USEPA Standard Method 314.0 (modified with filtered sample according to USEPA Standard Method 314.1)
Co-contaminants: Nitrate and TCE	Reduce nitrate-N to <1 mg/L and TCE to <5 µg/L	USEPA Standard Method 300.0 (for nitrate-N) and USEPA 3260 (for TCE and VOCs)
Overall system performance	Observe the presence of injected electron donor and/or negative ORP sampling wells throughout the test plot at appropriate time points (i.e. indicative of a broadly distributed treatment zone)	USEPA Standard Method 300.0m for electron donor (volatile fatty acids [VFA]) and field meter (ORP)
Minimal impacts to downgradient groundwater geochemistry	Maintain levels of Fe and Mn in downgradient monitoring well(s) <1 mg/L during Phase I	EPA Standard Method 200.7 for Fe and Mn analysis. Field meter measurements of dissolved oxygen (DO), Eh, and pH
Biofouling control	Redevelop well(s) receiving biofouling treatment with chlorine dioxide <1X per year	Pressure and flow measurements in wells receiving chlorine dioxide solution
SECONDARY CRITERIA (Performance Objectives) (Qualitative)		
Ease of use	Minimal operator training required.	Experience from demonstration operations
Versatility Use at other sites Use with other target contaminants	-Yes, with site-specific modifications (i.e. electron donor, pH buffering) -Predictive modeling	Experience from demonstration operation
Maintenance – required	-Minimal	Experience from demonstration operation
Scale-up constraints Pilot scale testing Engineering of full-scale design Installation	-Yes, with site-specific modifications (i.e. electron donor, pH buffering)	Monitor during demonstration operation
Process waste – generated	-None	Observation

7.2 PRIMARY PERFORMANCE OBJECTIVES

7.2.1 Perchlorate Treatment

7.2.1.1 Phase I

Fourteen groundwater sampling events were performed during Phase I operation, including five background events and nine events to measure system performance after initial electron donor addition (see Table 4). Between the final background monitoring event (Day -15—October 13, 2004) and the groundwater sampling conducted on August 1, 2005 (Day 275), perchlorate levels in the seven shallow monitoring wells (see Figure 4 for plot layout) declined by an average of 95% from the starting average of 2230 µg/L to 90 µg/L (Figure 13). Well 3632 reached <5 µg/L (method detection limit [MDL]) on Day 67, but most of the other wells showed stable perchlorate levels ranging from ~40–160 µg/L. These concentrations remained reasonably constant with electron donor dosages up to 2.5X stoichiometry added to the HFTW-U.

Like the shallow downgradient wells, the perchlorate concentrations in the deep downgradient monitoring wells at the site also declined significantly during Phase I operation, although the extent and consistency of the reduction was less than for the shallow wells (Figure 14). In the nine deep downgradient wells within the treatment zone, perchlorate concentrations declined by an average of 60% from a starting concentration of 3722 µg/L on Day 0 to 1780 µg/L on Day 275. However, in the five deep wells furthest downgradient—NMW-8, NMW-10, 3514, 3627, 3630—(see Figure 4), which are beyond the immediate influence of the upgradient water entering the system through the HFTWs, average perchlorate reductions exceeding 93% were achieved on Day 146 (the final sampling event in Phase I prior to intermittent operation). In addition, based on the tracer studies, several of the deep wells, including 3633, 3629, and 4440 were not well connected to the HFTW system (see Hatzinger and Diebold [2009] for tracer results).

As with the shallow zone, the citric acid concentrations applied to the deep zone were intentionally limited during Phase I (between 1.25X and 4X stoichiometry) to minimize secondary impacts to groundwater chemistry. In the absence of well fouling, the citric acid concentrations would have been increased consistently into Phase II. However, the significant biofouling of the HFTW-U prevented this planned increase. Rather, the system was shut down for biofouling mitigation tests, and then restarted several months later after perchlorate concentrations had rebounded in many of the wells.

7.2.1.2 Phase II & III

A total of nine groundwater sampling events were performed during Phase II & Phase II operation. These sampling events included one background event prior to each phase, four events to measure system performance in Phase II and three events to measure system performance in Phase III (see Table 4). As was observed in Phase I, perchlorate concentrations in all the downgradient shallow wells declined rapidly during Phase II (Figure 13). Perchlorate reached 12 µg/L in well 3632 on Day 555 (~80 days after injection commenced), but values generally did not go below detection, but rather ranged from ~30-110 µg/L in the various wells despite increased electron donor (~4X stoichiometry) in the HFTW-U through most of the Phase II treatment.

Perchlorate concentrations generally remained low in the shallow wells during the Phase III active-passive testing. Perchlorate concentrations in a few of the wells, including 3631 and 3632 , reached lower concentrations during Phase III than in either Phase I or Phase II testing. In fact, the perchlorate concentration in well 3632 was <4 µg/L during the final 3 sampling events in Phase III. The enhanced perchlorate reduction in these two wells during Phase III likely reflects an increased residence time of water in this region of the aquifer while the HFTWs were not pumping.

The consistent decline in perchlorate throughout the entire shallow aquifer during Phase II confirmed that, even with much more periodic dosing of electron donor (i.e., from daily during Phase I to 1 or 2 times per week during Phase II), the HFTW system operated well as a treatment technology in the shallow zone. Moreover, the data from Phase III suggest that perchlorate treatment can be achieved by using the HFTW system intermittently as a vehicle to mix electron donor with the contaminated groundwater. Even in side-gradient well NMW-5, perchlorate concentrations remained low (i.e., <100 µg/L) throughout Phase III despite the fact that the system was not pumped continuously. This suggests that the wide "capture" zone of the system was maintained during the active-passive phase. It should be noted, however, that longer term operation under this regimen is necessary to determine whether the wide capture zone remained consistent over several months or years. The ability to operate this system several days per month rather than continuously could appreciably reduce the O&M costs associated with biofouling and well redevelopment, which is the most significant issue with this design.

The perchlorate concentrations in the shallow zone on Day 801 represent a 96+4% reduction in dissolved perchlorate from the starting concentration in each well prior to Phase I (Day -7) and an average 94+3% reduction from perchlorate concentrations prior to Phase II (Day 472) (Figure 13). Thus, perchlorate treatment in the shallow zone was very effective. However, with the exception of well 3632, perchlorate concentrations <4 µg/L were not generally achieved in the shallow zone during Phase II and Phase III. Rather, perchlorate concentrations stabilized between ~40 to 80 µg/L in most wells. Interestingly, a low residual concentration of contaminant was also observed during cometabolic treatment of TCE using an HFTW system (McCarty et al., 1998). The low residual contaminant is attributed primarily to competitive interactions between toluene (the cosubstrate) and TCE during biodegradation by toluene-oxidizing strains. In this case, competitive inhibition between nitrate and perchlorate could contribute the low residual perchlorate concentrations observed in the shallow zone. Other factors that could contribute include the following: (1) inadequate or inconsistent concentrations of electron donor due to the periodic dosing regimen and/or competition with competing electron acceptors and (2) mixing of untreated and treated groundwater, potentially within the screen interval of the well (i.e., due to heterogeneities in the aquifer).

Despite the somewhat inconsistent decline in perchlorate among the deep downgradient wells, the overall percentage reduction in the deep zone on Day 801 was 80+39% from the starting perchlorate concentration in each well prior to Phase I (Day -7) (Figure 14), and an average 52+29% reduction from perchlorate concentrations at the end of Phase I (Day 275). If one only considers the Row 2 and Row 3 wells (i.e., the 6 deep wells furthest downgradient from the HFTWs as shown in Figure 4), the total perchlorate reduction during the 801-day demonstration was 88+9%. Thus, reasonable perchlorate treatment occurred in the deep zone, particularly considering results from the far downgradient wells.

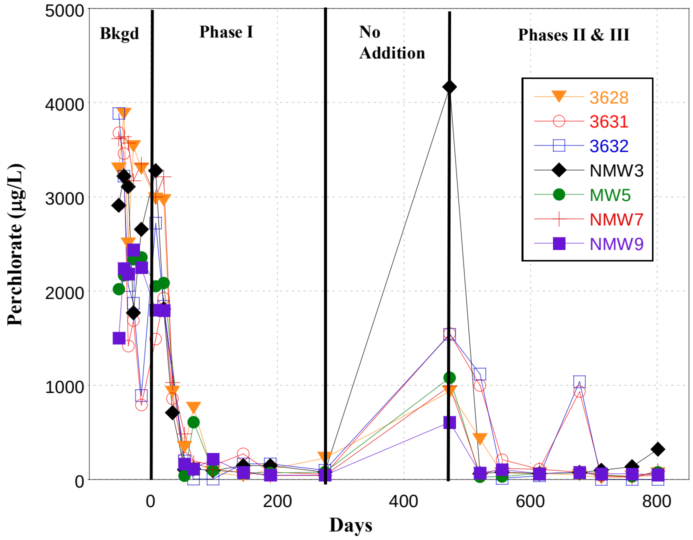

Figure 13. Perchlorate concentrations in shallow downgradient monitoring wells during the demonstration.

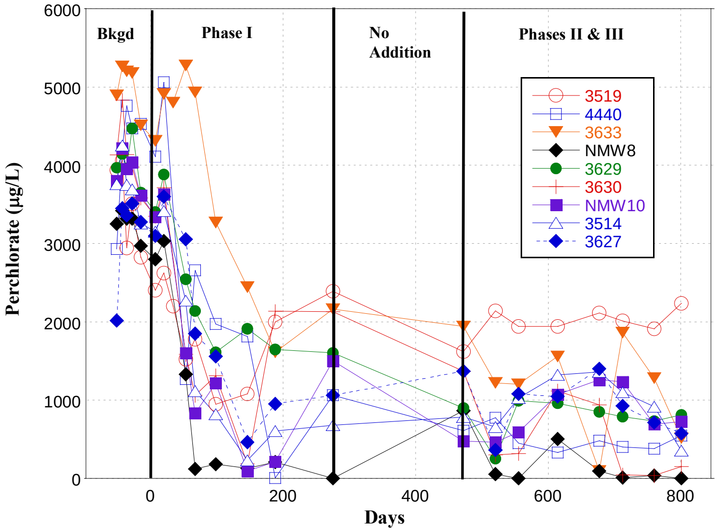

Figure 14. Perchlorate concentrations in deep downgradient monitoring wells during the demonstration.

7.2.2 Treatment of Chlorinated Solvents

The Phase I system operation was designed primarily to determine whether perchlorate reduction was possible without significant mobilization of Fe and Mn as secondary groundwater contaminants. To achieve this end, electron donor was added only in moderate stoichiometric excess. The quantities of electron donor and the redox conditions achieved were not generally low enough to promote significant reductive dechlorination. However, even under these conditions, appreciable losses of TCE were observed in several of the plot's shallow monitoring toward the end of Phase I operation (see Figure 15).

During Phase II, and more significantly, Phase III, the quantities of electron donor added to the plot were increased. The Phase II operation was used in large part to determine if the system operation could be optimized to provide perchlorate reduction with less biofouling, since this became the most important O&M consideration during Phase I. However, electron donor addition was increased appreciably in Phase III, and the system was shut down periodically so that upgradient water was not continuously brought into the treatment plot. In addition, a commercial culture containing Dehalococcoides spp. (Shaw Culture SDC-9) was injected into the HFTWs during Phase II to enhance reductive dechlorination.

TCE concentrations in many of the shallow wells declined significantly during Phase II and Phase III (Figure 15). There was a 76+23% reduction in total TCE in all the shallow wells from the beginning of Phase II (Day 472) to the end of Phase III (Day 801). If Wells NMW-3 (between HFTWs) and NMW-5 (side-gradient well) are excluded, so that only the downgradient wells are considered, then the percent loss increases to 87+14%, with average final concentrations being 323 μg/L. Among the shallow wells, the lowest TCE concentration was observed in the far downgradient well NMW-9, which reached 19 μg/L during the final sampling event. Cis-1,2-DCE (the initial reductive degradation product of TCE) was detected at high concentrations (>1000 μg/L) in three of the shallow wells (3628, 3632, and NMW-7). This degradation product was also observed in the other shallow wells at lower concentrations. Cis-1,2-DCE was not detected in the upgradient well (NMW-1). VC was detected only during the last sampling event (Day 801) in Well 3632. All other wells were below the reporting limit (RL) of 5 μg/L during Phase II and Phase III. The rapid and significant decline in TCE during the months after SDC-9 injection in many of the shallow wells suggests that the bioaugmentation procedure enhanced the dechlorination kinetics in the plot.

The TCE concentrations in a number of the deep downgradient monitoring wells also declined from the beginning of Phase II to the end of Phase III (Figure 16). Most notably, the TCE concentration in the far downgradient wells NMW-8 and 3514 declined significantly, with NMW-8 falling from 2500 μg/L at the beginning of Phase II to 42 μg/L at the end of Phase III (>98%). However, as with perchlorate, the average decline in TCE concentrations in the deep monitoring wells was appreciably less than in the shallow wells. As noted for perchlorate, this may reflect (1) the observation (based on tracer tests) that several of the deep wells were not well connected to either the HFTW-U or the HFTW-D or (2) that there was higher than anticipated interflow between the HFTWs, perhaps with significant short-circuiting of injected fluid from the HFTW-D to the HFTW-U.

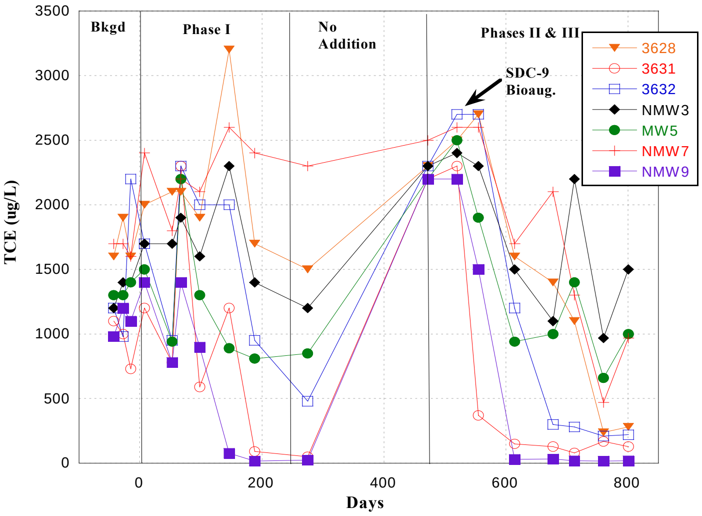

Figure 15. TCE concentrations in shallow downgradient monitoring wells during the demonstration.

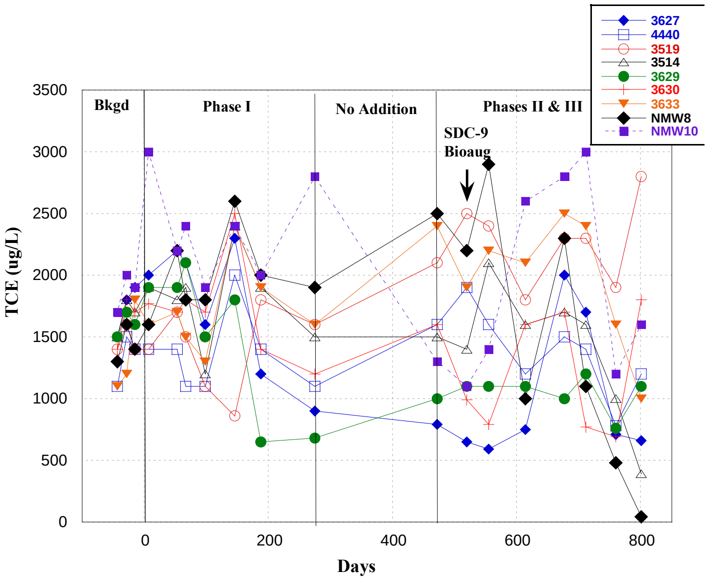

Figure 16. TCE concentrations in deep downgradient monitoring wells during the demonstration.

7.2.3 Overall System Performance: ORP and Electron Donor

7.2.3.1 ORP

The average ORP in the shallow monitoring wells during the sampling events prior to injection of citric acid was ~+250 millivolts (mV). At the end of the 275 days of Phase I, the average ORP in the shallow and deep downgradient wells was +72 mV (Figures 17 and 18). This average value increased slightly during the beginning of Phase II to +86 mV on Day 520 but then declined and remained between approximately –30 mV at the end of Phase II (Day 614) to ~+40 mV at the end of Phase III (Day 801). These lower values are expected due to the increased addition of electron donor in Phase II and Phase III, and they are within the range that is normally expected for reduction of perchlorate, nitrate, and sulfate. The decline in ORP was pretty consistent throughout the plot demonstrating that the system provided good overall mixing of groundwater. It is interesting to note that the ORP values in the upgradient wells NMW-1 & NMW-2, although generally higher than many of the treatment wells, did decline somewhat during system operation.

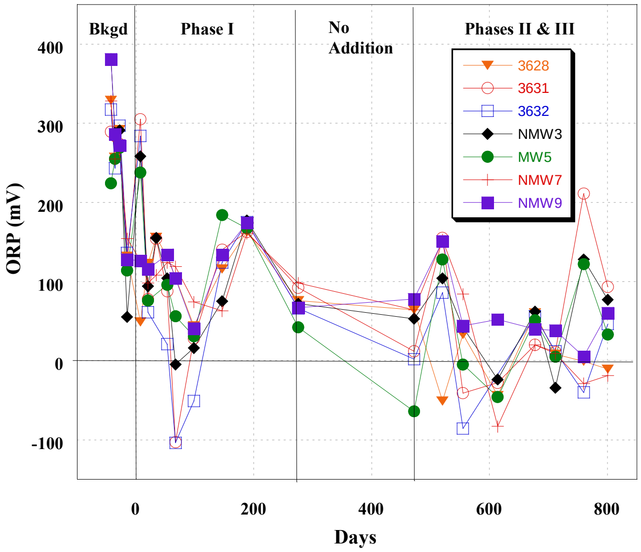

Figure 17. ORP in shallow monitoring wells during the demonstration.

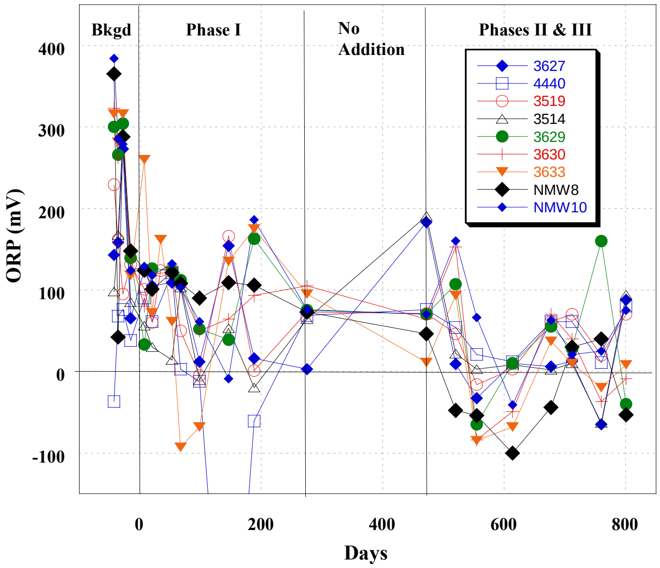

Figure 18. ORP in deep monitoring wells during the demonstration.

7.2.3.2 Electron Donor

Citric acid was added as the sole electron donor to the test plot during the various phases of this project. However, based on laboratory tests the citric acid is anticipated to be biodegraded to acetate in situ. During Phase I, low concentrations of electron donor were used intentionally to limit the extent of secondary reactions, such as Mn and Fe reduction. Thus, we did not generally expect to see measurable concentrations of electron donor in most downgradient wells. As expected, citrate was not consistently detected in any of the monitoring wells above the practical quantitation limit (PQL) of 2 mg/L during Phase I. Acetate was observed in several downgradient wells during the demonstration, particularly towards the end of Phase I. Concentrations ranged from <1 mg/L (J values) to >20 mg/L. During Phase II and Phase III, electron donor concentrations were increased, as detailed previously. At the end of Phase II, acetate was detected in wells NMW-7 and NMW-8, and during Phase III, the fatty acid was consistently present in shallow wells 3628, 3632, and NMW-7 and was detected at 78 mg/L in side-gradient well NMW-5 toward the end of Phase III. For the deep wells, acetate was consistently detected in NMW-8 and was detected on one occasion in both 3514 and 3630. Detailed results on electron donor concentrations are given in the final report (Hatzinger and Diebold, 2009).

7.2.4 Secondary Mobilization of Fe and Mn

7.2.4.1 Phase I

Overall, mobilization of iron and manganese was minimal during the course of Phase I operation. With the exception of two shallow wells closest to the upflow HFTW (monitor wells 3631 and 3632), soluble iron levels throughout the plot remained well below 500 µg/L (Figure 19). Moreover, based on the operational data, iron that was dissolved and mobilized during the active phase of operation (through Day 146) rapidly re-precipitated when the system was shut down. At the last sampling event in Phase I during which iron concentrations were measured (Day 188), iron was below detection (27 µg/L) in each of the eight shallow wells and three of the deep wells, and two additional deep wells were <34 µg/L. Thus, very little iron was mobilized, and what did come into solution was rapidly removed once the system was shut down.

Among the shallow wells in Phase I, manganese concentrations increased most significantly in wells 3631 and 3632, reaching a maximum of 1470 µg/L in well 3632 at Day 98 (Figure 20). However, concentrations in both these wells declined back to <50 µg/L by Day 188 of Phase I. During the final sampling event in Phase I in which manganese was measured (Day 188), levels of the metal were below 50 µg/L in 12 of the downgradient monitoring wells. The maximum concentration observed at this time was 715 µg /L in NMW-8. This well is directly downgradient of the nest with wells 3631 and 3632 (see Figure 4). The concentrations of Fe and Mn mobilized during this demonstration are appreciably lower than those produced during previous pilot work at the Aerojet site. During a previous pilot demonstration in which ethanol was tested as an electron donor with an active pumping system (groundwater extraction and reinjection design), Fe in a some monitoring wells exceeded 2.9 mg/L, and Mn levels reached 5 mg/L (Hatzinger et al., 2008). The dissolved iron rapidly re-precipitated based on data from a downgradient well, but the dissolved manganese remained mobile, at least through the ~30 m treatment plot.

7.2.4.2 Phases II & III

Soluble Fe and Mn were sampled on Day 472 at the beginning of Phase II to evaluate background concentrations of each metal after the system had been shut down for well rehabilitation. Fe concentrations were below 200 µg/L in all wells (except 4440 and 3514, which had naturally high background values and are excluded from further discussion) at the beginning of Phase II (Figure 19). The next sample for analysis of soluble Fe was collected at the beginning of Phase III (Day 677). At this time, all of the shallow and deep downgradient wells had Fe levels below 30 µg/L, except NMW-8, which had a concentration of 556 µg/L Thus, any Fe mobilized during the Phase II operation was below detection by the beginning of the active-passive operation in Phase III. During Phase III, significant quantities of Fe were mobilized in the treatment plot. Four of the shallow wells and three of the deep wells had concentrations exceeding 1000 µg/L on Day 760, with two wells exceeding 30,000 µg/L. These data are not surprising given that large doses of citric acid were added during Phase III, and the system was only operated intermittently. With higher electron donor concentrations and less thorough and continuous mixing, it is likely that an excess of electron donor would result in some regions of the treatment cell. These would subsequently promote biological reduction of Fe and Mn, as well as sulfate. It is important note however, that Fe concentrations declined significantly in most of the wells by the final sampling event on Day 801. This occurred between the final citric acid injection cycle, which was competed on December 1, 2006 (Day 763), and the final event. Thus, the mobilized iron appeared to quickly re-precipitate in the aquifer once the citric acid and daughter products were consumed.

With the exception of a few wells (3628, 3630, NMW-7), Mn concentrations were below 100 µg/L at the beginning of Phase II (Day 472) (Figure 20). However, as with soluble Fe, Mn concentrations increased significantly in numerous wells during the active-passive operation in Phase III. Concentrations in several wells, including 3628, 3629, 3632, 3633, NMW-7, NMW-8 were near or exceeded 3000 µg/L on Day 760 in Phase III. These were by far the highest Mn concentrations observed during the course of the 801-day operational period. As with Fe, however, Mn concentrations dropped significantly in most of these wells by Day 801, the final sampling event conducted approximately 40 days after the last citric acid injection was complete.

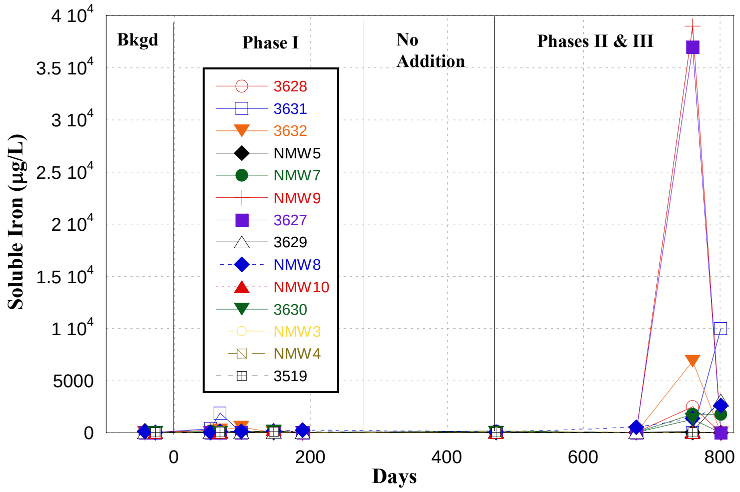

Figure 19. Soluble iron concentrations in downgradient monitoring wells during the demonstration.

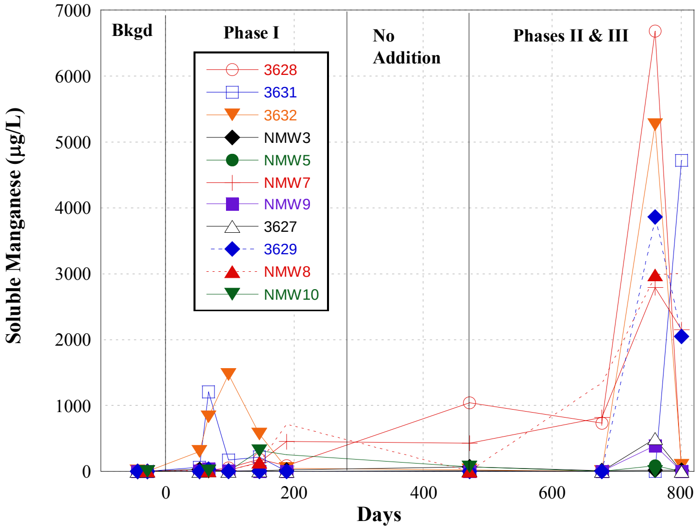

Figure 20. Soluble manganese concentrations in downgradient monitoring wells during the demonstration.

7.2.5 Biofouling Control

7.2.5.1 Phase I

During the initial period of Phase I operation (Day 0 to Day 105), the citric acid dosing was programmed to occur as a batch addition once per day. This addition was then followed by an injection of stabilized chlorine dioxide solution to achieve approximately 10 mg/L of chlorine dioxide in each well for 30 min. The hydraulic head near both screens of each HFTW (i.e., the injection and extraction screen) were monitored using transducers to assess biofouling. The pressure/hydraulic head levels near both screen intervals of each HFTW were stable through December 9, 2004 (Day 42), at which time the chlorine dioxide system experienced the first of two mechanical failures. The absence of chlorine dioxide during this period (with continued daily addition of citric acid) resulted in an appreciable pressure increase in the lower screen of the downflow HFTW. The head level increased by approximately 5 ft in the lower screen interval (injection screen) while the chlorine dioxide system was nonfunctional (Day 42-Day 54), and then continued to increase gradually thereafter. The pressure reading in this zone reached the maximal level of the installed transducer (~70 ft water) on Day 75. An increase in hydraulic head in the upper screen of the upflow well (injection screen) was also observed beginning around Day 50. The pressure in this zone gradually increased through Day 100, at which time the transducer reached its maximal pressure (~30 ft water). The lower screen of the upflow HFTW showed no appreciable increase or decrease in pressure during the initial phase of testing.

The system was operated under a constant pumping scenario at 6 gpm without issue despite the pressure increases until late March 2005 (~Day 150), at which time leakage was observed through the cap of the upflow well. At this time, the system was shut down, and various chemical and biological approaches were tested to decrease well pressure. Initially concentrated chlorine dioxide was added to each well followed by mixing and incubation for several days.

This approach was ineffective. Addition of concentrated citric acid also proved to be ineffective for decreasing pressure in the upflow well. A third approach, enzyme treatment, did however show significant promise for removal of biomass, but was not effective enough to prevent physical well redevelopment (including removal and cleaning of all downhole equipment from each HFTW), which occurred between Phase I and Phase II.

7.2.5.2 Phase II

During the initial 56 days of Phase II operations (Day 473–Day 529), excluding the days immediately before and after the injection of Dehalococcoides spp., electron donor injections were conducted every seventh day. During this same period (excluding the day of and following the injection of Dehalococcoides spp.) chlorine dioxide was injected in small doses several times per day. After 56 days, the amendment injection strategies were modified to inject a smaller pulse of electron donor every 3.5 days, followed by a single pulse of chlorine dioxide into each well. The regular pulsing of chlorine dioxide during the days between electron donor injections was discontinued. This mode of operation was maintained for the HFTW-D throughout the remainder of Phase II operations. For the HFTW-U, daily pulses of chlorine dioxide were restored on Day 544 (71 days into Phase II) and continued for the remainder of Phase II operations.

Ongoing mechanical issues impacted the injection of chlorine dioxide at various times throughout Phase II; however, some general trends appear to be represented by the pressure data. Both wells indicated an initial decline in injection zone pressures associated with the initiation of electron donor and chlorine dioxide injections, as compared to pressures measured during the second bromide tracer period proceeding Phase II (see Hatzinger and Diebold [2009] for tracer data). This pressure drop was most pronounced in the HFTW-U, which declined from a pressure of ~40 ft of water to ~25 ft of water. Both wells generally responded well to the initial operating mode (Days 1 through 56 in Phase II) where electron donor was added in a large infrequent pulse and chlorine dioxide was added in a series of small pulses several times per day. Based on the various pressure trends observed during Phase II operations, it appears that an operating mode that entails injection of large, infrequent doses (one or two per week) of electron donor coupled with small, frequent doses (several per day) of chlorine dioxide, can be utilized to provide relatively stable injection zone pressures and may provide a good long-term operating condition for this type of in situ treatment system.

7.2.5.3 Phase III

During Phase III, the HFTW treatment wells were operated in a 15-day cycle consisting of 3 days of active pumping followed by 12 days in passive (non-pumping) mode. During the active period, citric acid was added to both HFTWs as an electron donor in three 12-hour pulses (followed by chlorine dioxide as a biocide), resulting in the addition of approximately 60 L of electron donor per 12-hour cycle and 180-L per injection event. Each pulse of electron donor was followed by a 10-min pulse of chlorine dioxide. The 15-day cycle was repeated six times during the 3-month test period. The average Phase III injection pressures were similar to or less then the injection pressures observed during the initial Phase II operations (~25 to 40 ft of water in HFTW-U and 125 ft of water in HFTW-D) and were substantially below the pressures that were being observed during the final weeks of Phase II. This is believed to be related to the chelating effect created when the large doses of citric acid are being injected. The pressures did not increase enough during Phase III to impact system pumping or operation during the active phase.

The trends from Phase III indicate that, from an O&M perspective, an active/passive operating mode coupled with large doses of electron donor followed by doses of chlorine dioxide could be an effective long-term operating strategy for this type of treatment system.

7.3 SECONDARY PERFORMANCE OBJECTIVES

O&M issues were the most significant ones with the HFTW system due to biofouling of the two HFTWs, as detailed in Section 7.2.5 and discussed further in Section 9.0. The secondary performance objectives, which are listed in Table 6, were largely met during the demonstration. Apart from biofouling and problems associated with the pilot-scale chlorine dioxide system (which contributed to the biofouling problems with the HFTWs), the system was easy to operate and control (particularly due to the Calcon SCADA system) and required little maintenance. In addition, there was no environmental waste apart from water generated during the initial pump tests and cuttings from the installation of the HFTWs and monitoring wells. Scale-up of the system should also be readily achievable.

8.0 COST ASSESSMENT

The HFTW approach can be used to replace traditional groundwater extraction with above-ground treatment, and discharge or re-injection approaches. Other competing innovative technologies could include trench installed or injected permeable reactive barriers as well as paired extraction and re-injection wells where the extracted water is pumped to the ground surface, mixed with amendments, and then re-injected into the formation to deliver amendments and promote in situ degradation of the target dissolved phase contaminant(s) of concern. Detailed descriptions of these alternate approaches, their limitations, and relative costs are provided in Stroo and Ward (2008).

The HFTW approach is ideally suited for layered lithologic units where one or more of the target treatment zones are >50 ft below ground surface (bgs) and where re-injection of contaminated water (e.g., extracted groundwater with electron donor added) is either prohibited due to water usage or rights concerns or subject to regulatory injection permits. Longer treatment time frames, high contaminant concentrations, secondary reaction concerns (metals mobilization, sulfate reduction, etc.) may also present conditions favorable for utilizing an HFTW approach, since electron donor addition and mixing rates can be adjusted more easily than with injected or trench installed permeable reactive barrier approaches (which often utilize very high concentrations of slow-release electron donors, such as emulsified oils of mulch). For shallower target treatment zones and shorter treatment durations, trenched or injected permeable reactive barriers may be more cost effective then HFTWs. For sites where extracted water can be discharged directly to surface water, storm water systems, or sanitary sewer systems, groundwater extraction and ex-situ treatment may be more cost effective.

In order to evaluate the cost of a potential full-scale HFTW treatment system and compare it against traditional remedial approaches, costs associated with site selection, site characterization, treatability testing, site modeling, system design, system installation and start-up, operations, maintenance, monitoring, and reporting were tracked throughout the course of the demonstration project. Table 7 summarizes the total cost of the demonstration project. The costs have been grouped by categories as recommended in the Federal Remediation Technologies Roundtable (FRTR) Guide to Documenting Cost and Performance for Remediation Project (FRTR, 1998). Many of the costs shown in this table are a product of the innovative and technology demonstration/validation aspects of this project and would not be applicable to a full-scale site application. Therefore, as described below, these costs have been excluded or appropriately discounted from the subsequent remedial technology cost analysis and comparison.

Table 7. Demonstration cost components for HFTW in situ treatment of perchlorate in groundwater.

Capital Costs		Cost (US $)
1	Modeling (AFIT)	$ 152,400
2	System design	$ 55,700
3	System installation—material/subcontracts	$ 252,500
4	System installation—labor	$ 49,800
5	Travel	$ 5000
	Subtotal	$ 515,400
Operation and Maintenance Costs		
1	Sampling and system O&M—labor	$ 90,500
2	Equipment	$ 7900
3	Consumables	$ 4900
4	Analytical—in-house labor	$ 71,600
5	Analytical—outside lab	$ 7300
6	Travel	$ 3500
7	Reporting	$ 52,600
	Subtotal	$ 238,300
Other Technology-Specific Costs		
1	Site selection	$ 76,000
2	Site characterization	$ 119,400
3	Treatability studies	$ 74,800
	Subtotal	$ 270,200
	TOTAL COSTS	$ 1,023,900

8.1 COST MODEL

For purposes of this cost assessment, the costs associated with full-scale implementation of an HFTW barrier are discussed and compared against traditional groundwater extraction, above grade biological treatment using a fluidized bed reactor (FBR) design (groundwater treatment and extraction [GWET]-FBR), and re-injection of the treated water into the subsurface. Only those costs related the post remedial investigation (RI) and feasibility study (FS) elements have been considered for each remedial approach. Any elements that are standard industry practices and are deemed to be similar in scope and cost for the HFTW and GWET-FBR approaches (conceptual site modeling, treatability testing, etc.) are described briefly within this document but have been excluded from the cost analysis and comparison.

The following sections discuss the various post-RI/FS elements that are common to both remedial approaches and identify those elements that are included within the cost analysis/comparison portion. For comparison purposes, a base case has been developed using parameters similar to those present at the Aerojet HFTW demonstration site location. Costs have been broken into capital, O&M, and monitoring costs over a projected 30-year remediation period. The O&M and monitoring costs were discounted, using a 3% discount rate, to develop net present value (NPV) estimates of future costs (DoD, 1995) for each remedial option. Post remediation and decommissioning costs were not included in this analysis.

8.1.1 Hydrogeologic Testing

Prior to implementing HFTW or groundwater extraction and treatment systems, basic hydrogeological testing is recommended. This normally includes pump tests to confirm field-scale aquifer parameters such as hydraulic conductivity, storage coefficient, and zone of influence or capture for different pumping or injection scenarios. The amount and type of testing typically recommended is similar for both the HFTW and groundwater extraction and treatment remedial alternatives being considered in this cost assessment/comparison; therefore, this factor is not discussed in detail in this report.

8.1.2 Treatability and Pilot Testing

Since bacteria capable of degrading perchlorate are common to most sites, biological treatment is likely to be a viable approach for the in situ and ex situ biological treatment of this compound. However, biological degradation performance has been shown to be dependent on a number of factors such as the choice of electron donor, pH, and other conditions. Therefore, a simple bench-scale microcosm study where a series of replicates are run to compare the degradation achieved by a variety of common electron donor compounds is recommended to confirm the choice of electron donor and assess the potential need for additional amendments such as pH buffering compounds or others. The preliminary microcosm testing may include electron donor sources that are available locally and can be obtained inexpensively. In those cases where initial microcosm results indicate no or minimal biological degradation of perchlorate, further bench-scale testing may be required to assess other parameters affecting biological performance such as pH buffering, nutrient deficiencies, or other factors. Additionally, field-scale pilot testing may be necessary prior to finalizing the design of the remedial system to assess sizing, operational, and cost parameters (electron donor addition and consumption rates, metals mobilization, etc.) under actual field conditions.

Similarly, bench-scale treatability testing is normally recommended for assessing typical ex situ treatment technologies such as ion exchange (technology not discussed in detail in this report) or biologically based treatment systems such as FBRs. For FBR treatment systems, the same suite of microcosm studies described above may be sufficient. In some cases bench-scale or field-scale pilot studies may be recommended to refine equipment design, operating parameters, and costs (both capital and operating). Since both treatment approaches are biologically based, the basic elements and costs of the treatability and pilot studies are similar for each treatment technology, this cost factor is also excluded from detailed consideration and discussions in this report.

8.1.3 System Design, Installation, and Start-up (Capital Costs)

The design, installation, and start-up process and related costs vary considerably between the HFTW and GWET-FBR/re-injection approaches. Therefore, the various design, installation, and start-up elements and costs are described and compared within this document. Since these are one-time, up-front cost elements, they are collectively referred to as Capital Costs. The following sections highlight the key elements associated with each capital cost item.

8.1.3.1 **HFTW System Design**

The typical HFTW system design process includes the following elements:

- Refinement of the site conceptual model and development of groundwater flow, fate and transport, and biodegradation models. These models are calibrated using site-specific data obtained during the site characterization, treatability, and pilot testing phases and are used to estimate the final system layout, number and spacing of wells, HFTW pumping rates, and amendment addition dosing patterns and quantities.
- Development of process flow and detailed P&IDs for both the down-hole and above grade elements of the treatment system. A P&ID depicting the common elements of an HFTW system is provided in Figure 12.
- Equipment selection based on sizing, compatibility, operational, and system monitoring needs.

8.1.3.2 **GWET-FBR System Design**

The typical GWET-FBR system design process includes the following elements:

- *Refinement of the site conceptual model and development of groundwater flow and fate and transport models.* These models are calibrated using site-specific data obtained during the site characterization, treatability, and pilot testing phases and are used to estimate the final system layout, number and spacing of wells, groundwater extraction and re-injection pumping rates, FBR system inlet conditions (flow rate, contaminant loading, etc.), and FBR amendment addition dosing rates.
- *Development of process flow and detailed piping and instrumentation diagrams for both the down-hole and above grade elements of the treatment system.* A process flow depicting the common elements of a GWET-FBR system (courtesy of Envirogen Products of Basin Water) is provided in Figure 21.
- *Equipment selection based on sizing, compatibility, operational, and system monitoring needs.*

8.1.3.3 **HFTW System Installation**

For the base case analysis, the HFTW system installation includes the following elements:

- Two 8-inch diameter schedule 80 polyvinyl chloride (PVC) wells with dual screened zones
- Downhole equipment, including two pneumatic packers, two submersible process pumps (5 horsepower [hp], 10 gpm @ 150 total discharge head [TDH]) with variable frequency drives, four submersible sampling/mixing pumps, four

pressure transducers, two in-line flow meters, two in-line mixing valves, solenoid valves, two sealed well caps, one pressure gauge, and one pressure relief valve

- Above grade equipment, including two chemical metering pumps, one electron donor chemical storage tank, one liquid chlorine dioxide generation unit, liquid level sensors for all chemical storage and mixing tanks (total of three), water supply line, 220 volt 3-phase 100 amp power supply, control panel, desktop PC with PLC software, hard-wired or wireless modem, and climate controlled storage shed
- Plumbing, mechanical, electrical support to connect all equipment assuming 100 lineal ft of trenching for all piping and wiring runs.

8.1.3.4 GWET-FBR System Installation

For the base case analysis, the GWET-FBR system installation includes the following elements:

- Two 6-inch diameter, schedule 40 PVC wells screened from 40 to 100 ft bgs
- Downhole equipment, including one submersible process pump (5 hp, 50 gpm @ 125 TDH), one submersible sampling/mixing pump, two pressure transducers, one sealed well cap, one pressure gauge, and one pressure relief valve
- Above grade equipment, including one equalization tank, one post-treatment tank, one electron donor chemical storage tank, a nutrient tank, a pH control tank, an integrated FBR system per process flow diagram (Figure 8), liquid level sensors for all chemical storage and mixing tanks (total of five), water supply line, one booster pump for water re-injection, 460 volt 3-phase 200 amp power supply, control panel, desktop PC with PLC software, hard-wired or wireless modem, climate controlled storage shed, and a post treatment multimedia filter and aeration system (also included in the cost) to remove biomass and aerate water prior to reinjection.
- Plumbing, mechanical, electrical support to connect all equipment assuming 100 linear ft of trenching for all piping and wiring runs.

8.1.3.5 HFTW System Start-Up

For the base case analysis, the HFTW system start-up includes the following elements:

- Initiation of full system operations.
- Monitoring groundwater levels within centerline monitoring wells to check for vertical leakage or other flow short circuiting and to ensure flow balance between the upflow and downflow HFTWs.
- Observing and adjusting all system operational settings including pumping frequency, rates, sensors, and alarms.

- Based on the amount of mechanical components and monitoring variables, the HFTW start-up process is expected to require a two-person crew and approximately 100 man hours to complete over a period of 1 to 2 weeks.

8.1.3.6 GWET-FBR System Start-Up

For the base case analysis, the GWET-FBR system start-up includes the following elements:

- Phased initiation of system operations beginning with reduced system flows and the accumulation of contaminated groundwater within temporary storage tanks.
- FBR seeding and start-up in >90% recirculation mode for biomass growth, followed by a controlled transition to the full process flow inlet feed rate of 50 gpm from the recovery well to the equalization tank.
- Groundwater drawdown monitoring to confirm adequate plume capture and that control is being achieved under design pumping rate conditions.
- Based on the amount of mechanical components and the need for controlled seeding and growth of biomass within the FBR system, the start-up process is expected to require approximately 250 man hours to complete over a period of 3 to 4 weeks.

8.1.4 System Operations and Maintenance Costs

The O&M needs and costs vary considerably between the HFTW and GWET-FBR/re-injection approaches. Therefore, the various O&M elements and costs, are described and compared within this document. Since these are ongoing costs, they are collectively referred to as O&M costs and the NPV is estimated for the O&M costs for each remediation alternative using a 30-year operating period and 3% discount rate for comparison purposes. The following sections highlight the key elements associated with each O&M cost item.

8.1.4.1 HFTW System O&M

For the base case analysis, the HFTW system O&M includes the following elements:

- Electron donor consumption—annual
- Power consumption—annual
- Routine equipment maintenance and calibration—quarterly
- Non-routine equipment maintenance, repair, or replacement—every 3 years
- Chemical/mechanical well rehabilitation for HFTW—every 3 years.

Based on the amount of mechanical components and process variables, the HFTW O&M is anticipated to require approximately 120 man hours and $5000 for other direct costs (ODC), excluding power and electron donor, per year for routine items and 120 man hours and $25,000 for ODCs every 3 years for non-routine items and well rehabilitation (to be performed simultaneously).

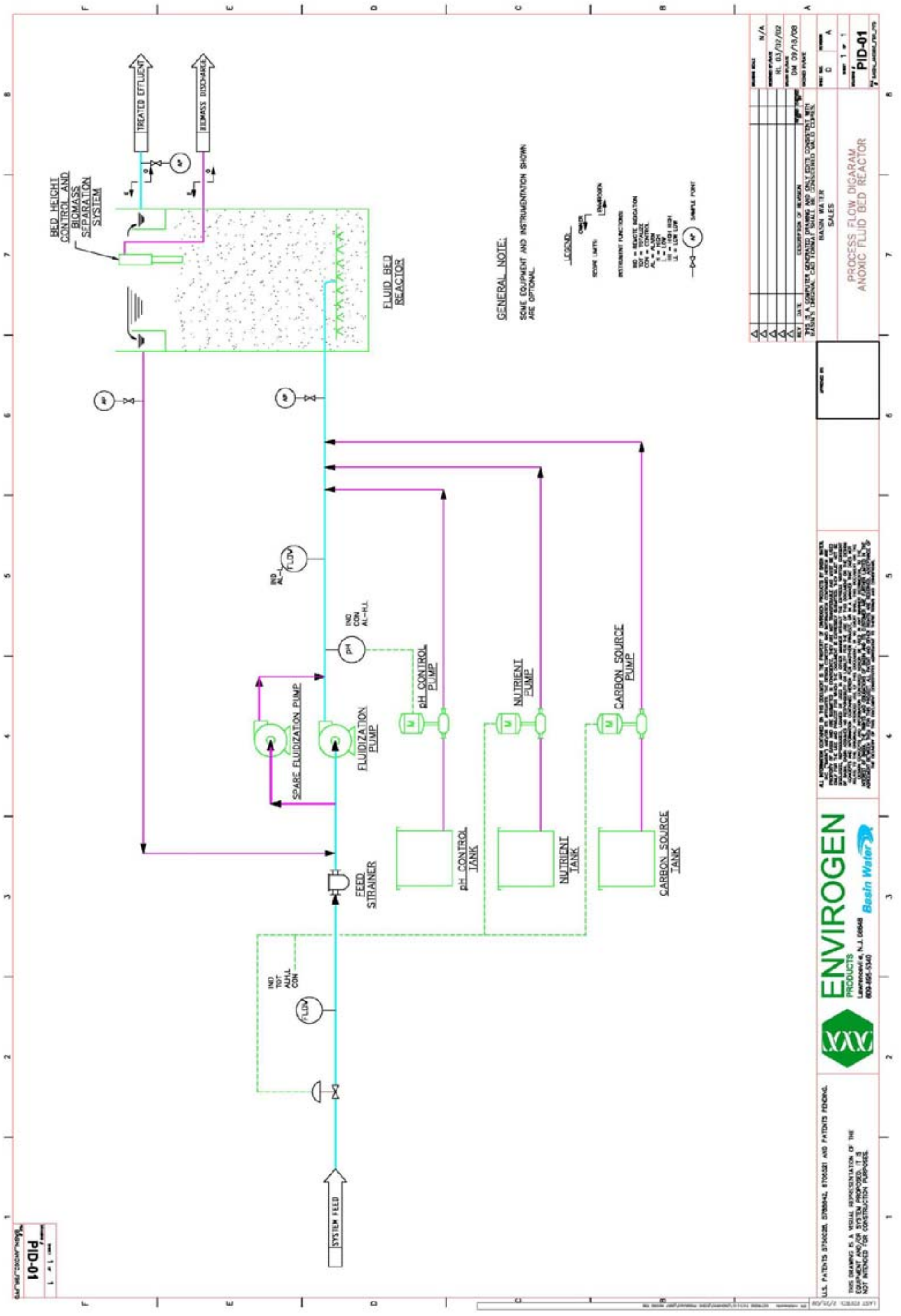

Figure 21. Process flow diagram for Envirogen anaerobic fluidized bed reactor.

8.1.4.2 GWET-FBR System O&M

For the base case analysis, the GWET-FBR system O&M includes the following elements:

- Electron donor consumption—annual
- Power consumption—annual
- Routine equipment maintenance and calibration—monthly
- Non-routine equipment maintenance, repair, or replacement—every 3 years
- Chemical/mechanical well rehabilitation for the extraction and injection wells—every 5 years.

Based on the amount of mechanical components and process variables, the GWET-FBR O&M is anticipated to require approximately 240 man hours and $5000 for ODCs, excluding power and electron donor, per year for routine items, 120 man hours and $25,000 for ODCs every three years for non-routine items, and 80 man hours and $15,000 for ODCs every 5 years for well rehabilitation.

8.1.4.3 HFTW System Monitoring

For the base case analysis, the HFTW system monitoring includes the following elements:

- Quarterly groundwater measurement and sampling for the first 5 years
- Semiannual groundwater measurement and sampling on four wells, with four additional wells monitored annually for the final 25 years.

Given that the HFTW process is designed to promote in situ biological treatment, more monitoring wells will need to be sampled and monitored on a more frequent basis throughout the duration of remediation. Monitoring costs are based on the collection of samples from an average of eight wells located near and downgradient of the HFTWs during the initial 5 years, including four screened within the upper and lower target treatment zones, and it is assumed each sampling event will require 20 man hours and $2500 in ODCs per event. From year 6 and beyond, 4 wells will be monitored semiannually, and four additional wells will be monitored annually requiring 30 man hours and $4000 in ODCs per year.

8.1.4.4 GWET-FBR System Monitoring

For the base case analysis, the GWET-FBR system monitoring includes the following elements:

- Monthly system effluent sampling for the first 5 years
- Quarterly system effluent sampling for the final 25 years
- Quarterly groundwater measurement and sampling for the first 5 years
- Annual groundwater measurement and sampling for the next 25 years.

GWET-FBR system effluent monitoring is anticipated to require approximately 8 man hours and \$500 for ODCs per sampling event. Groundwater monitoring is based on collecting measurements and samples from an average of four monitoring wells per event, and it is assumed each sampling event will require 12 man hours and \$1500 in ODCs per event.

8.2 COST DRIVERS

The expected cost drivers for installation and operation of an HFTW system and those that will determine the cost and selection of this technology over other options include the following:

- Depth of the perchlorate plume below ground surface
- Width of the perchlorate plume
- Thickness of the perchlorate plume
- Aquifer lithology
- Regulations and acceptance of groundwater extraction and re-injection
- Regulatory considerations concerning secondary groundwater contaminants
- Length of time for cleanup (e.g., necessity for accelerated cleanup)
- Concentrations of perchlorate and alternate electron acceptors (i.e., nitrate [NO_3] and oxygen [O_2])
- Presence of co-contaminants, such as TCE and N-nitrosodimethylamine (NDMA)
- O&M costs and issues, particularly injection well fouling.

A thorough cost analysis of various in situ treatment approaches, including active-pumping systems (such as a HFTW), passive systems, and active-passive designs is provided in a recent book chapter by Krug and Cox. (2008). These approaches are compared technically and economically with each other and with ex situ treatment under a variety of different contamination scenarios. The reader is referred to this chapter and others in this volume by Stroo and Ward (2008) for descriptions and economic comparisons of different in situ technologies.

In summary, the plume characteristics and those of the local aquifer will play an important role in the cost and applicability of an HFTW system. For shallow groundwater plumes (<50 ft bgs) passive in situ options, such as installation of a PRB consisting of either trench or Geoprobe applied slow-release substrates is likely to be the most cost-effective option. These systems require little O&M after installation and are not subject to the biofouling issues that impact active pumping designs. For deeper plumes (bgs) or those that are very thick, passive approaches are often not technically feasible (e.g., for trench-applied passive substrates) and/or are cost-prohibitive (e.g., injecting passive substrates at closely spaced intervals to >50 ft bgs). Active capture systems are technically and economically more attractive under these conditions. A layered lithography is particularly desirable for an HFTW system since this promotes horizontal rather than vertical flow between the paired pumping wells.

Other factors that will determine the cost and applicability of an HFTW system compared to other technologies, include regulatory constraints, particularly in scenarios where re-injection of contaminated groundwater is subject to regulation. Under this scenario, and particularly in a deep aquifer, an HFTW system is a desirable option because, although pumping occurs for plume capture, no contaminated groundwater is brought to the ground surface. Factors such as required clean-up time, contaminant concentrations, and presence of select co-contaminants can also affect costs and technology selection.

However, perhaps the most significant long-term O&M cost and obstacle for any active in situ pumping systems is biofouling control. During this active treatment project, as well as others that have recently been completed (e.g., Hatzinger and Lippincott, 2009; Hatzinger et al., 2008), control of injection well fouling is a key component of system design and operation. This issue remains a critical technical and economic constraint to active pumping designs for perchlorate treatment, including both HFTW systems and groundwater extraction and re-injection approaches. For this demonstration, chlorine dioxide was applied as a biofouling agent. This approach worked to slow the onset of system fouling (based on previous experience at Aerojet) but did not completely prevent the process, and the HFTWs required redevelopment. The wells also fouled and had to be redeveloped periodically when this approach was tested for aerobic, cometabolic treatment of TCE at a field site (McCarty et al., 1998).

The most effective and economical solution for biofouling control with active systems involves multiple approaches, including selection of electron donor, dosing regimen of electron donor, biocide application, water filtration, and system pumping operation. Based on experience from this demonstration and others, the best operational approach to control fouling and minimize O&M costs associated with this issue includes the following:

- Active-passive rather than continuous operation.
- Infrequent, high concentration dosing of electron donor during active phase.
- Selection of an acidic electron donor to assist in biofouling control. Citric acid is optimal as it serves as an acid and a metal chelating agent.
- Daily application of chlorine dioxide or other fouling control chemical.
- Installation of a filtration system to remove biomass from between the extraction screen (or wells) and the injection screen (or wells).

These approaches were proven to be effective in a recent demonstration at the former Whitaker-Bermite facility in California (Hatzinger and Lippincott, 2009). Although this was a groundwater extraction-reinjection system rather than an HFTW design, biofouling was significantly controlled throughout the 6-month demonstration period by implementing the approaches described above. Moreover, perchlorate was treated to <4 μg/L in many of the system monitoring wells, from an initial concentration of ~300 μg/L.

8.3 COST ANALYSIS

As described above, the HFTW approach is ideally suited for layered lithologic units where one or more of the target treatment zones are >50 ft bgs and where re-injection of the treated water is preferred or mandated due to water usage/water rights concerns. Therefore, we have included the following base assumptions for this cost model:

For both options:

- Depth to shallow groundwater is approximately 35 ft bgs.
- Depth to the base of the impacted zone is approximately 100 ft bgs.
- Plume width is at least 150 ft at the point of treatment or capture.
- The upper and lower target treatment zones are separated by a 5 ft thick layer of soil occurring between 60 and 65 ft bgs, which has a hydraulic conductivity at least one order of magnitude lower then the upper and lower treatment zones. (Note: In layered sedimentary formations where the naturally occurring ratio of horizontal to vertical soil hydraulic conductivity values are 10:1 or greater, the presence of a single low conductivity zone separating the upper and lower target treatment zones may not be needed.)
- The upper and lower target treatment zones have average hydraulic conductivity values of $1\text{x}10^{-3}$ centimeters per second (cm/s).
- All extracted groundwater must be re-injected into the same formation it was extracted from following treatment to remove perchlorate.

For the HFTW option:

- Two HFTWs, one operated in the upflow mode and the other operated in the downflow mode, will be sufficient to provide full plume capture and treatment.
- The following are average concentrations for common electron acceptors:
  - Dissolved oxygen – 1.9 mg/L
  - Nitrate (as N) – 4.6 mg/L
  - Perchlorate – 3.3 mg/L.
- The average pumping rate for each HFTW well process pump will be between 6 and 10 gpm.
- Each well will be completed at a depth of 105 ft bgs, will be screened from 35 to 60 and 65 to 100 ft bgs, and will be constructed using eight ID, schedule 80 PVC piping.
- The electron donor agent will be a food-grade citric acid.

For the GWET-FBR option:

- One extraction well and one re-injection well will be sufficient to provide full plume capture, treatment, and re-injection.
- The following are average concentrations for common electron acceptors:
    - Dissolved oxygen – 1.9 mg/L
    - Nitrate (as N) – 4.6 mg/L
    - Perchlorate – 2.0 mg/L (reduced from HFTW to account for plume capture at margins – assuming NO_3 and DO are consistent in concentration throughout aquifer).
- The average pumping/re-injection rate will be 50 gpm.
- Each well will be completed at a depth of 105 ft bgs and will be screened continuously from 35 to 100 ft bgs,
- The extraction and re-injection wells will be constructed using six ID, schedule 40 PVC piping.
- Treatment costs are based on the use of an FBR using published cost factors and/or based on discussion with an FBR vendor.

Tables 8 and 9 show the estimated capital costs, O&M costs, and long-term monitoring costs for implementation of the HFTW and GWET-FBR technologies under the base case. The NPV of the O&M and monitoring costs is also included. The capital costs and NPV of the other O&M and monitoring costs provides the respective life-cycle costs adjusted to take into account the time value of money.

8.3.1 HFTW Cost Analysis

The HFTW alternative assumes that a single pair of HFTWs will be installed in a perpendicular alignment with groundwater flow. These wells will be used to capture, circulate, and add electron donor amendments to the perchlorate impacted groundwater. The amended water is then released to the opposite portion of the aquifer zone (e.g., water captured from the upper zone is amended and released into the lower zone) causing the electron donor to be distributed within the saturated formation. A portion of this amended water is then recaptured by the opposite well pair, amended, and released into the opposite portion of the formation again. The remaining portion of this water and the unconsumed portion of the added electron donor continue moving downgradient with the natural groundwater flow regime promoting further breakdown of the target contaminants of concern (COC). The rate of capture and electron donor dosing can be adjusted to achieve the required target treatment levels, including levels at or below the current USEPA reference dose value of 24 µg/L as well as more stringent state standards or public health goals in the range of 1 to 6 µg/L, at the point of compliance boundary. The costing has been developed for the base case conditions and assumptions described previously and is based on circulating groundwater on a continuous basis and adding electron donor on a semi-continuous pulsed basis. The capital cost including design, installation of wells, installation of the downhole and above grade equipment and controls and system start-up and testing is approximately \$403,000, and the NPV of the O&M totals an additional \$785,000 of costs over a 30-year life.

The O&M costs include the costs for labor for system O&M, costs for equipment repair and replacement, and cost for electron donor. The NPV of the long-term monitoring costs is estimated to be $271,000, resulting in a total life-cycle cost for the HFTW alternative of $1,459,000 (Table 8).

Table 8. Cost components for HFTW in situ biobarrier treatment of perchlorate-impacted groundwater.

	Year Cost is Incurred										NPV of Costs*
	1	2	3	4	5	6	7	8	9	10-30	
Capital Costs											
System design	83,500										83,500
Well installation	87,725										87,725
System installation	216,480										216,480
Start-up and testing	15,500										15,500
Subcost ($)	403,205										403,205
O&M Costs											
System O&M	28,172	28,172	61,272	28,172	28,172	61,272	28,172	28,172	61,272	Year 7-9 costs repeat through year 30	784,944
Subcost ($)	28,172	28,172	61,272	28,172	28,172	61,272	28,172	28,172	61,272	Repeat 7-9	784,944
Long-term monitoring costs											
Sampling/analysis/reporting**	22,560	22,560	22,560	22,560	22,560	10,660	10,660	10,660	10,660	Years 10-30 costs same as year 9	271,342
Subcost ($)	22,560	22,560	22,560	22,560	22,560	10,660	10,660	10,660	10,660	Same	271,342
Total Cost ($)	453,937	50,732	83,832	50,732	50,732	71,932	38,832	38,832	71,932	Repeat 7-9	1,459,491

NPV – net present value

*NPV calculated based on a 3% discount rate

**Quarterly through 5 years, then annually

8.3.2 GWET-FBR/Reinjection Cost Analysis

The GWET-FBR/reinjection alternative assumes that a single groundwater extraction well will be installed to capture the perchlorate-impacted groundwater flow and a single injection well will be installed to reinject the FBR treated water downgradient from the extraction area. The extracted water will be pumped to an above ground FBR unit for treatment prior to reinjection. The groundwater treatment train for the base case assumes perchlorate is the only COC, thus avoiding the need for additional pre- or post-treatment polishing to remove COCs that are not amenable to anaerobic biological treatment. A multimedia filter is included in the cost to remove biomass from the groundwater prior to re-injection into the aquifer, and a chlorine dioxide system is included for maintenance of the injection well. The extraction and injection wells and FBR system will be operated on a continuous basis throughout the treatment period. The capital cost including design, installation of wells, installation of the downhole and above grade equipment and controls, and system start-up and testing for the base case is approximately \$843,000, and the NPV of the O&M totals an additional \$978,000 of costs over a 30-year life. The O&M costs include the costs for labor for system O&M, costs for equipment repair and replacement and cost for electron donor. The NPV of the long-term monitoring costs is estimated to be \$297,000, resulting in a total life-cycle cost for the GWET-FBR/reinjection system of \$2,117,000 (Table 9).

Table 9. Cost components for the GWET-FBR ex situ treatment system for perchlorate-impacted groundwater

	Year Cost is Incurred										NPV of Costs*
	1	2	3	4	5	6	7	7-30	9, 12, 15, 18, 21, 24, 27, 30	10, 15, 20, 25, 30	
Capital Costs											
System design	108,500										108,500
Well installation	61,483										61,483
System installation	657,247										657,247
Start-up and testing	15,500										15,500
Subcost ($)	842,730										842,730
O&M Costs											
System O&M	34,472	34,472	67,572	34,472	58,872	67,572	34,472	Repeat $34,472 annually through year 30	Add 33,100 for non-routine O&M in each year listed above	Add 19,400 for well rehab in each year listed above	977,663
Subcost ($)	34,472	34,472	67,572	34,472	58,872	67,572	34,472				977,663
Long Term Monitoring Costs											
Sampling/analysis/reporting**	28,080	28,080	28,080	28,080	28,080	10,930	10,930	Years 8-30 costs same as year 7			296,920
Subcost ($)	28,080	28,080	28,080	28,080	28,080	10,930	10,930	Same	Same	Same	296,920
Total Cost ($)	905,282	62,552	95,652	62,552	86,952	78,502	45,402				2,117,313

NPV – net present value

*NPV calculated based on a 3% discount rate

**Quarterly through 5 years, then annually

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9.0 IMPLEMENTATION ISSUES

As with many in situ treatment approaches, both biological and non-biological, biofouling and plugging of the injection well screens can be a significant concern. During this demonstration, biofouling issues occurred as a result of poor system design, equipment selection, and inadequate controls. For HFTWs, this problem can be quite costly and time-consuming to correct by traditional well redevelopment and rehabilitation methods due to the amount of equipment installed within each of the HFTWs.

When the chlorine dioxide production system was operational, the regular dosing of chlorine dioxide proved to be an effective means of controlling biofouling and maintaining stable injection pressures within each HFTW. As noted in prior sections, optimal pressure controls were achieved when electron donor was added in larger doses with several days between injection events, combined with frequent (multiple small doses per day) short duration injections of chlorine dioxide. However, biofouling occurred very rapidly during periods of system operation when the chlorine dioxide production unit malfunctioned, particularly during the earlier periods of operation when this condition occurred in conjunction with more frequent (daily or multiple times/day) pulses of the electron donor, resulting in poor or no delivery of this chemical. This was evident by the rapid increase in injection zone pressures that could be seen in pressure data logs beginning within a brief period (<24 hours) following these malfunctions. It was also noted that, once biofouling began, it was difficult to reverse through the use of chlorine dioxide pulses alone. In the case of this demonstration, it appeared that the rate of pressure increase within the injection well screens could be slowed or stopped if observed quickly following the onset of problems with the biofouling control system. However, the newly stabilized injection pressures would typically remain well above the initial baseline pressures and often close to the maximum pressures that were achieved during the chlorine dioxide malfunction.

One key suggestion for future implementation of a liquid chlorine dioxide control system is the use of sensors that are capable of monitoring the proper production (via pH measurement, as acidic pH is required for production of liquid chlorine dioxide using the Bio-Cide system) and delivery of chlorine dioxide (via flow or level sensors) is recommended, coupled with alarm logic that will cause the entire system to shut down if the correct parameters are not being achieved for each chlorine dioxide cycle.

Even with proper chlorine dioxide system design and operation, well fouling is likely to occur over time. Therefore, options for delivering chemicals to the fouled well screens and recovering the biosolids or mineral scale solids released during redevelopment, while the pneumatic packer and other down-hole equipment remain in-place, need to be considered during the design of the HFTWs. This may include the following:

- Installation of extra feed lines that would permit the delivery of anti-fouling chemicals to the injection zones while the pneumatic packer remains in place

- installation of high flow submersible pumps, solenoid valves, and injection nozzles that would allow water and chemicals to be recirculated within the injection zone to promote the scouring of solids, allowing them to be recovered

- Installation of a filtered flow loop to allow the water with recovered solids to be pumped to the ground surface, filtered, and the solids-free water to be returned to the formation.

The other key issue with implementing the HFTW system for perchlorate treatment was the inability of the system to consistently treat perchlorate to <4 μg/L throughout the demonstration plot. Although reductions in perchlorate concentration of >95% were achieved throughout the shallow aquifer, including side-gradient well NMW-5, during all three phases, very few wells achieved perchlorate concentrations <4 μg/L. During Phase I, a limitation in electron donor supply was suspected to have resulted in the residual perchlorate, since the citric acid was tightly controlled in an attempt to reduce the solubilization of Fe and Mn. However, during Phase III, the citric acid concentration was increased appreciably, such that some of the wells in the test plot had residual measured concentrations of acetate in the mg/L range for several weeks (acetate is the key citric acid degradation intermediate), yet perchlorate persisted in some of these wells at ~30-100 μg/L. The perchlorate was present even though there was evidence of significant generation of soluble Fe and Mn, as well as sulfate reduction in some of these wells. For example, well NMW-7 had perchlorate concentrations ranging from 26-90 μg/L during Phase III and nitrate-N ranging from 0.2 to 0.7 mg/L, yet sulfate concentrations declined from 14.2 to 6.4 mg/L during Phase III, and both Fe and Mn were present at >1000 μg/L. These data suggest that multiple electron-accepting processes were occurring, including perchlorate reduction and sulfate reduction.

There are several potential explanations for the persistence of low concentrations of residual perchlorate in wells downgradient from the HFTW system. Tracer testing clearly showed that some of the deeper wells were not well-connected to the HFTW system hydraulically (based on greater than expected dilution of conservative tracer (see project final report [Hatzinger and Diebold, 2009]). For these wells, the concentration of electron donor was certainly inadequate for significant treatment of perchlorate. Other wells, such as NMW-7, however, were hydraulically connected based on tracer tests and had residual electron donor in Phase III (acetate in this case), yet perchlorate and nitrate persisted at very low concentrations. The apparent persistence of low concentrations of these electron acceptors may result primarily from aquifer heterogeneity, and this effect may be exacerbated with the HFTW system design due to the complex groundwater flow patterns of the paired pumping wells (i.e., deep water being brought up in the HFTW-U and shallow water pushed down in the HFTW-D, with perhaps some static zones in between the wells). In some regions, electron donor may not mix with groundwater during the course of the demonstration due to low permeability, poor connectedness to the injection well, etc. As a result, little degradation of perchlorate is likely in these zones, while extensive degradation (probably to nondetect concentrations) occurs in other regions. When groundwater is sampled from a broadly screened well, zones with varying degrees of local reaction may be represented in the collected sample, as shown in Figure 22. As a result, partial degradation of various electron acceptors, including perchlorate, nitrate, and sulfate, may be observed in the sample. This appears to be the case for many wells in Phase II and Phase III of this HFTW demonstration.

It should be noted that during a previous test of an HFTW system at Edwards AFB, in which toluene was injected into an aquifer to cometabolically stimulate TCE oxidation, residual concentrations of TCE remained (~18–24 μg/L throughout the test plot) at the conclusion of the demonstration (McCarty et al., 1998). The TCE removal was 97–98%, similar to the perchlorate removal efficiency in this demonstration, but low residual contaminant remained in the treatment zone. Although TCE and perchlorate have different physiochemical characteristics and slow desorption may play a role in the residual TCE in the Edwards study, the comparative data do suggest that, while very effective for mass reduction, low residual concentrations of contaminant may persist when using an HFTW system design. This has been a characteristic of both bioremediation field studies conducted with this system to date. However, this condition may diminish over longer operating periods or at greater distances downgradient from the active mixing zone.

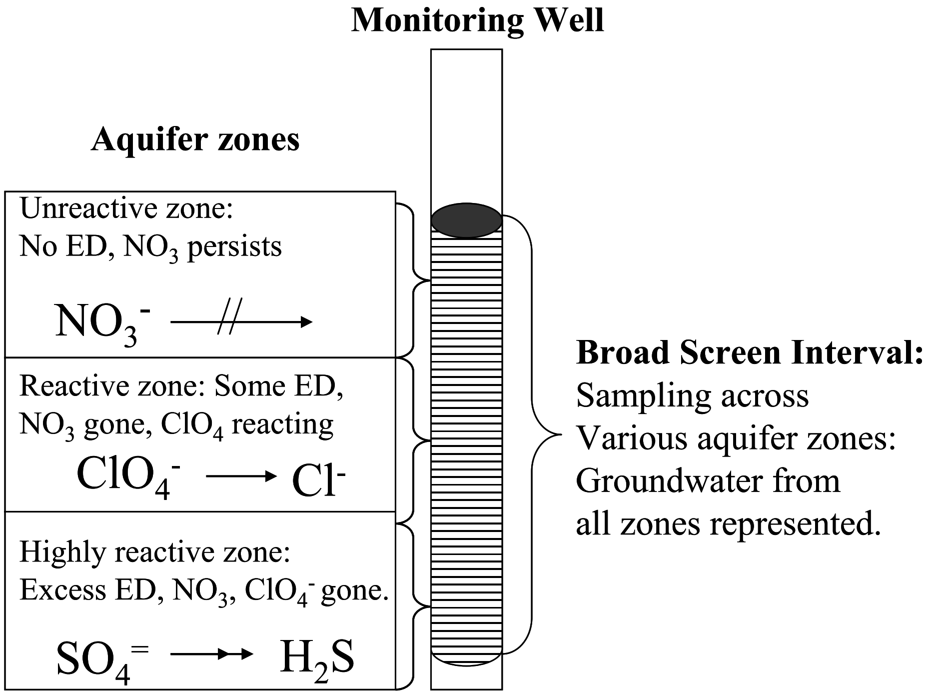

Figure 22. Simplified schematic of an aquifer with various reactive zones.
The monitoring well intercepts multiple zones, resulting in a mixture of groundwater from each zone in varying percentages.

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APPENDIX A

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