FINAL REPORT

In Situ Bioremediation of Perchlorate in Groundwater

ESTCP Project ER-0224

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A field demonstration was conducted to evaluate the in situ treatment of perchlorate using a horizontal flow treatment well (HFTW) system to mix electron donor into perchlorate impacted groundwater. The complete demonstration results are provided in this document.

15. SUBJECT TERMS

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Executive Summary

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 wide 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 perchlorate-reducing bacteria, 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 and 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.

During this ESTCP Project, an HFTW system was installed at Aerojet General Corporation's 8,500 acre site in Rancho Cordova, California (Aerojet). 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). The screen intervals for the HFTWs (each was screened in both intervals) were determined based on an extensive geological evaluation and groundwater modeling. 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. Based on laboratory microcosm and column studies, citric acid was utilized as an electron donor throughout the demonstration. This fatty acid was observed to effectively promote biodegradation of perchlorate (as well as nitrate and trichloroethene, which were co-contaminants in the aquifer), while creating less potential biofouling that alternate electron

donors, such as ethanol and acetate. In addition, chlorine dioxide was periodically added to each of the HFTWs as a biofouling control agent.

The demonstration was conducted in three phases (Phases I-III). During Phase I, each of the HFTWs was operated continuously at a net flow of 6 gallons-per-minute (gpm) and citric acid was added in daily pulses. The objectives of Phase I were as follows: (1) to evaluate the overall groundwater mixing and capture by the system; (2) to determine the extent of perchlorate and nitrate reduction possible without mobilizing significant quantities of Fe and Mn 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 Phase I based on stoichiometric requirements for the degradation of oxygen, nitrate, and perchlorate.

Fourteen groundwater sampling events were performed during Phase I operation, including 5 background events and 9 events to measure system performance after initial electron donor addition. Between the final background monitoring event (Day -15) and the final groundwater event in Phase I on Day 275, perchlorate concentrations in the 7 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 other 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 in the upflow HFTW (HFTW-U).

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 zone 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. In later testing (Phase III), low concentrations of residual perchlorate were detected in several downgradient wells even in the presence of excess electron donor.

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 9 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 5 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. In addition, based on the tracer studies, several of the deep wells, were not well connected to the HFTW system. Appreciable dispersion of the tracer cloud was apparent for these wells suggesting either (1) that the water from the HFTW-D was significantly diluted with untreated water prior to reaching these wells, or (2) that the quantity of water (and electron donor) reaching these deep wells was appreciably lower than anticipated due to significant recycling of the injected water from HFTW-D into HFTW-U with subsequent preferential delivery into the shallow aquifer.

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 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 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 & reinjection design), dissolved Fe in some monitoring wells exceeded 2.9 mg/L, and Mn concentrations reached 5 mg/L. Moreover, Dissolved Fe and Mn exceeding 70 mg/L and 40 mg/L, respectively, have been observed using slow release substrates for *in situ* perchlorate treatment.

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 (ClO_2) 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 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 a significant pressure increase in the lower screen of the downflow HFTW, while the chlorine dioxide system was non-functional, and then the pressure continued to increase gradually thereafter even when chlorine dioxide was added. 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 also gradually increased thereafter. The system was operated under a constant pumping scenario at 6 gpm without issue despite the pressure increases until Day 150, at which time water leakage was observed through the cap of the upflow well, and the system was shut-down. Various chemical and biological approaches (enzyme treatment, acid treatment, and physical rehabilitation) were tested to decrease well pressure during this period, and the system was operated intermittently. Electron donor was not injected from the end of Phase I (Day 275) until the beginning of Phase II operation (Day 472) to allow rebound of perchlorate throughout the demonstration plot. Each of the HFTWs was redeveloped via traditional chemical and physical methods prior to the commencement of Phase II.

The key objective of Phase II was to treat perchlorate without promoting significant well biofouling. 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 (4 – 8 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-h pulses during the active period, and 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.

A total of 9 groundwater sampling events were performed during Phase II & Phase III 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. Perchlorate concentrations rebounded appreciably in most shallow monitoring wells between Day 275, the last day for sampling in Phase I, and Day 472, (the background sampling event conducted just prior to the initiation of Phase II). Values in most wells increased from < 100 μg/L on Day 275 to > 900 μg/L on Day 472. Even after nearly 200 days without electron donor, however, perchlorate concentrations in most of the shallow wells were appreciably below their initial concentrations prior to system start-up and electron donor addition (i.e., Day 0), at which time most wells had concentrations exceeding 2,000 μg/L. As was observed in Phase I, perchlorate concentrations in all of 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 other shallow wells are further downgradient, and thus much less impacted by the pumping system.

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 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 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 represent a 96 $\pm$ 4% reduction in dissolved perchlorate from the starting concentration in each well prior to Phase I (Day -7) and an average 94 $\pm$ 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 a HFTW system for cometabolic treatment of TCE. The low residual contaminant was attributed primarily to competitive interactions between toluene (the cosubstrate) 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 6 deep wells furthest downgradient from the HFTWs, the total perchlorate reduction during the 801-day demonstration was 88 ± 9%. Thus, although non-detect concentrations of perchlorate were only achieved in a few wells, reasonable perchlorate treatment occurred in the deep zone, particularly considering results from the far downgradient wells.

There are several potential explanations for the persistence of low concentrations of residual perchlorate in the shallow and deep 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. For these wells, the concentration of electron donor was certainly inadequate for significant treatment of perchlorate. Many other wells, however, were hydraulically connected based on tracer tests, and had residual electron donor in Phase III, yet perchlorate and nitrate persisted at very low concentrations. The 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 non-detect 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. 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 of 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 percent loss was 87 ± 14%, with average final concentrations being 323 μg/L. Cis-1,2-DCE (the initial reductive degradation product of TCE) was detected at high concentrations (>1,000 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 injection of the *Dehalococcoides* spp. in many of the shallow wells suggests that the bioaugmentation 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 of the deep monitoring wells was appreciably less than in the shallow wells, averaging 71 $\pm$ 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 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 re-develop the HFTWs on a periodic basis, but this operational regimen should significantly increase the time between re-development events.

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, while biofouling was more readily controlled, "active-passive" operation appears to be the most desirable operational approach for this type of *in situ* design.

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LIST OF ACRONYMS AND ABBREVIATIONS

Aerojet—Aerojet General Corporation
AFB—Air Force Base
AFCEE—Air Force Center for Environmental Excellence
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
CH_4—methane
Cl—Chloride
ClO_2—chlorite
ClO_3—chlorate
ClO_4—perchlorate
cm—centimeters
CO_2—carbon dioxide
COR—Certified Organizational Representative
DCE—dichloroethene
DOD—Department of Defense
ED—electron donor
ESTCP—Environmental Security Technology Certification Program
Fe—Iron

Ft—feet
GCW—groundwater circulation wells
GET D—Groundwater Extraction Treatment Facility D
gpm—gallons per minute
h—hours
in—inch
HFTW—Horizontal Flow Treatment Well
H_2O—water
H_2S—hydrogen sulfide
HRC—hydrogen release compound
IC—ion chromatography
ID—inner diameter
IHDIV—Indian Head Division Naval Warfare Center
in—inches
ITRC—Interstate Technology and Regulatory Council
KV—kilovolts
L—liter(s)
µg—micrograms
µL—microliters
M—meters
MADEP—Massachusetts Department of Environmental Protection
MCL—maximum contaminant level
mg—milligrams
mL—milliliters
Mn—manganese
msl—mean seal level
N_2—nitrogen
NAICS—North American Industry Classification System
NaOH—sodium hydroxide
NAS—National Academy of Sciences
NASA—National Aeronautics and Space Administration
HN_4ClO_4—ammonium perchlorate
NMED—New Mexico Environmental Department
NO_3—nitrate
O_2—oxygen
O&M—operations and maintenance

ORP—oxidation reduction potential
P&G—Proctor and Gamble
P&ID—Piping and Instrumentation Diagram
PLC—programmable logic control
PRB—perchlorate-reducing bacteria
PVC—polyvinyl chloride
RfD—reference dose
RI—Remedial Investigation
s—second
SCADA—Supervisory Control and Data Acquisition
SEM—Scanning electron micrographs
SERDP—Strategic Environmental Research and Development Program
Shaw—Shaw Environmental, Inc.
SIC—Standard Industrial Classification
SO_4—sulfate
TCE—trichloroethene
TDS—total dissolved solids
UCMR—Unregulated Contaminant Monitoring Regulation
UNM—University of New Mexico
US—United States
USCS—Unified Soil Classification System
USEPA—United States Environmental Protection Agency
USGS—United States Geological Survey
VC—vinyl chloride
VOC—volatile organic compound

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1.0 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 GenCorp Aerojet 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 (horizontal flow treatment wells; HFTW) 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, California (McCarty et al., 1998). This project represents the first application of this design for *in situ* perchlorate remediation.

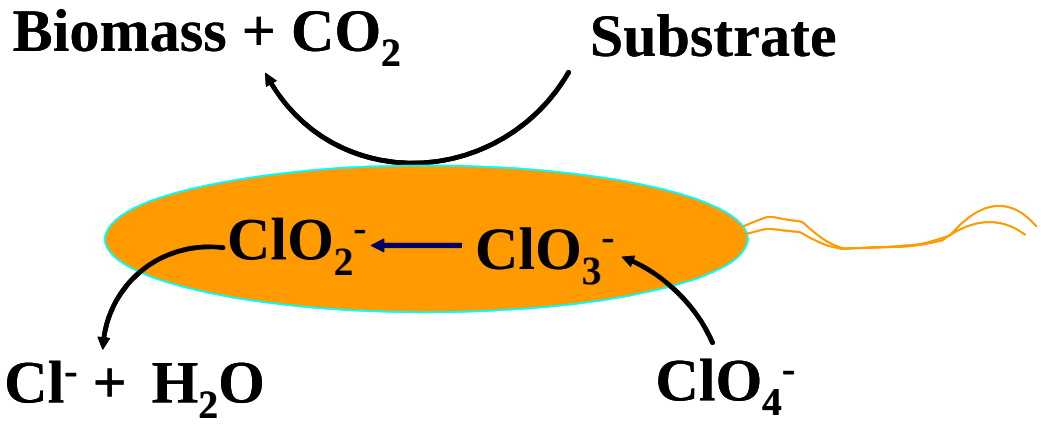
1.1 Background

Ammonium perchlorate (NH_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, including California, Texas, Maryland, Utah, and Nevada (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 US (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). The most extensive sampling for perchlorate has been conducted in California. According to data compiled by the California Department of Public Health (CDPH), perchlorate has been detected at concentrations exceeding 4 μg/L in 479 of 9,500 sources tested in the state during at least one sampling event over the past 5 years (CDPH, 2009).

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 can not 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 ground 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 (ITRC, 2008; Coates and Achenbach, 2004; Achenbach et al., 2001; Coates et al., 1999; Rikken et al., 1996).

The enzymatic pathways involved in perchlorate reduction have been studied in various strains. A perchlorate reductase enzyme catalyzes an initial two-step reduction of perchlorate (ClO_4^-) to chlorate (ClO_3^-) and then chlorite (ClO_2^-) (Coates and Achenbach, 2004; van Ginkel et al., 1996; Kengen et al., 1999). The chlorite is further reduced by chlorite dismutase to chloride (Cl^-) and oxygen (O_2), the latter of which is reduced to water (H_2O) (Coates and Achenbach, 2004; Coates et al., 1999). Thus, microbial degradation of perchlorate yields two innocuous products, chloride and water (Figure 1.1).

Figure 1.1. 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 (5) and wastewater (2) (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 perchlorate reducing bacteria 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. Perchlorate-reducing bacteria (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, wells, or using direct-push methods and rely upon 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 upon 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. An example of the plume depths for several significant DoD, DoD-contractor, and NASA sites is presented in Table 1.1. Many of these plumes are greater than 100 ft below ground surface. 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.

Table 1.1. Depth to Groundwater Perchlorate Contamination at Several Sites.

Site	Location	Plume Depth (ft below surface)
Jet Propulsion Laboratory	Pasadena, CA	200[1]
Thiokol Propulsion	Brigham City, UT	60 - 400[2]
Edwards AFB (Site 285)	Edwards, CA	125 - 190[1]
American Pacific Corp.	Henderson, NV	50 -300[2]
GenCorp Aerojet	Rancho Cordova, CA	100 - 300[2]
Los Alamos National Labs	Los Alamos, NM	50 - 740[2]
White Sands Missile Range	White Sands,NM	70 - 200[3]
Holloman AFB	Alamogordo, NM	300 - 400[3]
Boeing Corp.	Rancho Cordova, CA	100 - 300[2]
Mass. Military Reservation	Cape Cod, MA	40 - 150[1]
Melrose Bombing Range	NM	110 - 135[3]
Cannon AFB	Clovis, NM	300[3]

[1] From Remedial Investigation (RI) or other site report.
[2] Personal communication with site personnel.
[3] New Mexico Environmental Department (NMED). From USGS quarterly reports.

In addition to providing effective mixing, contaminated water passing through the HFTW system is not brought to the surface. As a result, regulatory concerns are reduced, and the requirement for an injection or waste discharge permit, which is common for *in situ* systems bringing water to the surface prior to reinjection (i.e., so that electron donor can be added) can often be avoided. Finally, this technology has a very small aboveground "footprint" which may be a requirement at many sites. In essence, this technology combines the advantages of pump-and-treat and *in situ* technologies. HFTWs have the advantages of active containment and groundwater capture provided by traditional pump-and-treat systems while simultaneously having the advantages of *in situ* treatment (cost/risk reductions of subsurface contaminant destruction and minimal aboveground infrastructure). A zone of influence of 80 meters was documented for the two-well HFTW system previously tested at Edwards AFB (McCarty et al., 1998). Another important advantage of the HFTW system is that it causes recirculation of contaminated water. This recirculation means that the system, in effect, acts as a recycle reactor, resulting in both flexibility (the extent of recycle can be controlled by controlling the flow of water through the wells) and increased efficiency (very low contaminant concentrations downgradient of the system may be achieved by increasing the extent of recycle). Thus, while the HFTW system is not designed for shallow sites, it is expected to be a viable and cost-effective option at many DoD sites with deep perchlorate-contaminated groundwater.

A large number of DoD facilities and DoD contractors presently have groundwater contaminated with perchlorate, often at multiple locations (e.g., hogout facilities, burn and disposal areas, live fire ranges). If or when firm EPA and/or state regulatory limits for perchlorate are established, groundwater at many of these locations will have to be treated. Current treatment technologies for this contaminant are limited largely to *ex situ* pump-and-treat systems in which water is passed through a bioreactor or ion exchange system to remove perchlorate. These systems, although very effective, require a large initial capital expenditure and the removal and reinjection of large volumes of groundwater. The testing and verification of electron donor addition using the HFTW technology provides DoD with an alternative *in situ* approach for perchlorate remediation. Although site-specific conditions must be taken into account, this technology is expected to be dramatically less expensive than current *ex situ* options at many sites, because an ion exchange or reactor system is not required and water does not have to be pumped above ground. A recent economic analysis of various *in situ* remedial approaches is provided in Stroo and Ward, (2008). The HFTW technology already has proven to be effective for addition and mixing of an electron donor for TCE remediation (McCarty et al., 1998; Goltz et al., 1998; Gandhi et al., 2002a, 2002b). Thus, this treatment technology is mature, expected to be very cost effective compared to *ex situ* options, and should be widely applicable for *in situ* perchlorate remediation at DoD facilities.

Another treatment option for perchlorate-contaminated groundwater is the injection of slow-release or complex substrates such as emulsified vegetable oils and polylactate (HRC) within zones in a contaminant plume. This approach, particularly using emulsified oils, has proven to be very effective for perchlorate treatment in shallow groundwater aquifers (Borden, 2007a; 2007b; Stroo and Ward, 2008). However, the application of this technology for deep aquifers can be technically challenging and cost-prohibitive. Because slow-release substrates do not mix well with water, they must be applied at close spacing to provide treatment efficacy for a soluble contaminant such as perchlorate. Thus, multiple, closely spaced wells must be drilled to apply slow-release electron donor (e.g., Borden 2007a; 2007b). Such application will be expensive at deep sites where drilling costs often drive remediation. In addition, once a slow-release substrate is applied to an aquifer, it cannot be recovered and the resulting redox of the aquifer cannot be controlled. This may result in aquifer redox conditions becoming much more reducing than minimally required for perchlorate treatment (redox similar to nitrate reduction) and yield hydrogen sulfide (from sulfate reduction), methane (from methanogenesis), and possibly result in the mobilization of manganese, iron, and arsenic (as arsenate is bioreduced to the more mobile, more toxic arsenite species). These endpoints are undesirable, particularly in an aquifer supplying drinking water. With circulation or injection/extraction systems, good mixing and regulation of contaminated groundwater with electron donor is achieved, reducing the quantity of donor used and

allowing appropriate control of the reduction potential within the treatment zone. In addition, electron donor addition can be quickly stopped or modified (i.e., change donors, donor application rate, etc) if unanticipated endpoints are observed. One of the key objectives of this demonstration was to determine if perchlorate treatment in a drinking water aquifer can be conducted with minimal mobilization of secondary groundwater contaminants, primarily iron and manganese.

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 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 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 one or several 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. The demonstration was designed to validate the use of HFTWs and electron donor addition for *in situ* perchlorate treatment and to determine the potential problems and costs associated with implementation. This information will be made available to interested DoD and regulatory personnel through technology transfer efforts.

1.3 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 EPA under the Safe Drinking Water Act, 1996 amendment. According to this act, EPA 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, EPA published an extensive toxicological review on perchlorate in 2002 (USEPA, 2002). This review suggested a reference dose (RfD) of 0.00003 mg perchlorate/kg body wt/day as a protective level for humans. Assuming 2L of water consumption per day, and an average body weight of 70 kg, this RfD corresponds to a drinking water standard of 1 μg/L. In 2005, after reviewing the available toxicological literature and EPA reports, a special committee of the National Academy of Sciences (NAS) recommended a RfD of 0.7 μg perchlorate/kg body wt/day for perchlorate (NAS, 2005). This RfD equates to a

drinking water standard of 24.5 μg/L using the assumptions made by EPA in 2002. In October 2008, the EPA decided not to promulgate a federal MCL for perchlorate based on Safe Drinking Water Act criteria. However, at the publication of this report, this decision still remains the topic of scientific and political debate.

Although there is presently no federal MCL, 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 (MADEP, 2009). California followed suit in 2007, setting a slightly higher regulatory standard of 6 ug/L (CDPH, 2009).

1.4 Stakeholder/End-User Issues

This ESTCP demonstration evaluated the efficacy of HFTWs for perchlorate remediation under hydrogeological and geochemical conditions that are typical of many perchlorate-contaminated aquifers in California. The demonstration also quantified the basic capital and operational cost of the technology, including maintenance costs and approaches to control well biofouling. In addition, the impacts of the technology on the geochemistry of treated groundwater (e.g., mobilization of iron and manganese) were evaluated. This issue was one of the most significant interests of the Central Valley Regional Water Quality Control Board during their review of the workplan for this project. Thus, the main issues of concern for end-users of the technology, performance, cost, and potential groundwater impacts were addressed during the project.

2.0 TECHNOLOGY DESCRIPTION

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 perchlorate-reducing bacteria 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.

2.1 Technology Development and Application

2.1.1 Electron Donor Addition for Perchlorate Bioremediation

During the past several years, laboratory studies have revealed the following: (1) perchlorate is utilized by a variety of bacteria as a terminal electron acceptor in a form of anaerobic respiration (similar to denitrification or sulfate reduction); (2) perchlorate-reducing bacteria (PRB) are indigenous to many natural environments, including groundwater aquifers; (3) the addition of one or more organic (or inorganic) electron donors is sufficient to promote the biological reduction of perchlorate in groundwater and other environments; and (4) perchlorate is completely reduced to chloride and water during biodegradation. These findings all indicate that biological reduction of perchlorate through electron donor addition (i.e., biostimulation) is a promising technology for remediation of the contaminant. The success of this approach, however, depends on adequate mixing and distribution of the electron donor with perchlorate-contaminated groundwater. In this demonstration, we have chosen to utilize HFTW technology to mix electron donor with groundwater in the subsurface.

2.1.2 Horizontal Flow Treatment Wells (HFTWs)

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 2.1, and photos of the pumps and packers being installed into one of the HFTWs are provided in Figure 2.2. As shown in Figure 2.1, 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 2.1. Schematic of HFTW Design.

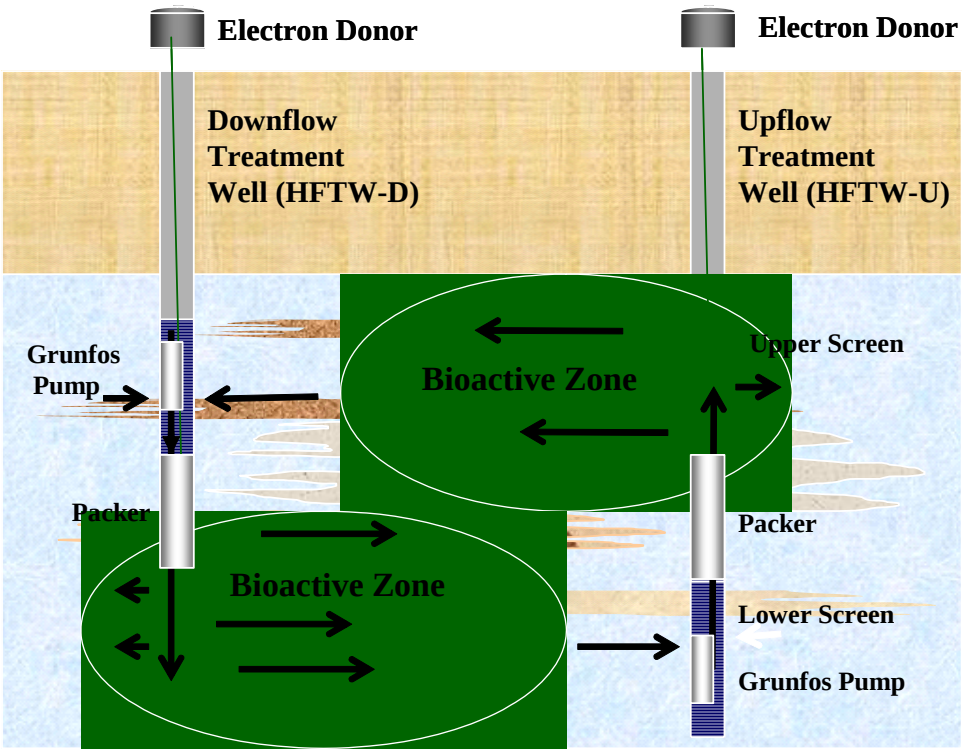


Figure 2.2. Photograph of Equipment Installation into the Downflow HFTW at Aerojet. The packer is visible in panel A and the wiring, tubing, and equipment present in the HFTW is seen in Panel B.

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 (GCWs) 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 recent publications and theses (Parr, 2002; Knarr, 2003; Chosa, 2004; Secody, 2007). The thesis of Secody (2007), which utilizes the model to simulate data from this demonstration, is provided as an appendix to this document (Appendix F).

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 (see Section 3.4). 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 (see Figures 3.18 and 3.19). 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, the distance between the wells, and to design the monitoring well network. A detailed description of the system components is provided in Section 3.5.1.

2.1.3 Biofouling Control

Microbial biofouling is a significant issue in many *in situ* bioremediation applications. In a previous demonstration at Edwards AFB with HFTWs to evaluate aerobic degradation of TCE, hydrogen peroxide was used to control fouling of well screens (McCarty et al., 1998). However, because perchlorate reduction is an anoxic process, hydrogen peroxide (which degrades to O_2) cannot be used an anti-fouling agent in this project. As part of this project, the University of New Mexico quantified biofouling mitigation options. Based on this work as well as previous testing at the Aerojet site during other demonstrations (Hatzinger et al., 2008; Chopra et al., 2004; 2005), chlorine dioxide was chosen as a biocidal agent.

Several chlorine dioxide systems were evaluated, including systems supplied by CDG Industries (creates chlorine dioxide from chlorine gas and acid), Pureline (creates chlorine dioxide electrolytically), Bio-Cide International (creates chlorine dioxide by mixing sodium chlorite and citric or phosphoric acid) and Proctor & Gamble (prototype electrolytic system). The chlorine dioxide production system supplied by CDG Industries has been used successfully by Aerojet to control biofouling in injection wells. However, the CDG system requires chlorine gas, which is a hazardous material. Because of this potential hazard, automation of the CDG system was deemed unacceptable by Aerojet personnel; thus the gas would have to be manually injected. Automation is necessary for the long-term technical and economic viability of this approach for biofouling control. Thus, the CDG system was not considered further for this project. By contrast, the chlorine dioxide systems developed by Pureline, Bio-Cide International, and Proctor and Gamble (P&G) do not require chlorine gas (rather a non-hazardous sodium chlorite solution is used as the precursor), and all are easily automated.

The Bio-Cide system was chosen for use in this demonstration based on low cost, simplicity of operation, commercial availability, and absence of waste products requiring disposal (the Pureline system produces a solution of 20% NaOH). The Bio-Cide system produces chlorine dioxide as a stabilized solution by mixing aqueous sodium chlorite (sold as "Oxine" solution) with small amounts of citric acid to produce ClO_2 in solution (Bio-Cide International, 2009). Once activated (by mixing with acid), the chlorine dioxide solution was applied to the HFTWs using metering pump. The quantities of solution added and the timing of addition were varied during the demonstration in an attempt to optimize biofouling control as detailed in Section 4.4.4.

2.1.4 Treatment Well and Monitoring Well Design and Placement

A generalized overhead view of the demonstration plot is provided in Figure 2.3. This version is not to scale. An overhead view of the plot to scale, and three cross-sectional views are provided in Figures 3.24 – 3.27. Additional details concerning HFTW and monitoring well construction and location are provided in Section 3.5.1.1 and 3.5.1.2. The two HFTWs were placed ~ 34 ft apart cross-gradient to groundwater flow (see Figure 2.3 for HFTW locations and Figure 2.4 for a photograph of the demonstration site). A series of groundwater monitoring wells were installed to quantify levels of perchlorate and 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. There were 3 pre-existing wells at the initiation of this demonstration that were screened within the perchlorate-contaminated zone of the aquifer (Aquifer B). These wells included a 6-inch-diameter pumping well (Well 4440), a single 2-inch-diameter monitoring well (3519) and one well in a nested set of three 2-inch-diameter monitoring wells (3514). The other wells in this nest (3515, 3516) were screened below the contaminated zone. These wells were not routinely sampled. An additional 16 wells were installed for the demonstration. Seven of these wells were completed during site assessment for this project (to obtain detailed geological and hydrogeological data). Well 3627, a single-completion 2-inch-diameter monitoring well was installed during initial site assessment work in January, 2003. In addition, two triple-completion wells/piezometers (3628 - 3630 and 3631 – 3633) were installed in August, 2003 using rotosonic drilling. Intact cores were obtained during these installations in order to verify previous geological data from the location. Each of these triple-completion wells included a single 1-inch-diameter piezometer screened at a shallow depth, and two 2-inch-diameter monitoring wells.

Figure 2.3. General Layout of Demonstration Plot. Distances between all monitoring wells is not to scale. The HFTWs are placed 34 ft apart, cross-gradient to the general direction of groundwater flow.

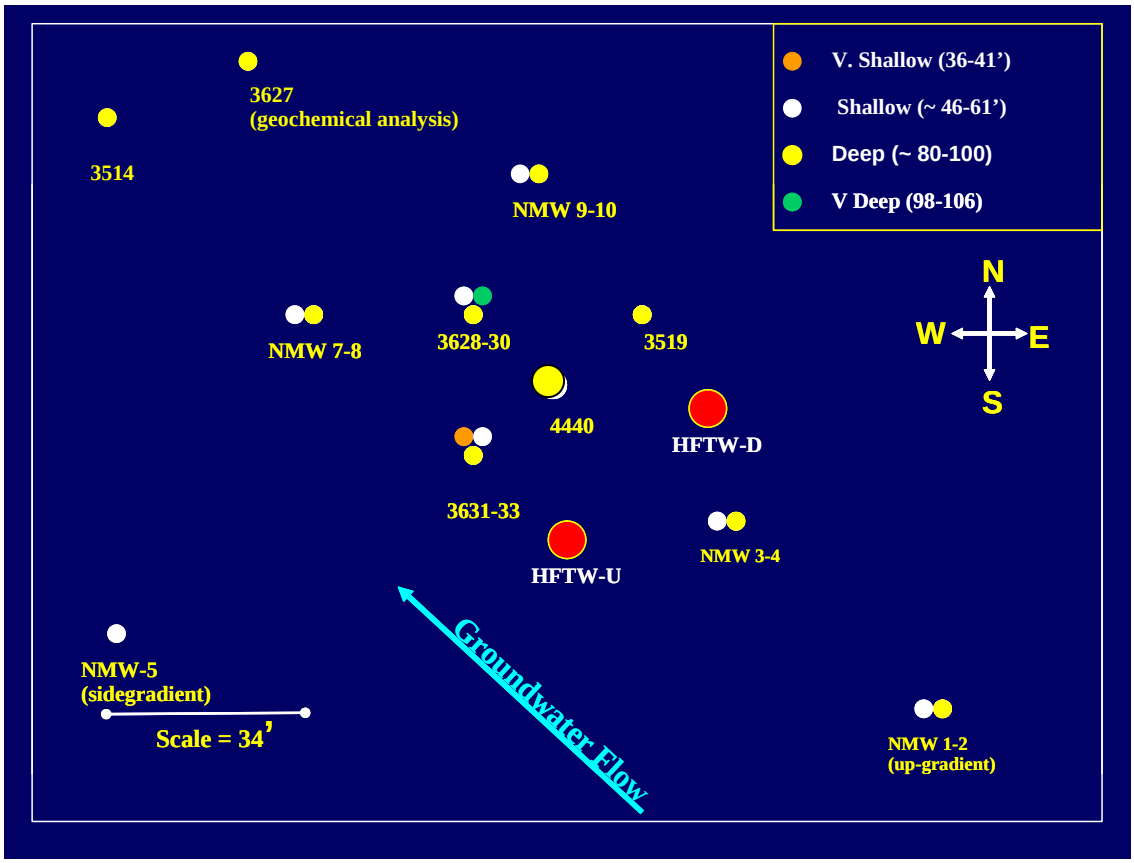


Figure 2.4. Photograph of the Aerojet HFTW System Showing Location of HFTWs and All Monitoring Wells.

Nine additional wells were installed at 5 locations (4 nested pairs and a single well), as shown in Figure 2.3 (NMW 1-5 and 7-10). These well locations were selected based on model simulations (Appendix E) as described further in section 3.5.6.3. An additional well (NMW-6) location was evaluated in early simulations, but based on model results, this well was not installed. Details of monitoring well/piezometer installation are provided in Section 3.4.6.3 and Appendix E. One of these locations, NMW 1-2, which is approximately 60 ft upgradient of the HFTWs, was designed to monitor concentrations of perchlorate entering the Test Plot. The dual-completion well nest NMW 3-4 was placed slightly upgradient of the HFTWs. This well is directly within the zone of influence of the pumping wells. Single-completion well MW-5, a shallow side-gradient well, was installed to evaluate the extent of influence of the HFTW system. The completions NMW 6-7 and NMW 8-9 were each approximately 45 ft downgradient of each HFTW. These wells were used to monitor contaminant degradation and changes in groundwater geochemistry after the water and electron donor mixture had reacted for a period of approximately 30 to 50 days (see Section 3.4.6.3 and Appendix E). Existing wells 3514 and 3627, which are located 70 ft downgradient of the HFTWs, were used to monitor 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 two to three months of groundwater travel time. The details of well construction and installation are provided in Sections 3.5.1.2 and 3.5.1.3.

2.2 Previous Testing of the Technology

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 VOCs. 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 1,000 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 (SERDP Project CU-1064 and ESTCP Project CU-0012). SERDP Project CU-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 CU-0012, evaluated the utilization of HFTWs to effect abiotic destruction of a TCE plume (ESTCP, 2007).

The concept of amending electron donor into perchlorate-contaminated groundwater to effect *in situ* biodegradation has now been tested successfully at the field-scale at several locations, primarily through funding from SERDP and ESTCP. A summary of these projects is provided in Hatzinger, (2005), and detailed descriptions of various remedial designs are given in Stroo and Ward, (2008). Active pumping systems

(in which groundwater is actively pumped to the surface and mixed with a soluble electron donor) have been tested at the Indian Head Division Naval Warfare Center (IHDIV) in Indian Head, MD (Hatzinger et al., 2006), Aerojet in Rancho Cordova, CA, just downgradient of this demonstration (Hatzinger et al., 2008; Geosyntec Consultants, 2002; Cox et al., 2001), the former Whittaker-Bermite Site in Santa Clarita, CA (Shaw Environmental, Inc., 2009), the Longhorn Army Ammunition Plant, Karnack, TX (Krug and Cox., 2008), and a few other locations (ITRC, 2008). None of these demonstrations employed HFTWs to apply electron donor to groundwater, rather water was pumped to the surface, amended with electron donor, then reinjected into the aquifer via one or more reinjection wells. Summaries of recent demonstrations are provided in the subsequent paragraphs. Additional details are given in the references provided for each demonstration.

An early SERDP and US Navy-funded field demonstration of in situ perchlorate treatment using soluble electron donor addition was completed at the Indian Head Division, Naval Surface Warfare Center in Indian Head, MD (Cramer et al., 2003; Hatzinger et al., 2006). An initial field investigation at the site revealed a shallow, narrow plume of perchlorate contamination behind IHDIV Building 1419 (Hog-Out), with perchlorate levels ranging from 8 to 430 mg/L, and nitrate varying from 4 to approximately 50 mg/L. The pH of site groundwater was generally below 5.0. A field-pilot demonstration employing a recirculation cell design was undertaken based on site geochemical and hydrogeologic data. Two field plots (Test Plot and Control Plot) were installed, each consisting of two extraction wells, two injection wells, and 9 groundwater monitoring wells. In the Test Plot, groundwater was removed from the site, amended with electron donor (lactate) and buffer (carbonate/bicarbonate mixture), and then reinjected into the aquifer. In the Control Plot, groundwater was extracted and reinjected without substrate or buffer amendment. During the 5-month study, approximately 20,000 gallons of groundwater was re-circulated through each plot. Groundwater pH was elevated to >6.0 in all Test Plot wells during the demonstration, and lactate was measured throughout the Test Plot within 3 weeks of system operation. Perchlorate levels were reduced by >95% in 8 of 9 monitoring wells within the Test Plot during the demonstration, with 5 wells reaching below 1 mg/L, and 2 below the 4 μg/L practical quantitation limit. Nitrate levels were also been substantially reduced throughout the Test Plot, with 7 of 9 wells showing nondetectable levels within 7 weeks. Conversely, there was no significant increase in pH or reduction in either perchlorate or nitrate within the Control Plot. The data from this demonstration indicate that *in situ* biostimulation using electron donor addition is a viable remediation option for treating high levels of perchlorate in groundwater. During the course of this field study, appreciable biofouling was not observed in the injection wells. However, the study was of relatively short duration (111 days of pumping), and water (and electron donor) was pumped intermittently rather than continuously. At the conclusion of the study, biomass was observed associated with the

screens on both the injection and extraction well pumps. Thus, with a longer operating time, biofouling may have become a significant issue.

A second project was completed by Geosyntec, Inc. at a perchlorate-contaminated location downgradient of the HFTW demonstration system installed for the current study, at the Aerojet Facility in Rancho Cordova, CA (Geosyntec Consultants, 2002). Details of this demonstration are also provided as a case study in Hatzinger et al., 2008. In summary, groundwater was extracted from the subsurface, amended with acetate or ethanol as electron donors and then reinjected into the aquifer. Initial perchlorate concentrations of 220 µg/L were reduced to below 4 µg/L within 25 to 75 ft of the reinjection well. Biofouling of the reinjection wells, which was anticipated to be a problem, was adequately controlled by chlorine dioxide injections. The results from the Geosyntec project, including the application of chlorine dioxide gas for biofouling control, were considered and applied where relevant during the design of this HFTW evaluation. One of the key secondary groundwater effects observed during the previous demonstration was the mobilization of appreciable quantities of iron and manganese in the aquifer due to biological reduction of these metals to more soluble species (Geosyntec Consultants, 2002). Based on these results, and a discussion with the Regional Water Quality Control Board in Sacramento, one of the early objectives of our demonstration (Phase I of testing) was to determine whether the mobilization of these two metals could be reduced by limiting the quantity of electron donor added to the aquifer.

Thus, in summary, HFTWs have been previously implemented as an *in situ* mixing technology for aerobic TCE treatment (McCarty et al., 1998; Gandhi et al., 2002a; 2002b), and electron donor addition using groundwater extraction/reinjection systems has been successfully applied to stimulate biodegradation of perchlorate by indigenous microorganisms (Cramer et al., 2003; GeoSyntec, 2002; ITRC, 2008; Stroo and Ward, 2008). This demonstration combines these two approaches. The desired result is extensive *in situ* mixing of electron donor with groundwater, and subsequent in situ biodegradation of perchlorate, without the need to extract the groundwater or contaminant from the subsurface. In addition to perchlorate treatment, treatment of TCE as a co-contaminant is evaluated, minimization of secondary groundwater impacts is addressed, and biofouling control and mitigation strategies are tested.

2.3 Factors Affecting Cost and Performance

A technology model was recently developed at the Air Force Institute of Technology to predict cost and performance for a number of HFTW technology configurations under differing site conditions (Knarr, 2003). In this study, it was observed that engineering variables such as HFTW treatment well pumping rate, distance between the paired treatment wells, and electron donor injection schedule all impacted technology cost and performance. Performance, defined as contaminant mass removal and attainment of regulatory contaminant concentrations downgradient of the treatment system, was also a

function of aquifer hydraulic conductivity, regional groundwater velocity, and initial contaminant concentrations. Other issues affecting cost of the HFTW system include biofouling and biofouling control measures. Section 5.0 of this report provides additional details concerning the costs of this demonstration and the predicted cost of implementing the HFTW system for full-scale treatment of perchlorate, as well as the variables expected to impact system performance.

A cost analysis of the HFTW concept, which was accomplished in support of SERDP Project CU-1064, demonstrated that HFTWs are cheaper than injection/extraction approaches to achieve mixing when the water table is deeper than about 30 ft (as one of the main cost savings of HFTWs is due to the fact that contaminated water need not be pumped to the ground surface) (SERDP, 2003). Results of the recently completed project CU-1064 showed the costs (operating plus capital) of an HFTW system used to remediate a trichloroethylene plume source area at Edwards AFB were about $30 per 1000 gal, conservatively calculated by assuming only a single year of system life. The cost per pound of TCE removed/destroyed was also very conservatively calculated at $7200. These figures compare extremely well to conventional pump-and-treat technologies.

2.4 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 DoD installations, where space is sometimes limited. As discussed above in Section 2.2, 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 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., HRC) (see Section 1.1). 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 TOC addition, such as sulfate reduction and methanogenesis, to the extent possible. During Phase I and Phase II operation, the electron donor was controlled at 1.5X – 4X the calculated stoichiometric requirement for reduction of perchlorate, nitrate, and dissolved oxygen in order to minimize secondary groundwater impacts, particularly mobilization of

Fe and Mn, 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/limitation with this technology is that microbial fouling may have a significant impact on HFTW performance and long-term operational cost. Because HFTWs have not previously been applied to promote contaminant biodegradation under anaerobic conditions, the potential for biofouling during this application is currently unknown. However, in a previous test of the system for aerobic degradation of TCE at Edwards AFB, biofouling was a significant issue during the demonstration. The HFTWs were initially redeveloped to reverse the impacts of fouling. The problem was then controlled through the periodic addition of hydrogen peroxide to the treatment wells. This technique was not applicable during this demonstration because the peroxide produces oxygen, which increases electron donor demand, and can subsequently inhibit perchlorate reduction if provided in high doses. However, as part of this project, laboratory column studies were conducted at the University of New Mexico to determine the following: (1) if specific electron donors promote less biofouling than others (ethanol, citric acid, lactate, and acetate were evaluated); and (2) whether specific biofouling control agents, including chlorine dioxide are likely to be effective for controlling biofouling at the injection well screens. The details of these studies are summarized in Section 3.4.4 and detailed further in Chopra et al., (2004 & 2005).

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 is not present between HFTW screens. A thorough geological assessment of the aquifer, including collection of intact cores using rotosonic drilling were used to size and place the treatment well screens in conductive zones within the aquifer. Moreover, a detailed site model developed at AFIT was implemented to estimate and minimize (based on distance between HFTWs and pumping rates) short-circuiting of the pumped groundwater.

3.0 Demonstration Design

3.1 Performance Objectives

The performance objectives for this project are listed in Table 3.1. 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 & Phase II; (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 3.1 and full details are provided in Section 4.

Table 3.1. 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, Inconsistent reduction in deep wells
	Reduction of trichloroethene levels (TCE) 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' 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

3.2 Test Site Selection

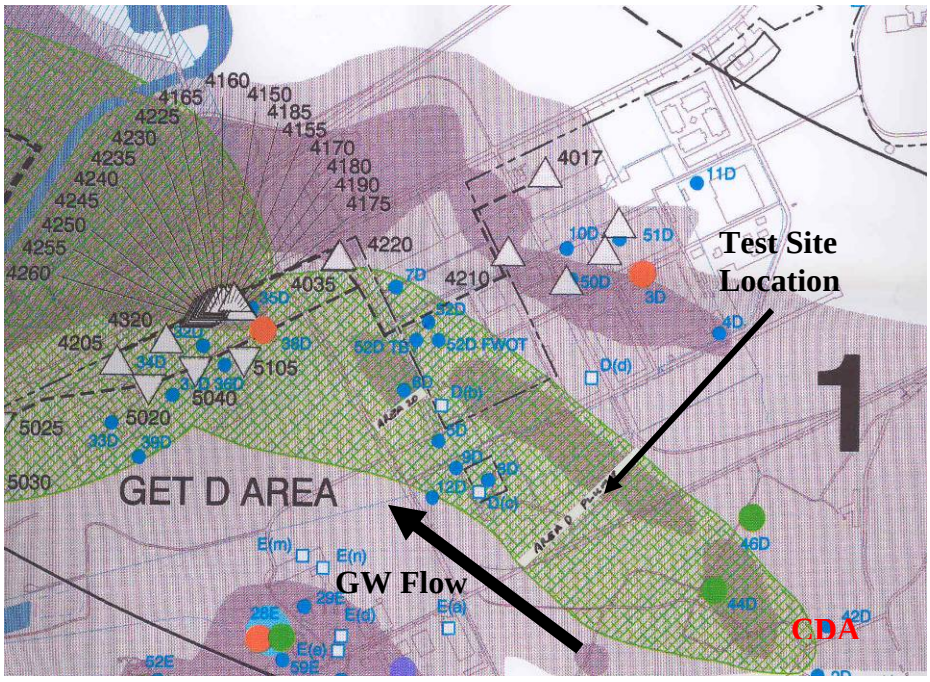
Several field sites for the demonstration were evaluated during the first three months of the project. These sites included the Jet Propulsion Laboratory (Pasadena, CA), two locations at Edwards Air Force Base, (Edwards, CA), and two locations at the Aerojet Corporation (Rancho Cordova, CA). Available contaminant and hydrogeological data were reviewed for each site. The selection criteria for a field demonstration site included the following: (1) depth to contamination >30 ft; (2) anisotropic aquifer (i.e., low vertical compared to horizontal flow) with overall hydraulic conductivity >1 x 10^{-3} cm/s; (3) perchlorate concentration >0.3 mg/L; and (4) aquifer pH >6.0. The initial two criteria are defined by the optimal conditions for efficient and cost-effective operation of a horizontal flow treatment well (HFTW) system. The second two criteria (perchlorate concentration and pH) are microbiological considerations. To ensure that a perchlorate-reducing population can be maintained and than reductions in concentration can be easily verified, an initial perchlorate concentration of at least 0.3 mg/L is desired for the demonstration. Laboratory studies have indicated that perchlorate reduction is inhibited at pH values less than 5.7, therefore, an aquifer with neutral pH and reasonable alkalinity is also required for the field site.

Based on a review of relevant site data, "Area D" at the Aerojet facility was chosen for the demonstration. The details of the demonstration site are given in the subsequent sections. A generalized map of the site showing the perchlorate and TCE plume is provided in Figure 3.1. The two sites at Edwards AFB were not chosen for the following reasons: (1) the first location, Site 285, was selected by site personnel for an ion exchange demonstration in conjunction with Los Alamos National Laboratory, and there was no way to adequately separate the two demonstrations; and (2) the perchlorate concentrations at the second site were in the low part-per-billion range, which was deemed too low for demonstration purposes (see previous paragraph). Data from the Jet Propulsion Laboratory (JPL) were also reviewed. Although the site conditions at JPL appeared to be generally appropriate for the demonstration, the depth to groundwater at this site is generally greater than 200 ft below land surface (bls). Because of the depth, combined with the urban location of the facility (and associated utilities, etc), drilling costs for well installation were anticipated to be too high for the current project budget.

Data were obtained and reviewed from two locations at the Aerojet facility. The first location is a plume emanating from Aerojet's Hog Out facility. Perchlorate contamination in this area is significant, with groundwater levels exceeding 50 mg/L in one well. However, a large portion of the vadose and saturated zone to 80 ft bls was hydro-mined for gold in the past, and now consists of dredge tailings rather than undisturbed sediments. Because the efficiency of horizontal flow treatment wells depends, in part, on preferential horizontal flow (i.e., anisotropic aquifer conditions), and the flow characteristics in the dredge tailings are unknown, this site was removed from further consideration as a demonstration site.

The source of the Area D plume at Aerojet is a former propellant burn area known as the "Central Disposal Area" (CDA). A description of the site geology and groundwater geochemistry and contamination is provided in the following sections. However, in general the geology beneath Area D consists of inter-bedded layers of sandstone, siltstone, silty sand, sandy silt, and clayey silt. The depth to groundwater in this area is approximately 30 ft bls, and this level had remained reasonably consistent (within 2 – 4 ft) during the 5 yr period preceding the demonstration. A clay confining layer at approximately 110 ft bls separates an upper and a lower aquifer. There were several existing monitoring wells within the chosen demonstration area from which historical data were available. Perchlorate levels in Wells 3514, 3519, and 4440, each of which are screened at different depths within the 70 – 100 ft region of the upper aquifer, ranged from approximately 3100 to 3600 µg/L. In addition, TCE is present within these wells at concentrations ranging from 400 to 2200 µg/L. The groundwater pH is neutral.

Figure 3.1. Location of the Test Site.



3.3 Test Site History / Characteristics

The Test Site is located within Aerojet General Corporation's (Aerojet) 8,500-acre Sacramento, California 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 Standard Industrial Classification (SIC) code for this facility has been replaced by the NAICS (North American Industry Classification System) code. This code for Aerojet is as follows: 336415 – Guided Missile and Space Vehicle Propulsion Unit and Propulsion Unit Parts Manufacturing.

As mentioned previously, 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 3.1. The CDA, specifically Site 42D, is the apparent source of the perchlorate and VOC (primarily trichloroethene) plume that underlies the Test Site. The CDA is an area where, during the 1950's, 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 5,800 ft long and 3,000 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 1,000 GPM Groundwater Extraction Treatment Facility D (GET D).

3.3.1 General 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 (Figure 3.2). 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 2,000 ft thick. Table 3.2 presents the site stratigraphy beginning from oldest to youngest geologic formations.

Figure 3.2. Map Showing the Geomorphic Provinces of California and the Location of the Aerojet General Corporation Facility.

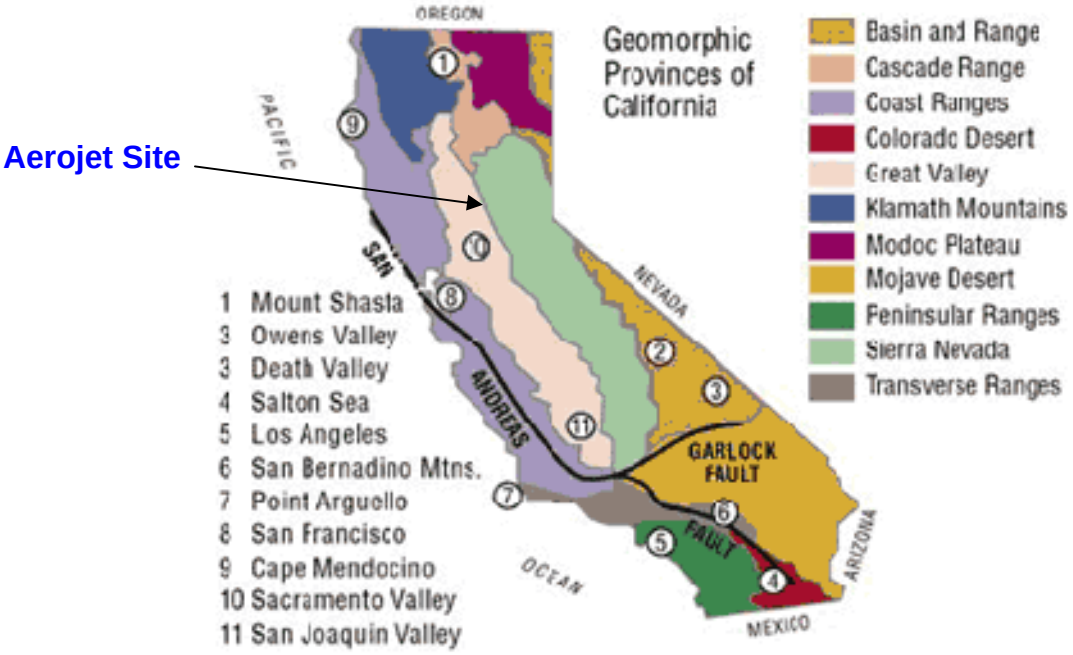


Table 3.2. Geology of the Aerojet Site.

Formation Name	Age	Thickness (ft)	Characteristics
Basement Rocks	Jurassic	unknown	Primarily metamorphic dominated by slates and meta-volcanic rocks.
Chico Formation	Cretaceous	200-400 ft	Chico Formation encountered at –1,180 ft. Composed of marine sandstone and shale with small amounts of saline water.
Ione Formation	Tertiary middle Eocene	100-400 ft	Ione Formation encountered at –830 ft. Composed of marine or transitional quartz sandstone and thick beds of clay.
Valley Springs Formation	Tertiary Oligocene-Miocene	75-300 ft	Valley Springs Formation encountered at –530 ft. Composed of volcaniclastic ash, tuff, quartz sand, pebble conglomerates and clay beds. Generally low water yielding aquifer.
Mehrten Formation	Tertiary Miocene-Pliocene	200-400 ft	Mehrten encountered at –190 ft . Fluvial volcaniclastic sediments composed of black sands, gravels and interbedded clays. This Formation contains the deepest fresh water aquifer.
Laguna Formation	Tertiary Pliocene-Pleistocene	100-200 ft	Laguna Formation is encountered at surface. Fluvial sediments derived mainly from silica-rich granitic rocks. Composed of silica-rich sands, gravels intermixed with clays and silts. Most of the surface deposits of the Laguna have been disturbed by dredging operations. High yield aquifers are found in the Laguna.
Dredged Tailings and Undifferentiated Fluvial Deposits	Pleistocene to Recent	0-100 ft	Dredge Tailings are unconsolidated heterogeneous mixture of sand, silt, clay and gravels. Undifferentiated Fluvial Deposits are unconsolidated clay, silt, sand and gravel. May contain discontinuous zones of perched groundwater.

The single most dominant surface features at the Aerojet facility are the dredge tailings that cover approximately 80 percent of the land surface. The Aerojet facility and surrounding areas have been subjected to historic gold dredging operations beginning in the early 1900's and continuing into the 1960's. The fluvial gold-bearing sediments of the Laguna Formation were the target for the dredges and areas within the site have been dredged to depths of up to 100 ft (from ground surface). As a consequence of this dredging the Aerojet site has become a significant groundwater recharge zone for the underlying groundwater bearing zones.

The Laguna and Mehrten Formations contain the most productive aquifers underlying the Aerojet site and serve as the principle 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 ft. 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 six 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.

3.3.2 Test Site Geology and Hydrogeology

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 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. Some of the sands and silts display moderate induration and 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. With the installation of the two nested piezometers in June 2003, a total of eleven groundwater wells are present at the Test Site. Nine of these wells are screened at various intervals from 30 to 105 ft bls, where perchlorate contamination is present. These nine wells will be used for groundwater monitoring during the demonstration. Table 3.3 summarizes perchlorate and VOC results from the existing monitoring wells 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 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 3,920 μg/L.

Table 3.3. Perchlorate and VOC Levels 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	1,500	600	80 – 85
3630	3,140	1,200	96 – 101
3631	65	14	36 – 41
3632	155	78	52 – 57
3633	3,350	650	98 – 103
3627	970	1,200	75 – 95
3519	2,320	1,700	78 – 103
3514	3,920	2,100	77 – 90
4440	3,300	2,200	75 – 93 and 98 – 106

[1] All data are from 2003 sampling except Well 4440 - 1995 data.

3.3.3 Present Operations

As mentioned in Section 3.3, the TCE and perchlorate plume that is present beneath the Test Site extends approximately 3000 ft to the southwest where it is intercepted by GET D. GET D currently extracts 1000 GPM of groundwater from 24 wells. Influent total VOC and perchlorate concentrations are 300 and 230 μg/L respectively. VOCs are treated with air strippers and perchlorate is removed with disposable ion exchange resins (Figure 3.3). The treated water is re-injected via six groundwater injection wells located 4000 ft west of the GET D facility. GET D has been in almost continuous operation since 1981 and has treated approximately 12 billion gallons of water (2003 data). The implications associated with successful plume treatment via *in situ* HFTWs include reducing the operating life of the GET D system components which will save money related to various elements including power consumption, system operations and maintenance, and resin replacement and disposal. These cost savings could prove to be quite substantial.

Figure 3.3. Current Remedial Operations at the Aerojet Facility GET D Area: (A) Air-Stripper for VOC Removal and (B) Ion-Exchange Vessels with Disposable Resin for Perchlorate Removal.

3.4 Pre-Demonstration Testing and Analysis

3.4.1 Monitoring Well Installation and Sample Collection

On January 28th 2003, a single borehole was advanced to 101'bls using an air rotary casing hammer-drilling rig to collect soil samples for microcosm studies. Wet sediments were first recorded at approximately 30'bls, which is consistent with previous data concerning groundwater elevation in this region. Layered sediments varying from sandy gravel (23-35'bls) to sandy silt (60-70'bls) to cemented sandstone/siltstone (70-93'bls) were observed during drilling. These materials are consistent with alluvial deposits in this region, and confirm that the location in Area D was not previously hydro-mined for gold. During the drilling, a split-spoon sampler was used to collect sediments from 40-42', 50-52', 60-62', 80-82', and 90-92'bls. The sediment samples were removed from the split-spoon into glass jars, which were then placed at 4°C for shipping to Lawrenceville, NJ. Following completion of the borehole, a two-inch diameter PVC groundwater monitoring well was constructed (MW 3627). The well was screened from 75-95'bls.

Groundwater samples were collected from the newly-installed well and from previously-installed monitoring wells in the demonstration area (MW 3514 and MW 3519) for contaminant and geochemical analysis and for use in microcosm studies. The groundwater collected from monitoring wells in the region had perchlorate levels ranging from 1.0-3.9 mg/L, nitrate from 13.0-19.4 mg/L, and TCE ranging from 1.7-2.1 mg/L. The pH of the site is neutral (6.8) and DO levels are in the 4-6 mg/L range. Thus, based on contaminant concentrations, and site geology and geochemistry, this location was determined to be suitable for the HFTW demonstration.

3.4.2 Aquifer Testing – 8-Hour Pump Test at Well 4440

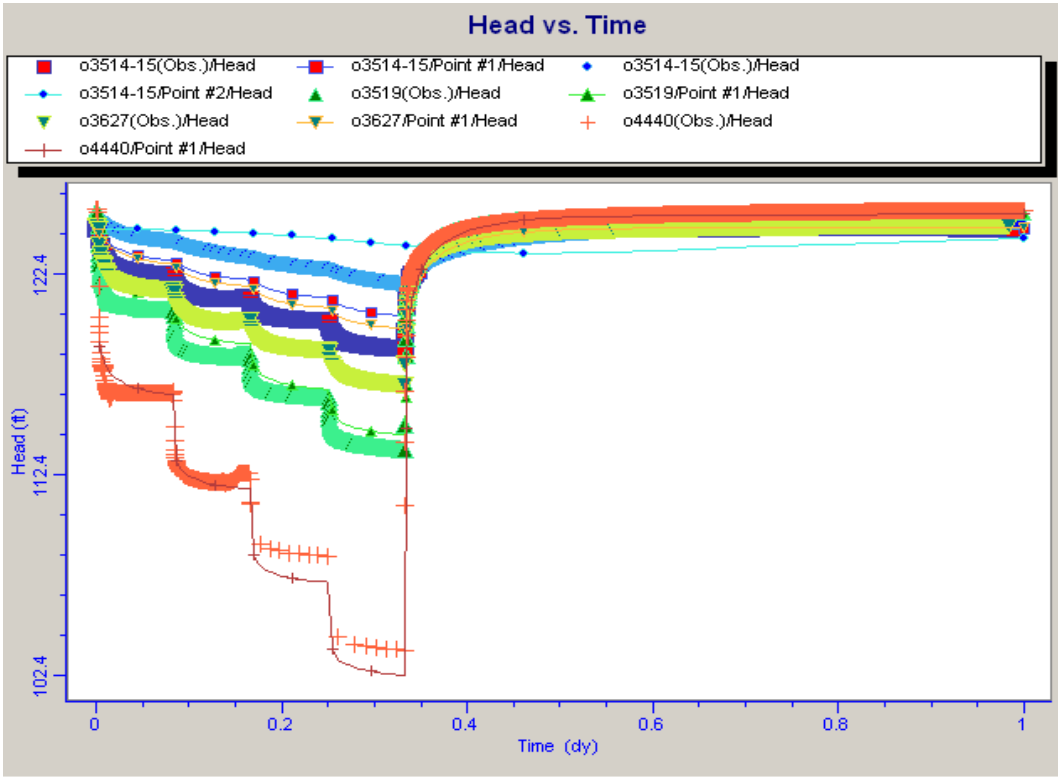
A pump test (step draw-down) was performed in the demonstration area in February, 2003 to assess pumping levels achievable in the region and to estimate hydraulic conductivity in the aquifer. Well 4440, which is an unused 6" pumping well located in the center of the proposed demonstration plot, was redeveloped and used as the pumping well for the test. Data loggers were placed in Wells 3627 (53'from pumping well), Well 3519 (12.7' from pumping well) and Well 3514-3516 (nested well 62' from pumping well) to record groundwater elevation. Well 4440 was then pumped at rates of 20, 30, 40, and 50 gpm, respectively, for 2 hrs each. The pump was then shut off and groundwater recharge in each well was recorded. The pump test data were then simulated using MODFLOW. Based on the test, it was estimated that pumping rates as high as 40-50 gpm are feasible with the HFTWs without causing significant draw-down in the aquifer. Much lower pumping rates (< 10 gpm) were used during the demonstration. Initial fitting of the pump test data yielded a hydraulic conductivity estimate of 15 ft/day. However, the data in one well could not be readily simulated using the model. A layered model (with regions of differing conductivity) was subsequently tested based on the

general characteristics of aquifer as inferred by the geological analysis of Well 3627. This model provided a better fit to the pump test data (Figure 3.4) from each of the wells than the initial model and gave a maximum K_h value of 13.1 ft/day.

The site model which was constructed based on fitting MODFLOW draw-down simulations to the pump test data was subsequently used to predict groundwater flow induced by the proposed HFTWs. In the model simulation, two HFTWs were screened at depths of 73 – 95' (shallow screen) and 98' – 106' (deep screen). These areas are anticipated to be zones of high conductivity based on the previous core analysis as well as existing well log data from well 4440. Each zone was assumed to be isotropic with a k-value of 13 ft/day. The 5' separation zone between the well screens was assumed to have a k-value of 0.3 ft/day. These values were determined from the MODFLOW simulations described above as well as interpretation of site lithography data. The capture zone of the wells and the movement of water through the 4 well screens was then simulated as a function of flow rate (10 – 50 gpm) and well spacing. Representative simulations are given in Figures 3.5 and 3.6. At a flow rate of 30 gpm, and a well spacing of 34', the flow model predicted appreciable vertical flow (~ 20/30 gpm) between adjacent screens on each individual well. Although some flow between screens of each individual treatment well is acceptable (injection screen to extraction screen), it is desirable for the primary flow within the demonstration system to be between screens on the adjacent wells in a horizontal rather than a vertical direction. The ratio of vertical/horizontal flow decreased with closer well spacing. However, the capture zone (i.e., amount of contaminated water captured by the HFTW system) is also anticipated to decrease as wells become more closely spaced. The most obvious reason for the vertical "short-circuiting" of flow induced by the HFTWs was the relatively small interval between the upper and lower screen of each well as well as the conservative assumption that each zone in the model was isotropic.

Based on the results of the initial modeling, it was determined that increasing the vertical separation distance between the screens of each HFTW was desirable. However, the geological and geochemical data on the upper portions of the aquifer were very limited. Therefore, additional site characterization work was undertaken to fully evaluate the lithology and contaminant concentrations within the upper portion of the aquifer. This site assessment work included the following: (1) rotosonic drilling to > 100 ft at two locations with complete core recovery and logging; (2) installation of nested piezometers with three completions within the rotosonic boreholes in regions of high conductivity, including particularly any shallow zones showing high conductivity; and (3) an additional pump test and specific slug tests to better define hydraulic conditions within the aquifer. The rotosonic drilling, core characterization and piezometer installation were completed in June, 2003. This work is described in Section 3.4.5. The pump and slug tests were completed in August 2003. These tests are described in Section 3.4.6.

Figure 3.4. (A) Pump Test Results with Modeling Data; and (B) Model Assumptions and HFTW Screen Placement.



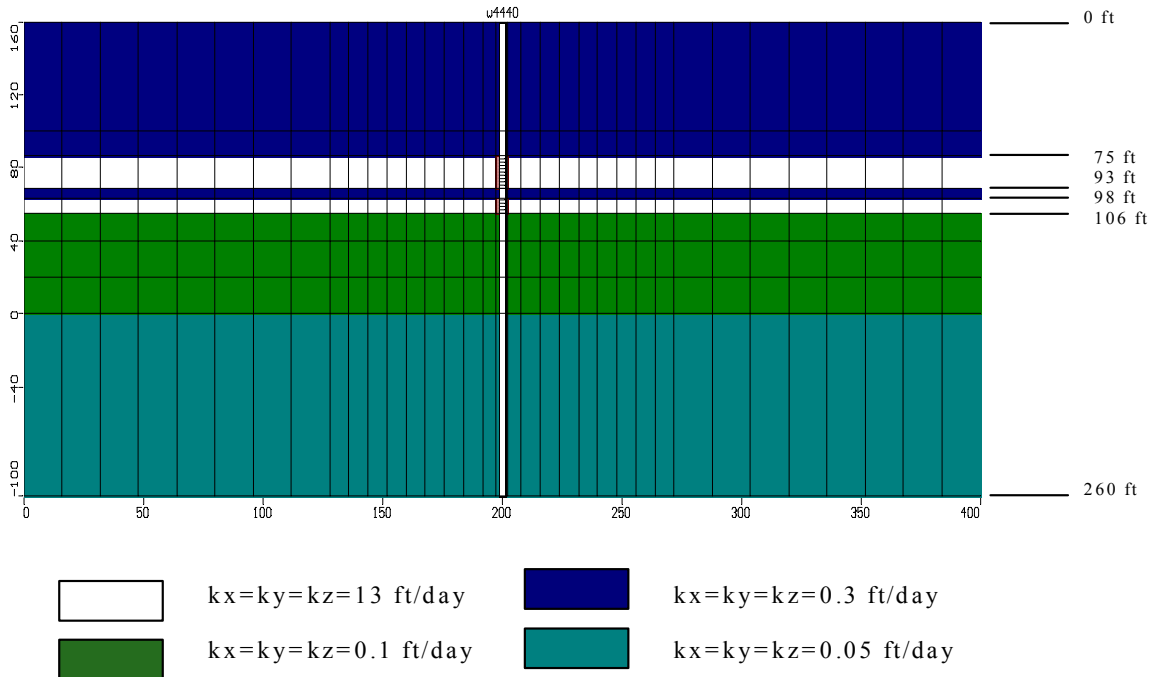


Figure 3.5. Model Simulation of the Capture Zone of HFTWs.

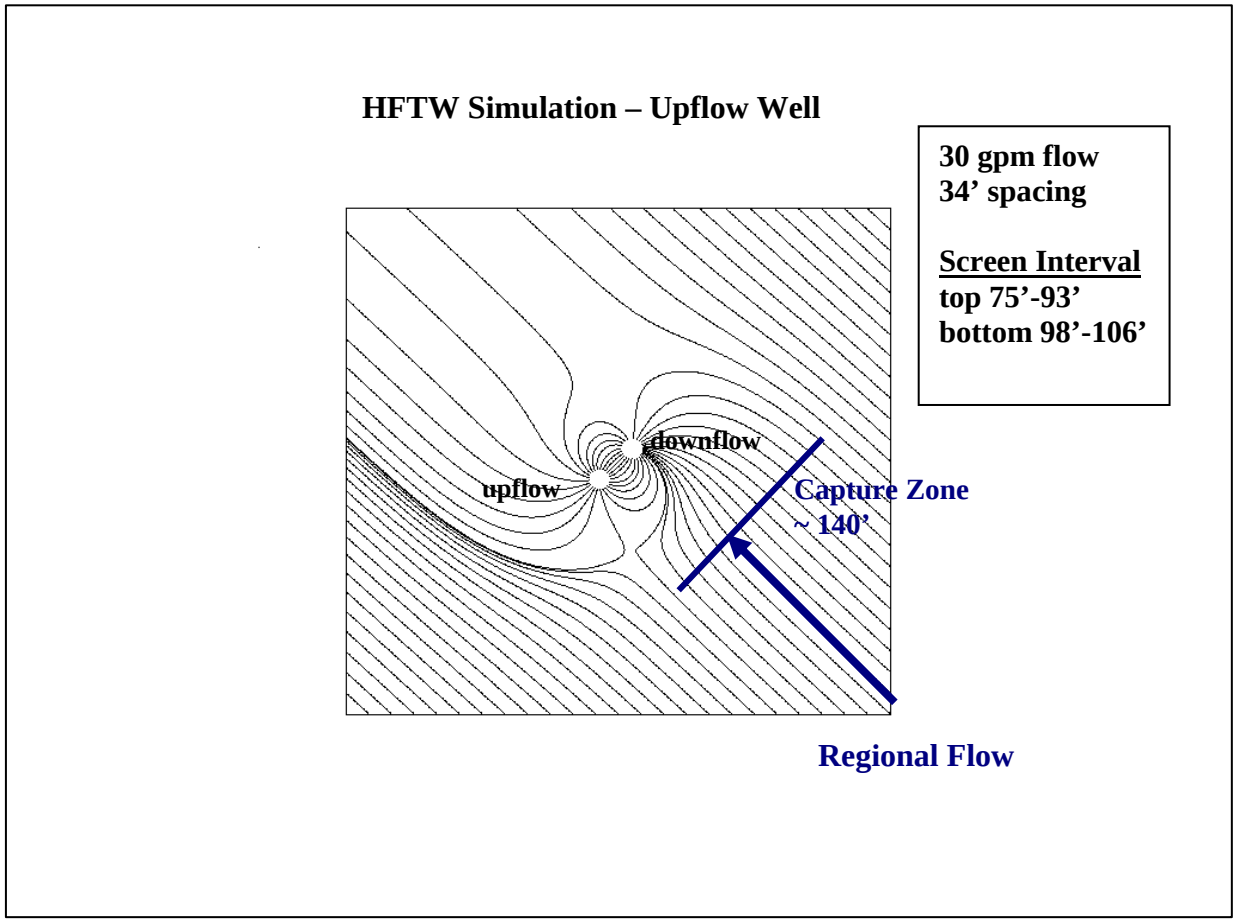
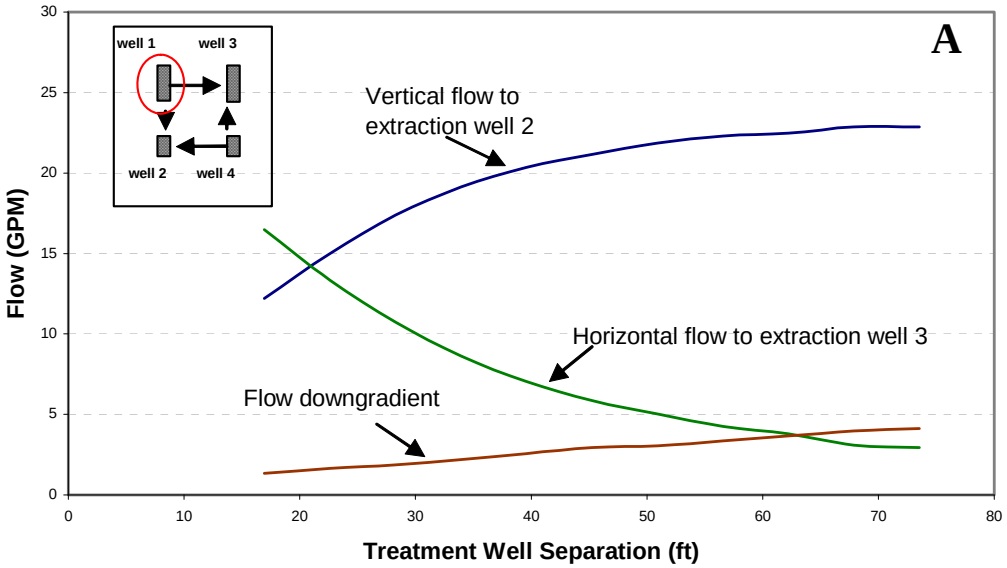
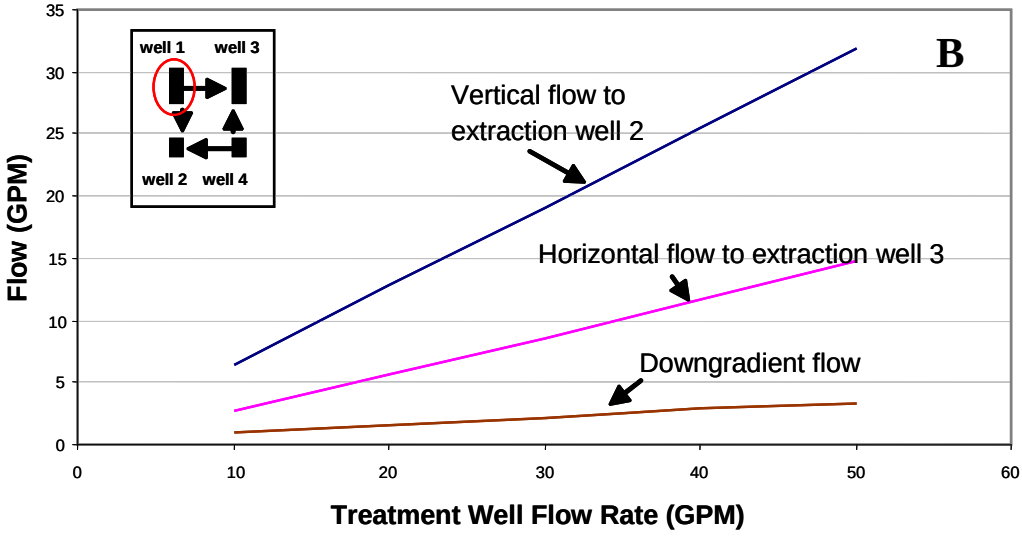


Figure 3.6. (A) Simulated Fate of Water Injected through Upper Screen of the Upflow Treatment Well (Well 1) at a 30 gpm Pumping Rate; and (B) Impact of Flow Rate on Simulated Fate of Water.





3.4.3 Biodegradation Microcosm Studies

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 is also being evaluated in these studies (ongoing). Sediments from the installation of well 3627 (from 40-42', 50-52', 60-62', 80-82', and 90-92') were homogenized and placed at 4^{o}C. These sediments were combined in 160-ml serum bottles with groundwater collected from Well 3519, then quadruplicate samples were amended with 3mM 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. A positive pressure of nitrogen gas was used to replace water during sample collection.

Nitrate levels 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 (Figure 3.7). Perchlorate levels declined in the same samples to below detection after approximately 15 days of incubation. Thus, both denitrifiers and perchlorate-reducing strains are present in the demonstration area, and these strains can be stimulated to degrade each contaminant to below detection. 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 is present in the site sediments (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 levels in bottles with citrate, acetate, and lactate were below detection. Perchlorate levels in bottles with no electron donor and those receiving formaldehyde to inhibit microbial activity remained near 4-6 mg/L (Figure 3.8). 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 levels in any of the active treatments (amended with electron donor) compared to the unamended or killed controls (Figure 3.9). 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 (Figure 3.10). This process should generate hydrogen to support reductive dechlorination. Similarly, acetate, formate, and propionate were detected in the citrate-amended samples, suggesting that fermentation was also occurring in bottles treated with this electron donor (Figure 3.11). This study was discontinued after 88 days.

Figure 3.7. Effectiveness of Different Electron Donors for Stimulating Biological Denitrification in Aquifer Samples from the Demonstration Area.

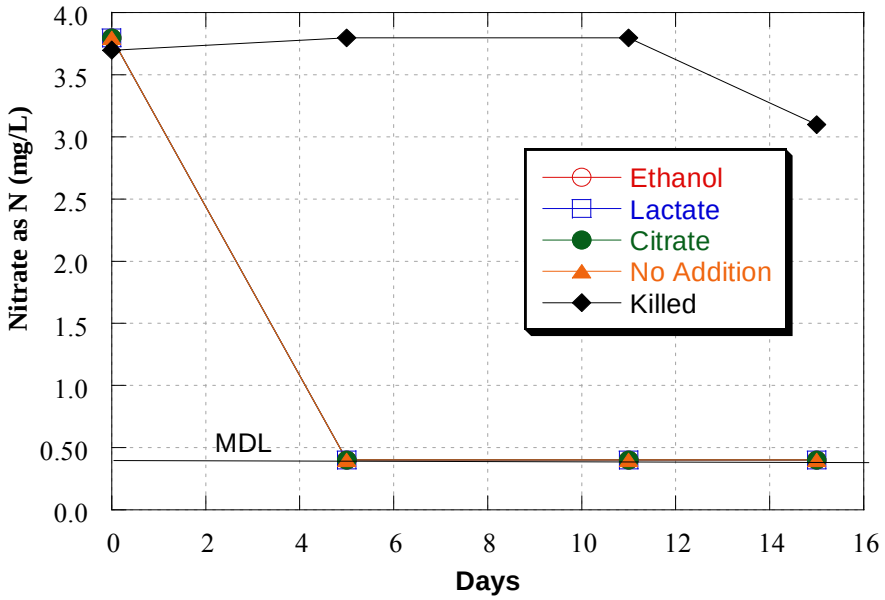


Figure 3.8. Effectiveness of Different Electron Donors for Stimulating Biological Perchlorate Reduction in Aquifer Samples from the Demonstration Area.

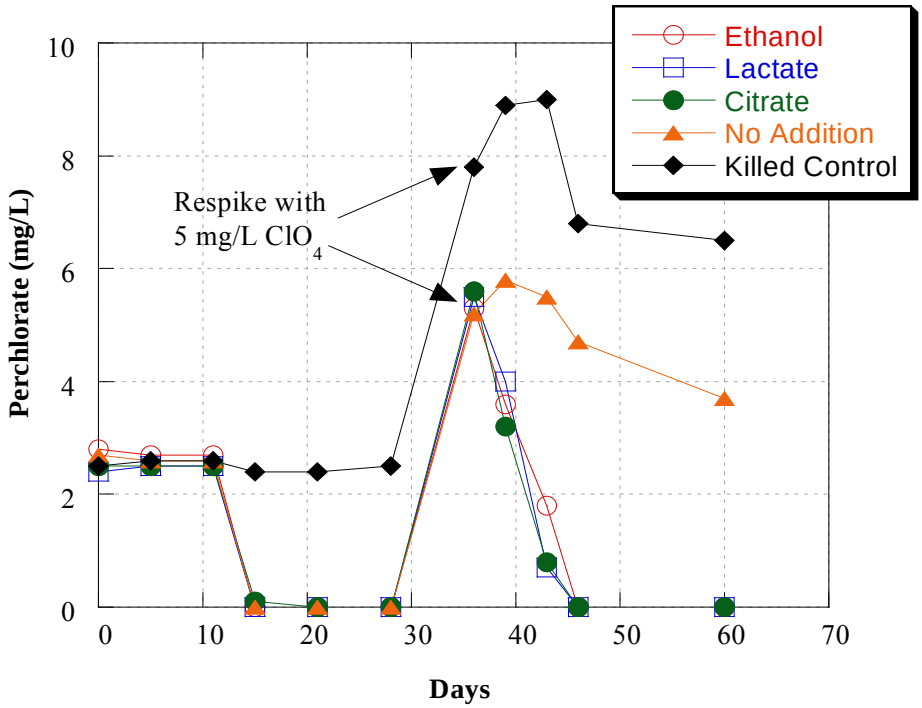


Figure 3.9. TCE Levels in Electron Donor Amended Microcosms.

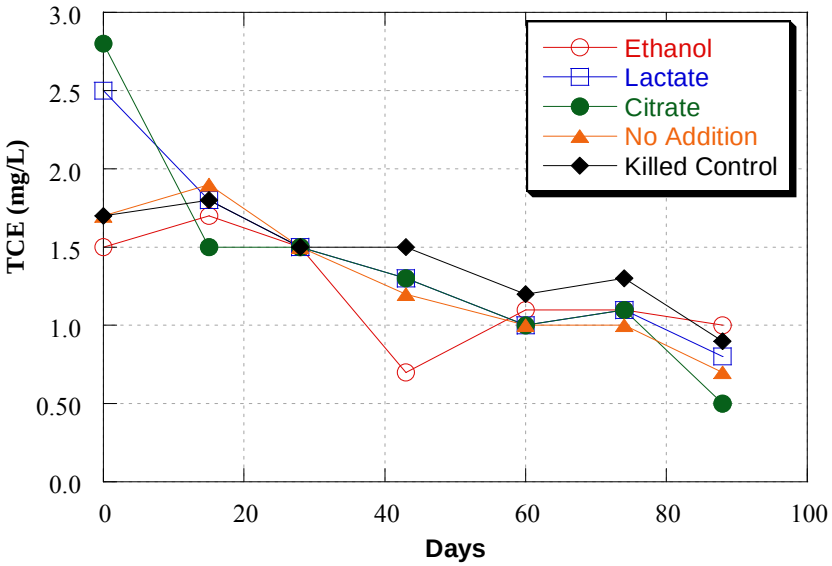


Figure 3.10. Fatty Acid Levels in Lactate-Amended Microcosms.

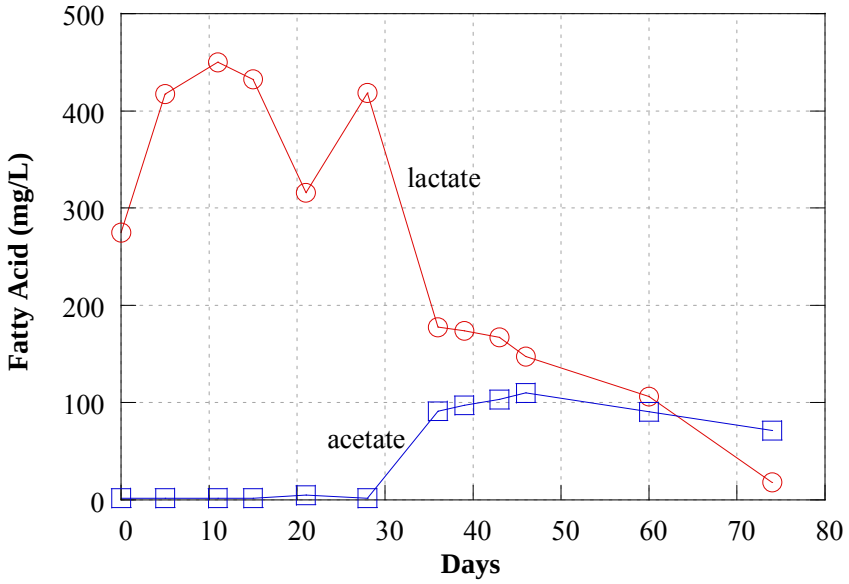
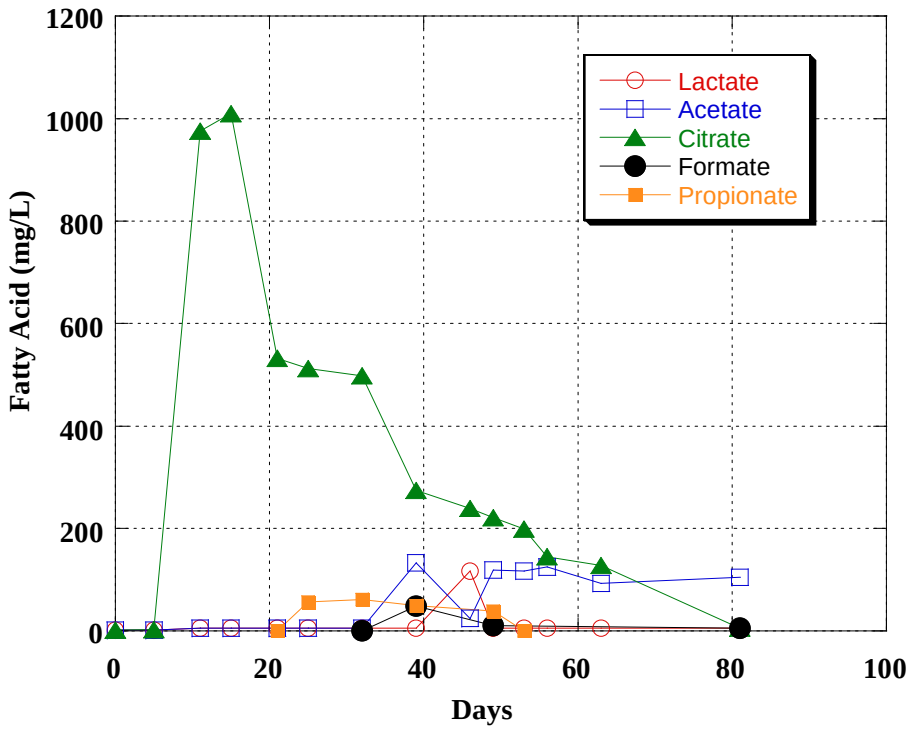


Figure 3.11. Fatty Acid Levels in Citrate-Amended Microcosms.



An additional microcosm study was set-up in an anaerobic chamber (Coy Environmental chamber with N_2 headspace) to look specifically at TCE degradation over a longer period of time. In this study, 16 g of homogenized Aerojet sediment and 55 mL of site water from Well 3519 was 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 levels 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 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 grown in mineral medium containing lactate as a carbon source and TCE as the sole electron acceptor. After growth to OD_{550} of ~ 0.5, the cultures were centrifuged and concentrated ten-fold to an OD_{550} of ~ 5.0. 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 suggest that bioaugmentation may be a viable strategy to reduce TCE concentrations in the demonstration plot.

3.4.4 Column Studies – Biofouling Control and Choice of Substrate

In addition to biodegradation studies, small-scale column studies were conducted in the laboratory of Dr. Eric Nuttall at the University of New Mexico (UNM) to simulate aquifer biofouling. Dr. Nuttall and graduate students designed laboratory columns to determine which electron donors promote the greatest extent of biofilm formation and to assess chemical and enzymatic methods to remove biofilms from the aquifer materials in the columns.

A schematic of the basic column system used to evaluate biofouling is shown in the Figure 3.12. Borosilicate columns of 15 cm length x 2.54 cm ID were initially packed with a washed sand (180 μm average diameter). The inlet and outlet ports at the end of each column were connected to a peristaltic pump and water reservoir using Nalgene tubing. A syringe pump was used to supply electron donors and/or biofouling

control and mitigation agents. A pressure sensor capable of measuring changes in the range of 0-30" of water was used to quantify biofouling effects within the column (i.e., increases in pressure across the column caused by microbial growth in pore space). The pressure sensor was interfaced with computer software to acquire the pressure readings from the sensor every 30 min. and record the data continuously on an Excel spreadsheet.

Containers, tubing and columns were washed with 75% solution of ethanol for sterilization. An artificial groundwater containing oxygen and nitrate as primary electron acceptors was fed into the columns at a fixed rate of 55 mL/hr, and electron donor solution was fed via the syringe pump at the rate of 1ml/hr. The electron donors tested to assess biofouling potential were ethanol, sodium lactate, sodium acetate, and sodium citrate. The quantities added were equalized on a stoichiometric basis. Pressure in the columns were measured as a function of time. The pressure in columns receiving ethanol, acetate, and lactate as electron donors each increased to > 30" of water within 5 d, which is indicative of rapid biofilm growth and pore plugging (Figure 3.13). Scanning electron micrographs (SEM) of the pure sand and the biofouled sand are provided in 3.14. The growth of biomass on the sand grains, and the subsequent reduction in porosity, is apparent in this SEM photo. In contrast to the columns with the three aforementioned electron donors,, the column that received citrate, appeared to foul much more slowly, reaching 30" of water only after nearly 13 days of operation. These data suggest that the rate of biofouling/column plugging with citrate as an electron donor is less than with the other substrates. Previous experiments showed that citrate is a suitable electron donor to promote the biological reduction of perchlorate at the Aerojet site (Figure 3.8). Thus, based on the reduced rate of biofouling, as well as the potential for citrate to act of a chelator of metals in the vicinity of the injection well screens (which is why it was initially selected as a potential electron donor), this fatty acid was chosen for use during the HFTW demonstration. The citric acid form, rather than sodium citrate, was used to reduce the quantity of sodium (and thus TDS) added to the aquifer, and to create acidic conditions in the vicinity of the injection well screen, once again removing any precipitated metals and potentially slowing the rate of biological growth. Additional details on electron donor choices are provided in Hatzinger et al. (2008).

A second series of column studies were conducted to determine effective methods to prevent and/or treat biofouling. In these experiments, a liquid chlorine dioxide solution (Oxine) was applied to columns receiving ethanol as a substrate. The columns received ethanol continuously, and then received either no Oxine (control) or 1 hr pulses of Oxine a 10 mg/L concentration. The pulse of Oxine was applied at 55 mL/hr via the syringe pump. The pressure across the column receiving ethanol only increased from ~ 2 to 30" of water in 6 days whereas the pressure in the column receiving the daily dose of Oxine remained < 10 " of water through this period, and showed no trend of increase (Figure 3.15). The data suggested that periodic dosing with Oxine (chlorine dioxide)

could be used as a preventative measure for biofouling. This approach was implemented in the field.

The final experiments conducted at UNM evaluated the potential for commercial enzymes to remove biomass, and reduce pressure drop, in the plugged sand columns. These studies employed the enzyme Pectinex Ultra, a multi-component pectolytic enzyme preparation produced by the fungus *Aspergillus niger*. The enzyme mixture contains protease and a wide range of carbohydrases, including pectinase, arabanase, cellulase, hemicellulase, beta-glucanase, and xylanase activities (Johansen et al, 1997). These enzymes are capable of hydrolyzing components of biofilms, particularly polysaccharides. Prior to addition of the enzymes, sand columns were fouled by treating for approximately 2 weeks with citrate at ~ 700 mg/L. After the pressure across the columns reached 30" of water, the substrate feed was discontinued for 10 h. The plugged column was then pulsed with 4 ml of Pectinex Ultra^{TM} dissolved in 9 ml of sample water and held for 48 h. The pressure was observed for next 10 h by keeping the column parameters in accordance with the values at time of plugging. In the untreated column, pressure remained near 30" of water, whereas in the column treated with the mixed enzyme solution, a pressure drop from > 30" to 8" of water was observed (Figure 3.16) The data indicate that the enzyme solution successfully penetrated and removed the biofilm, resulting in increased permeability of the sand column, and the resulting decrease in pressure.

In summary, the results from UNM indicate the following: (1) among several common organic electron donors citrate appears to promote the least rapid biofouling of sand columns; (2) a liquid solution of chlorine dioxide (Oxine) applied in 1 h daily pulses at 10 mg/L serves to appreciably reduce the potential for column fouling; and (3) application of a mixed enzyme solution (Pectinex Ultra) can be used to remove accumulated biomass from a sand column, resulting in increased permeability and reduced pressure across the column. Each of these laboratory findings were utilized during the field demonstration.

Figure 3.12. Schematic of the Apparatus used to Quantify Pressure Increase across a Sand Column.

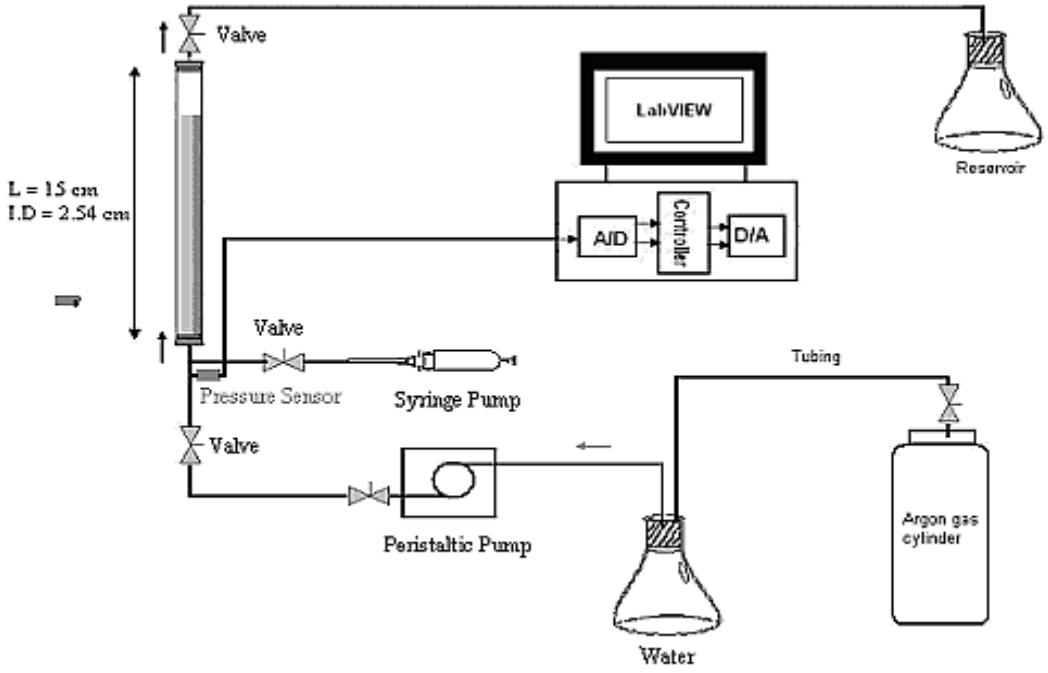


Figure 3.13. Pressure Increase Across Sand Columns Receiving Artificial Groundwater Amended with One of Four Different Electron Donors.

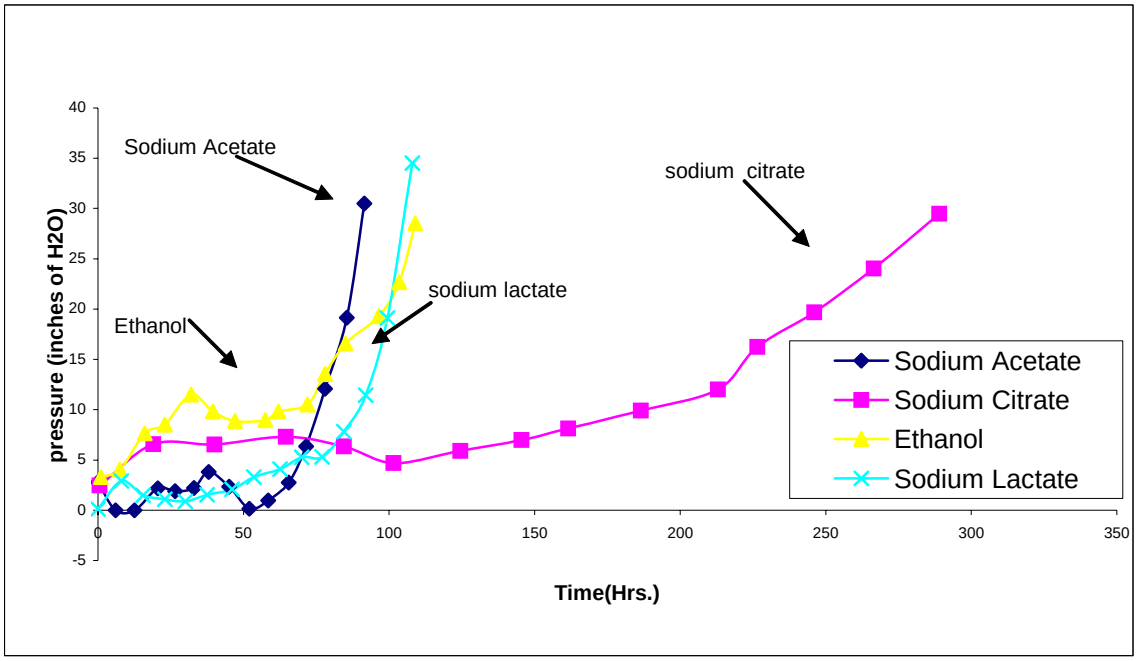


Figure 3.14. Environmental Scanning Electron Micrographs (SEM) of Sand Particles (A) Before and (B) After Column Biofouling. The magnification was 130X and the accelerating voltage was 20.0 KV.

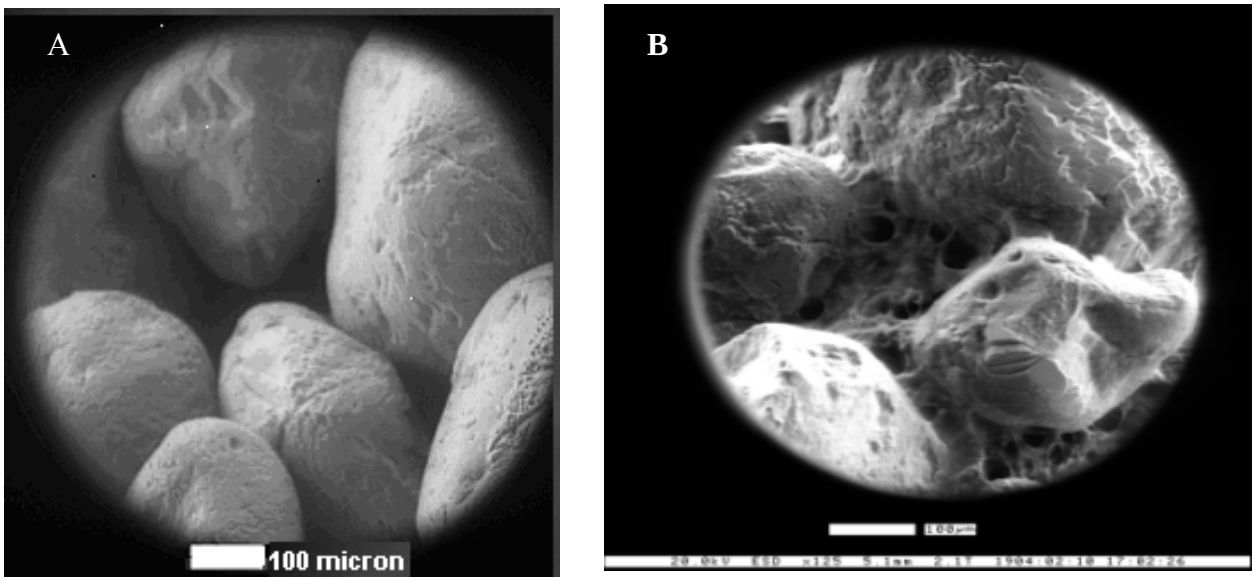


Figure 3.15. Influence of 10 mg/L Chlorine Dioxide Solution (Oxine) on the Pressure Increase across Sand Columns. The Oxine was pulsed into the column for 1 h per day.

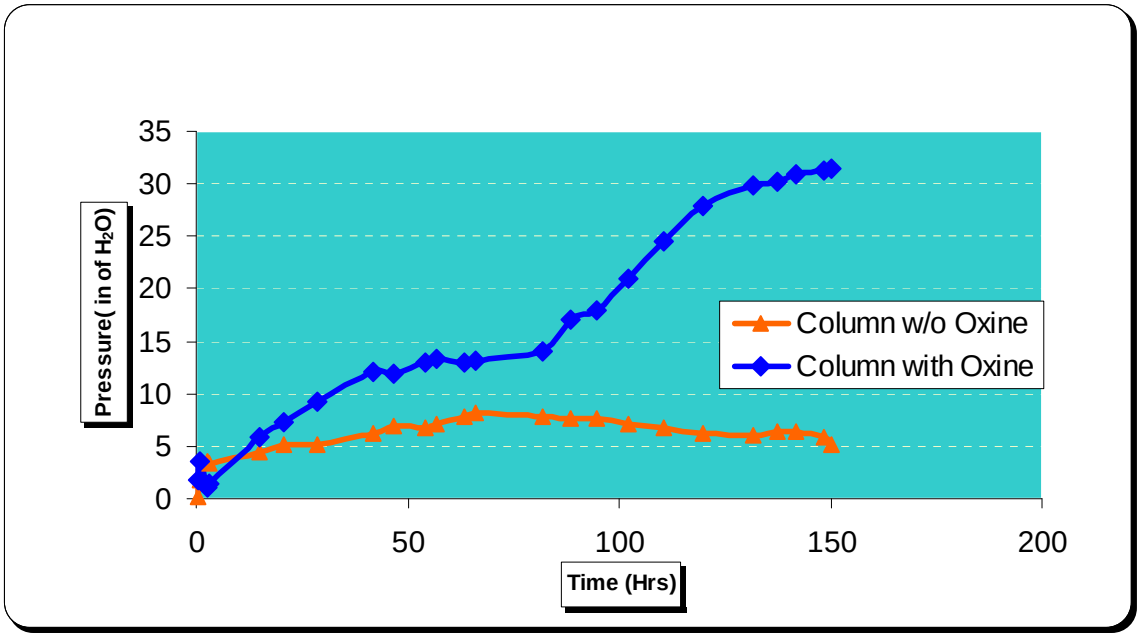
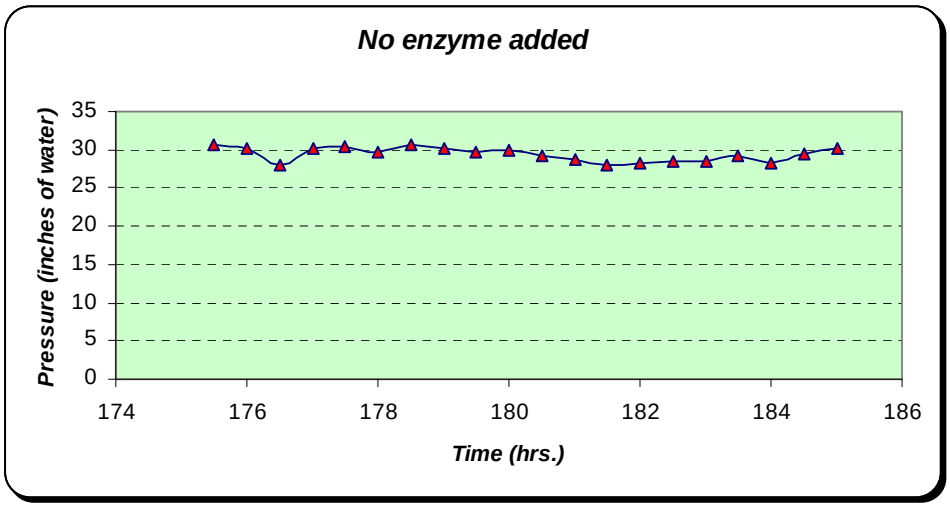
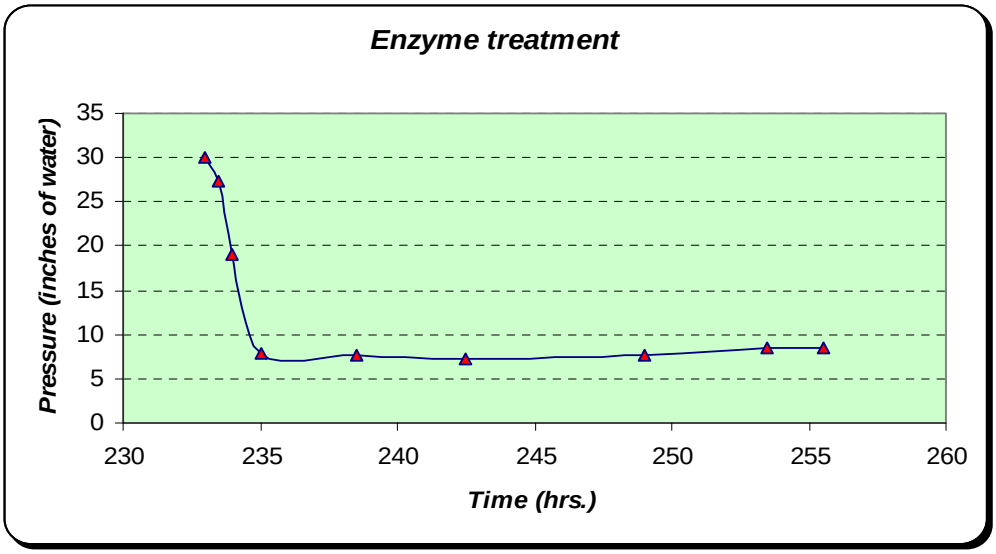


Figure 3.16. Influence of Pectinex Ultra Enzyme Treatment on Pressure in Biofouled Sand Columns. The enzyme was added to the column influent and allowed to soak statically for 10 h prior to reinitiating groundwater flow.





3.4.5 Additional Site Assessment and Piezometer Installations

As previously noted in Section 3.4.2, additional site assessment work was performed during June - August 2003. Two additional piezometer nests were installed in the vicinity of well 4440. Each of these piezometer nests contains three discreetly screened intervals to allow for monitoring of different aquifer zones. Rotary-vibratory drilling, also known as rotosonic drilling, was used to advance soil borings, collect soil samples, and install the piezometers (Figure 3.17). Rotosonic drilling is a dual cased drilling system, which utilizes high frequency mechanical vibration to drill through unconsolidated soils and bedrock. Using the specially designed hydraulically powered drill head, soil borings are advanced through fracturing, shearing, and/or displacement. Soils can be continuously sampled using a sonic core barrel. The core barrel is advanced ahead of the inner drill rods and collects a representative soil sample (usually in five-ft sections). The core barrel is removed and the soil sample is deposited into a plastic sleeve, stainless steel tray, or wooden core box. The core barrel is much wider than traditional split-spoon sampling tools, providing increased soil volumes. Adequate soil volumes allow field personnel to more accurately depict the stratigraphy and lithology of the soil formations.

Field personnel characterized soil samples in two-foot intervals using the Unified Soil Classification System (USCS). After the core barrel was removed and the soil sample was collected, an 8-inch outer casing was advanced down the borehole to the same depth. This sampling procedure and casing advancement was repeated until the desired boring depth was reached (~ 101' bls). The outer casing provides borehole stability and ensures there is no contamination from uphole material by sealing it off prior to each sample run. Once the desired borehole depth was reached, the inner drill rods and core barrel were removed.

The nested piezometers were installed using two 2-in and one 1-in inside diameter (I.D.) polyvinyl chloride (PVC) casings. The combination of casing diameters was chosen to allow for maximum use and versatility of the piezometer nests during future monitoring events while maintaining sufficient annulus to install a competent seal between the discreetly screened intervals. The piezometers were completed with 5-ft long 0.020 slotted casing sections. 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 3.18). Based on this field observation, the piezometers in this well were screened from 52 – 57 ft, 80 – 85 ft, and 96 – 101 ft bls. The designation of the three wells in sonic borehole # 1 are 3628, 3629, and 3630 going from the shallow to the deep completion. 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. In the second borehole, there was poor recovery of core material from 36 – 51 ft bls (Figure 3.19). This usually signifies a good water-bearing zone with saturated, unconsolidated materials.

This observation is reasonably consistent with the previous lithology in this region. 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 Demonstration Site. The designation of the three wells in sonic borehole # 2 are 3631, 3632, and 3633 going from the shallow to the deep completion.

The piezometer nests were completed by installing the screen and casing section for the lowest screen interval first. Filter pack sand (#3) was used to fill the annular space around the screen and 24" above and below the screen. Bentonite chips were then added via gravity to 24" below the next screen interval. The filter pack sand was then applied again from 24" below to 24" above the middle screen. The process was repeated until all three screened intervals had been installed. Upon completion of the filter pack sand associated with the upper most screen interval the annulus was filled with bentonite to within 24 inches of the ground surface. Above that, a concrete grout was poured. Depths were measured using a weighted tape measure once the outer casing was withdrawn past the area of interest. Each of the piezometer casings was extended to approximately 24 to 30 inches above grade. A 6-ft long, 10-in ID protective steel casing with a removable locking cap was installed over each piezometer nest. Casing tags were sealed to the outside of each piezometer casing to provide well identification during future sampling events.

Figure 3.17. Rotosonic Drilling at the Demonstration Site.

Figure 3.18. Lithography of Sediment Core from Borehole #1.

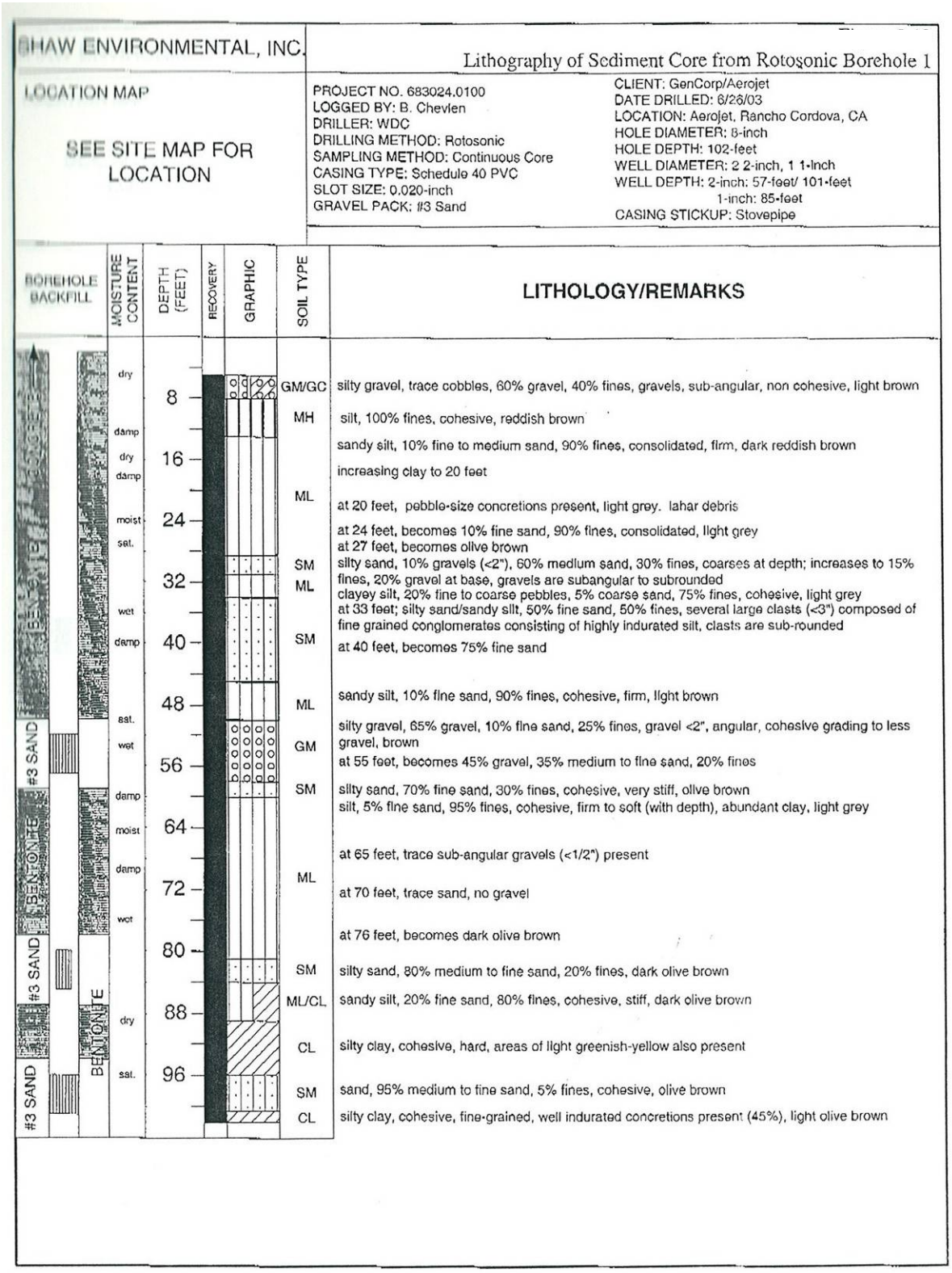
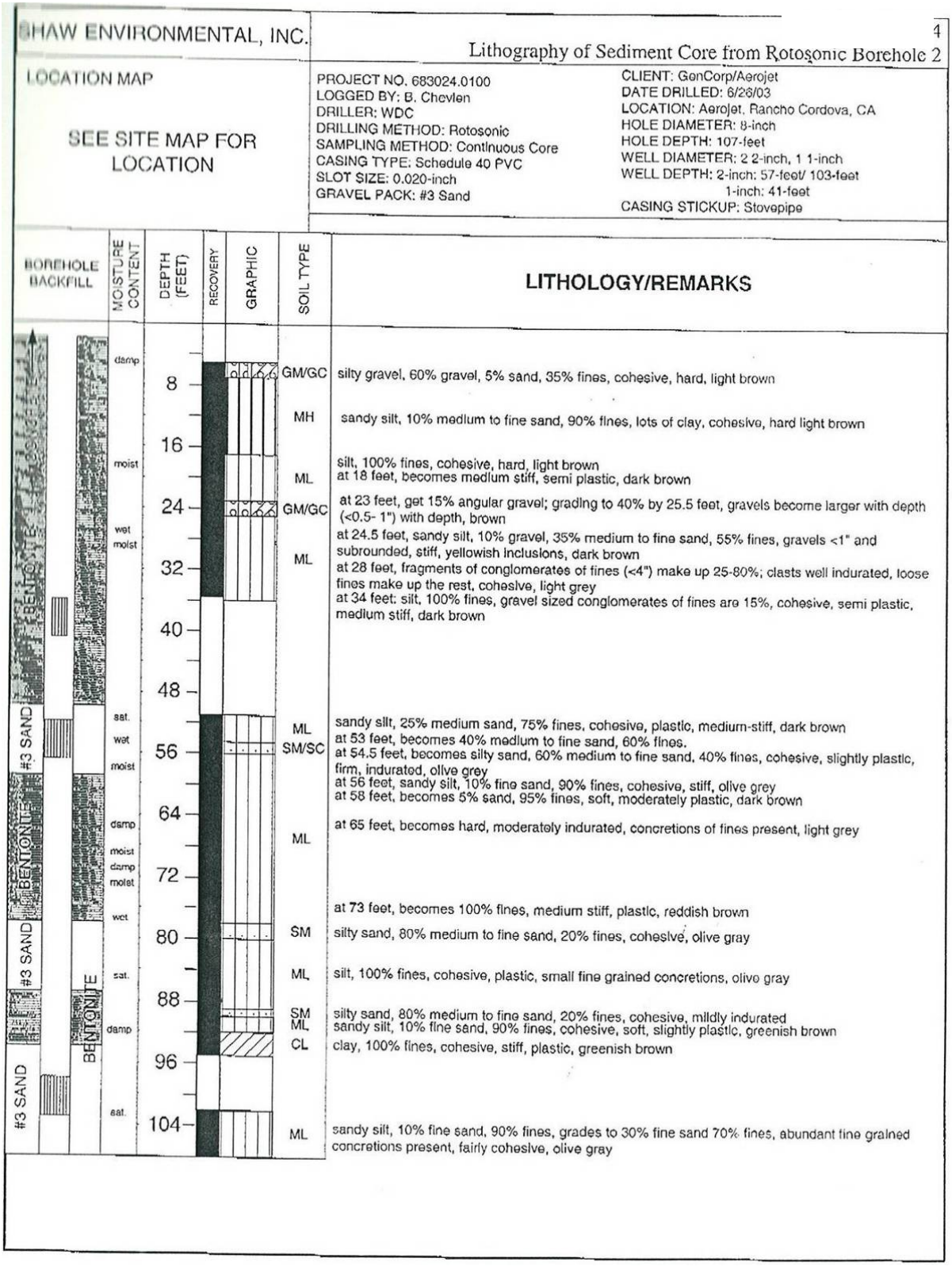


Figure 3.19. Lithography of Sediment Core from Borehole #2.



3.4.6 Additional Pre-Demonstration Activities

3.4.6.1 Groundwater Sample Collection

Groundwater samples were collected from the 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 volatile organic compounds (VOCs). The levels 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 3.3. The sample collection techniques used during this sampling event are described in Section 3.5.7. These baseline samples better establish the vertical distribution of perchlorate and co-contaminants in the demonstration area and aid in the selection of proper screen intervals for the HFTWs.

3.4.6.2 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 the pump testing. The stepped pumping method described in Section 3.5.2 was repeated during this test. Draw-down measurements were obtained using electronic data-loggers (trolls) from newly installed 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" piezometers (Wells 3628 and 3631). Slug testing was also performed on the newly installed 2-inch ID wells. The rate of water level decrease or increase was measured for both falling head and rising head tests, respectively. The rate of water level decrease or increase was measured using a pressure transducer and an electronic data-logger. Prior to placing any equipment in the piezometers, the initial water level was measured relative to the top of the piezometer casing, and the transducer was placed in the piezometer within the screened section or at a level that is within the pressure range of the transducer. The transducer was secured such that the slug could be added without allowing the transducer depth to change. After placement of the transducer, the water level in the well was allowed to equilibrate and the slug was placed and secured in the well casing above the water level. Once the water level was stable, slug testing was conducted.

To conduct the falling head test, the slug was instantaneously lowered into the water and the data-logger was activated to begin recording. Data were collected until the water level recovered at least 80% of the rise in water level caused by the slug. The data-logger was then set to begin recording the data for the rising head test. To conduct the rising head test, the slug was instantaneously removed from the water and the data-logger was activated. This test was performed until the water level recovered to the initial water level or until at least 80% of the fall in water level was recovered. After all of the tests were complete, the data were transferred electronically to a computer for formatting and

analysis. The data were then analyzed by the Bouwer and Rice slug test solution using commercially available computer software. The 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 (as described in Section 3.4.6.3).

3.4.6.3 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, 4-zone model. Layer depths and conductivities for the 15-layer site model are shown in Figure 3.20. 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. Figure 3.21 shows the goodness of fit of the model simulation to the draw-down data at Well 3633.

After completing the model calibration and validation, the multi-layer flow model was used to simulate the flow regime created by the pair of HFTWs. Early simulations focused on establishing the horizontal flow cells entirely within the lower water-bearing zone (75 to 105 ft bls). However, due to the potential for vertical short-circuiting between the upper and lower screens within the HFTWs, this design was abandoned. A revised design involving the use of the lower portion of the upper water-bearing zone (~ 46 to 61 ft bls) for the upper HFTW screens coupled with the entire lower water bearing zone for the lower screens (~ 80 – 100 ft bls) was subsequently selected for evaluation. The 15-layer, 4-zone site model was used to represent geologic and hydrogeologic conditions observed within the study area and to simulate groundwater flow between the HFTWs.

As previously noted, model simulations were performed assuming screen intervals for the HFTWs of 46 to 61 ft bls (shallow screen) and 80 to 100 ft bls (deep screen). Several model simulations were run to assess the impact of varying the spacing between the HFTWs and the pumping rate on the interflow ratios (i.e. short-circuiting of water between screens of the same HFTW). As shown on the interflow versus distance graphs, increasing the spacing between HFTWs results in a decrease in horizontal flow, an increase in farfield flow, and has very little impact on vertical short-circuiting (Figure 3.22). The interflow versus pumping rate comparisons indicate that increasing the pumping rate above 10 gpm has only marginal impact on the flow ratios (Figure 3.23).

Additional details concerning the modeled flow for the system are given in Section 3.6.3 *(Rate of Treatment/Expected System Performance Analysis).* Draw-down observations in model cells near the downflow HFTW indicated the potential for dewatering within layer 3 from 49.5 to 57 ft. Based on the observed draw-down and flow ratios associated with different spacing and pumping scenarios, a spacing of 34 ft (10 meters) and an initial pumping rate of 10 gallons per minute (gpm) (37.85 liters per minute) were selected. These design parameters also result in substantial capture of contaminated water from upgradient. Based on the streamline and tracer results obtained for each model layer, plume capture and treatment widths of approximately 175 ft and 120 to 145 ft have been predicted for the layers within the upper and lower treatment zones, respectively. Streamlines showing expected capture zones for each well within each of the 15 layers of the site model are provided in Appendix E. Bromide tracer simulations, which are described in the next section, are also provided in Appendix E. An additional discussion of groundwater capture and treatment is provided in Section 3.5.3.

Figure 3.20. Conceptual Model of Demonstration Site Aquifer Based on Rotosonic Logs and Pump Tests.

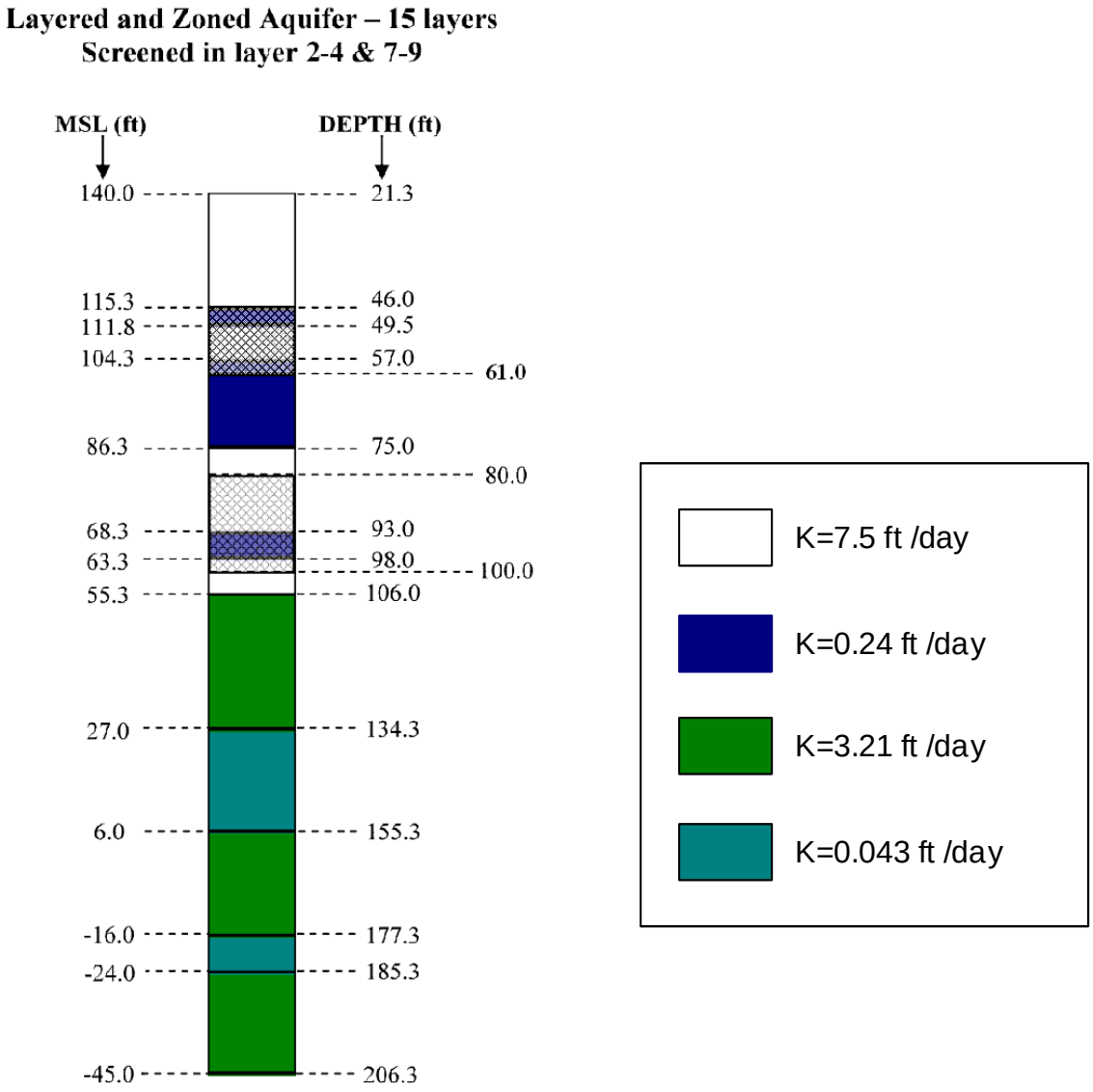


Figure 3.21. Goodness of Fit of the MODFLOW Simulation to the Pump Test Drawdown Data at Well 3633.

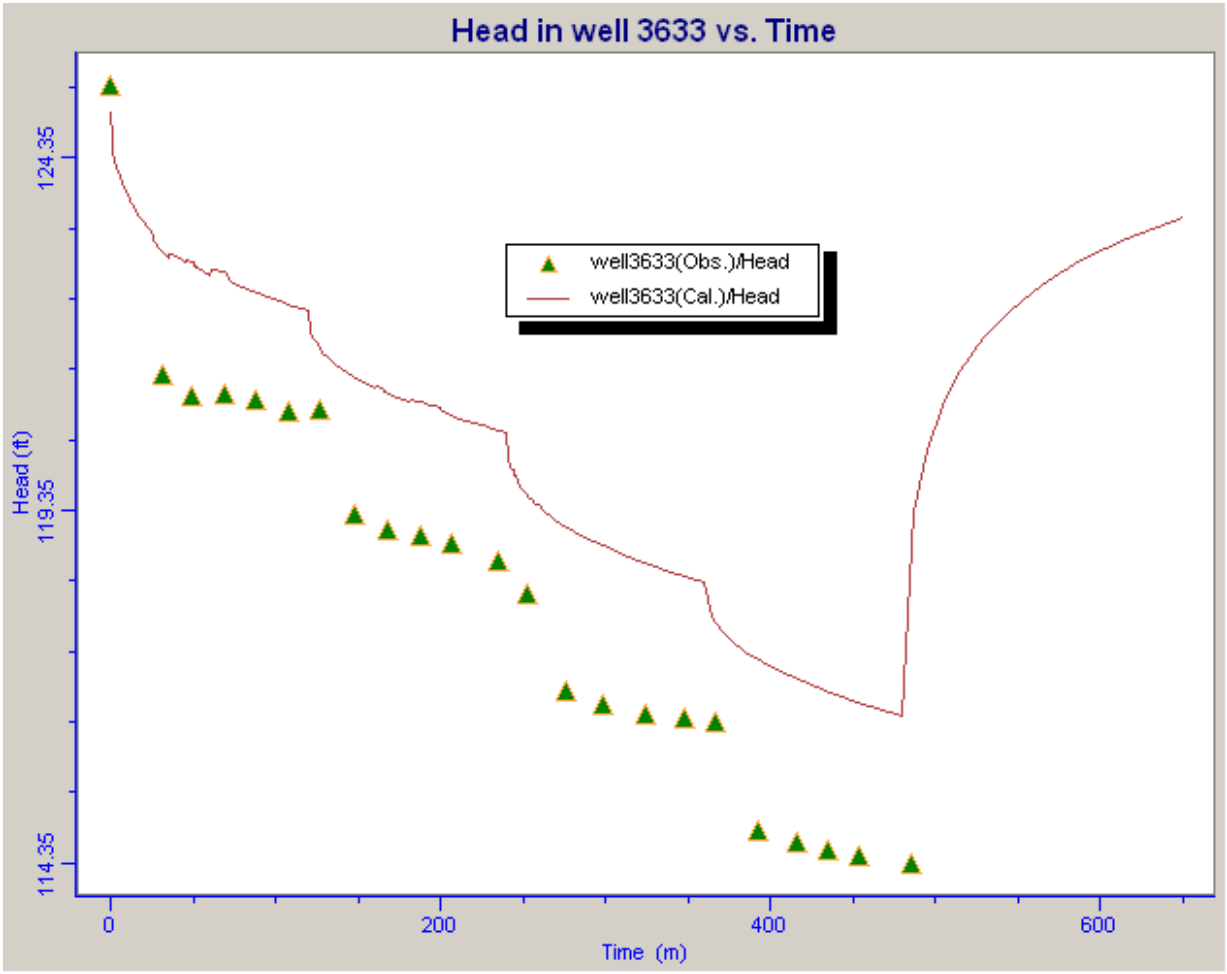


Figure 3.22. Model Simulation of Interflow vs. Spacing between the Paired HFTWs Pumping at 10 gpm.

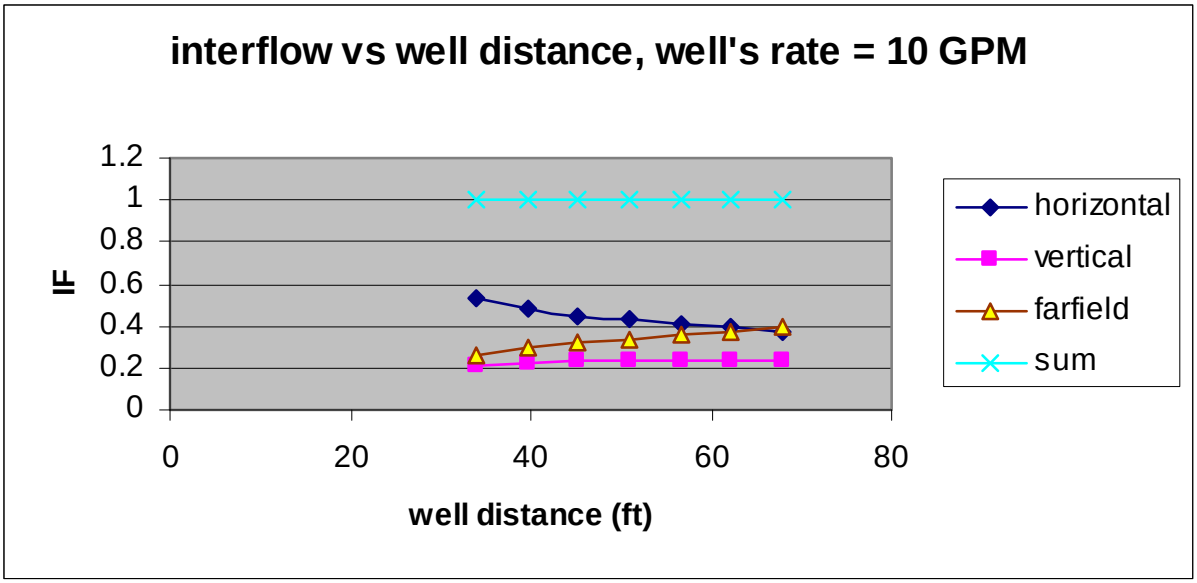
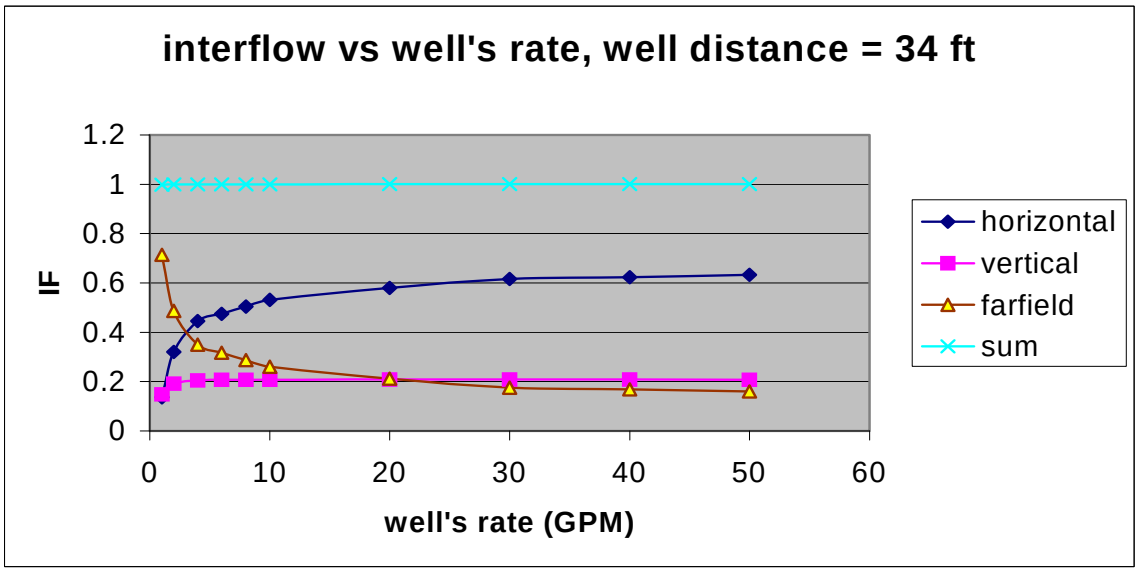


Figure 3.23. Model Simulation of Interflow vs. Pumping Rate with the Paired HFTWs Spaced at 34 ft.



3.5 Testing and Evaluation Plan

3.5.1 Demonstration Installation and Start-Up

3.5.1.1 Final Location of HFTWs and Additional Wells

The flow and tracer transport model was used to establish the final layout of the two HFTWs and nine additional monitor wells in the demonstration site area. Figure 3.24 provides a generalized plan view of the wells and Figures 3.25 – 3.27 provide cross-sections demarcating well screen intervals and interpreted geologic units. As shown on Figure 3.24, 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 following section (3.5.1.2). Two sets of monitor wells (NMW-1&2 and NMW-3&4 on Figure 3.24) 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 (Appendix E). These simulations are based on a continuous injection of a mass of 1 kg/day of bromide in the upper screens of the upflow HFTW (HFTW-U on Figure 3.24) and continuous injection of 1 kg/day of chloride into the lower screen of the downflow HFTW (HFTW-D on Figure 3.24).

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. The existing nine monitor wells found at the original six drilling locations in the demonstration area will be within 15 and 70 ft downgradient of the proposed HFTWs. With the exception of well 3631, screened between 36 and 41 ft bls, each of these wells is screened in either the upper or lower treatment zone layers.

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 two to three months of groundwater travel time. Figures 3.25 – 3.27 provide cross-sections depicting the interpreted geologic units (as used in the flow model simulations) and the basic well construction details. The graphic logs and well completion details for the existing borings/wells intersected by these cross-sections have also been included on these figures. Variations in layer depths and thicknesses can be seen when comparing the graphic logs to the geologic layer interpretations used for the model simulations.

Figure 3.24. Plan View of Wells in Test Plot.

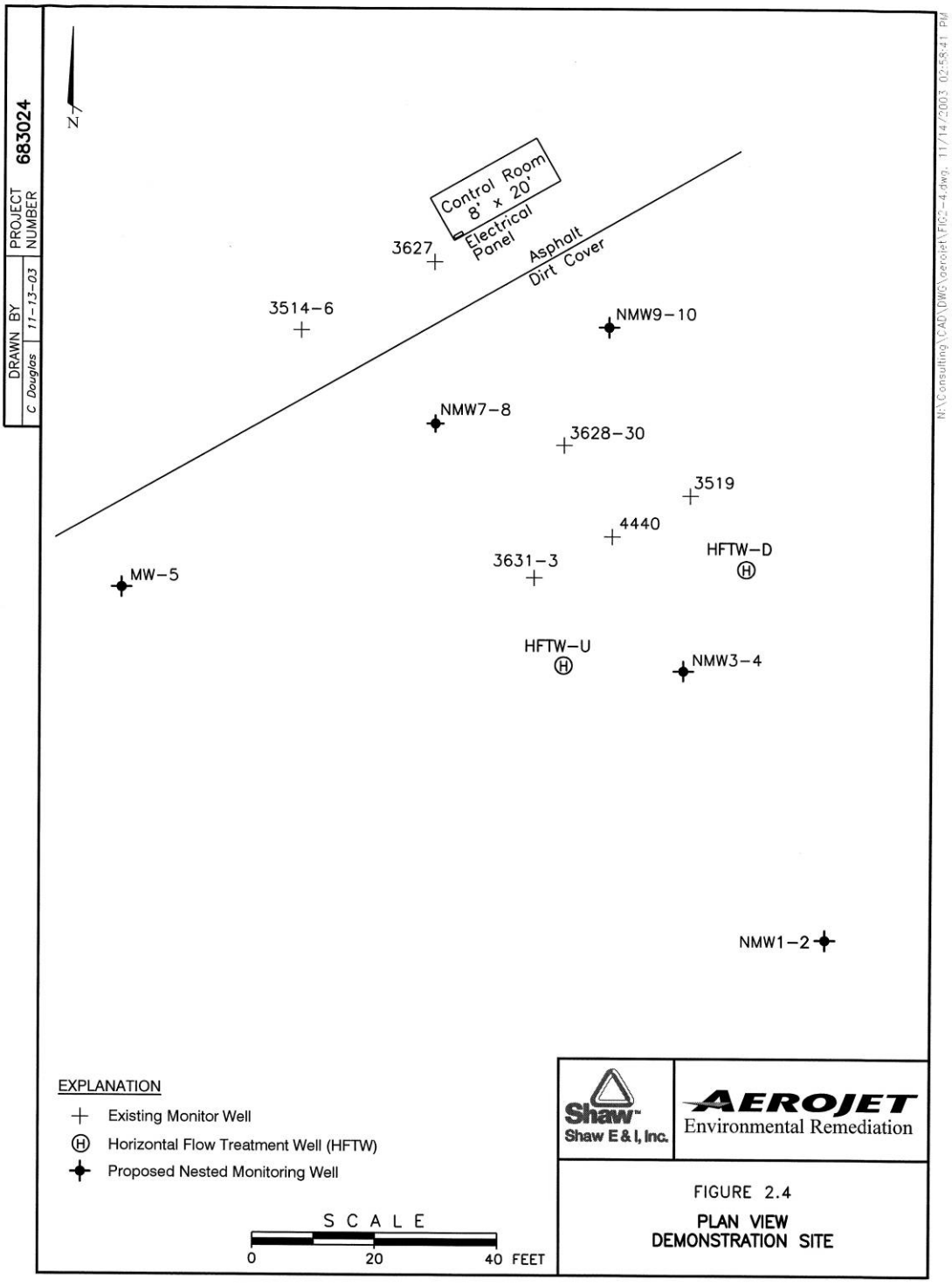


Figure 3.25. Cross-Sectional View (A-A') of Test Plot Wells Detailing Screen Intervals and Interpreted Geologic Units.

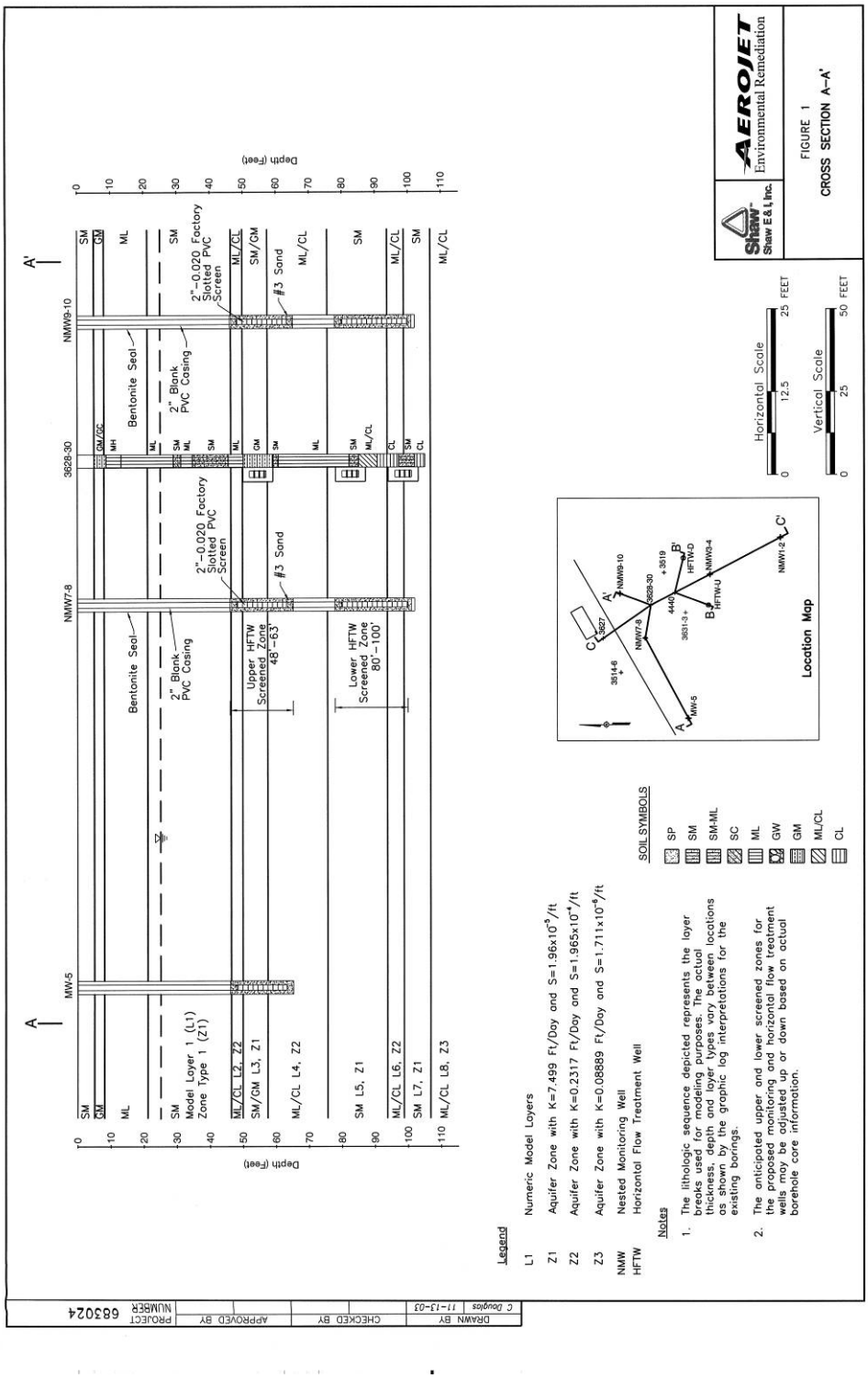


Figure 3.26. Cross-Sectional View (B-B') of Test Plot Wells Detailing Screen Intervals and Interpreted Geologic Units.

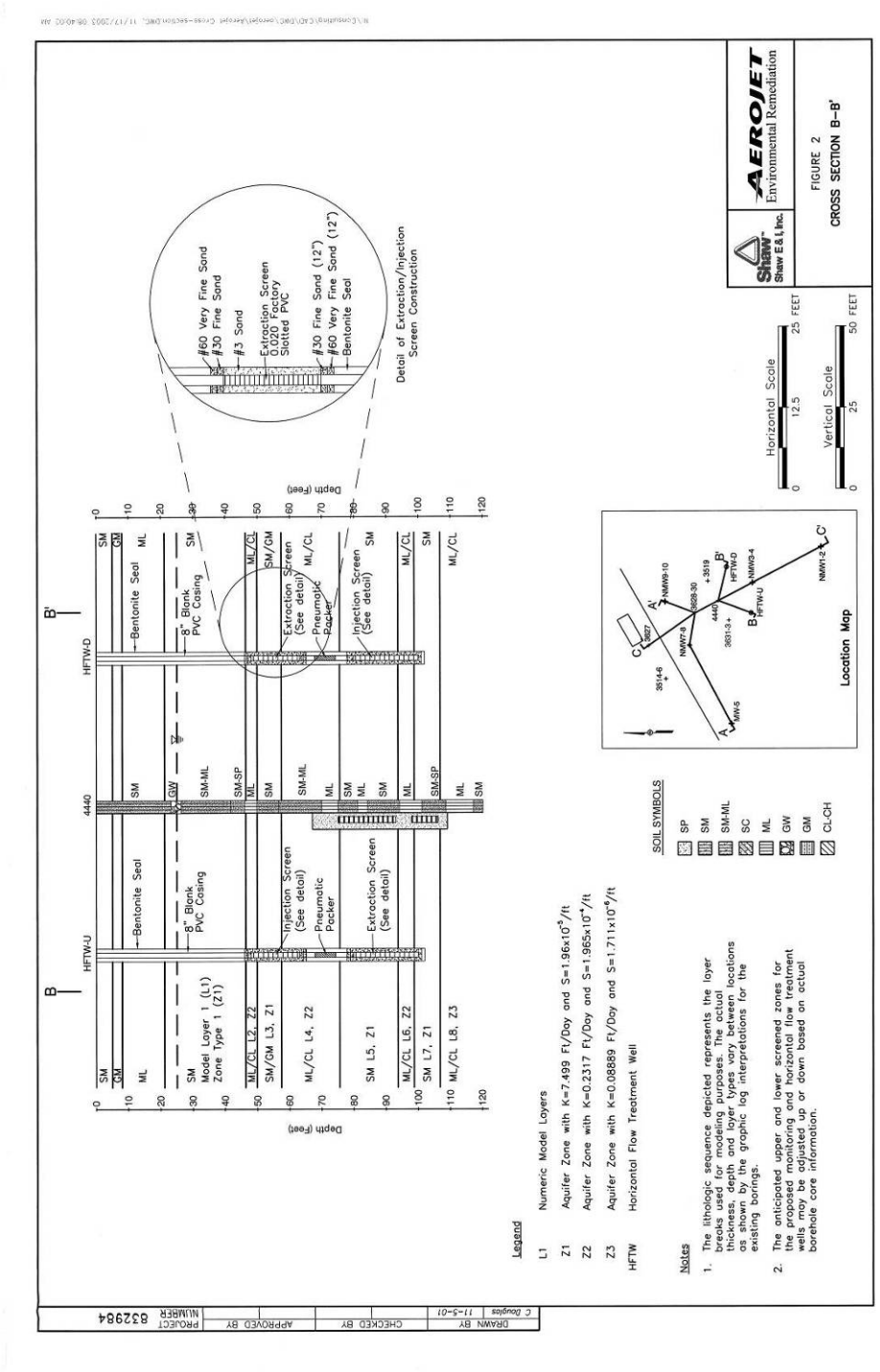
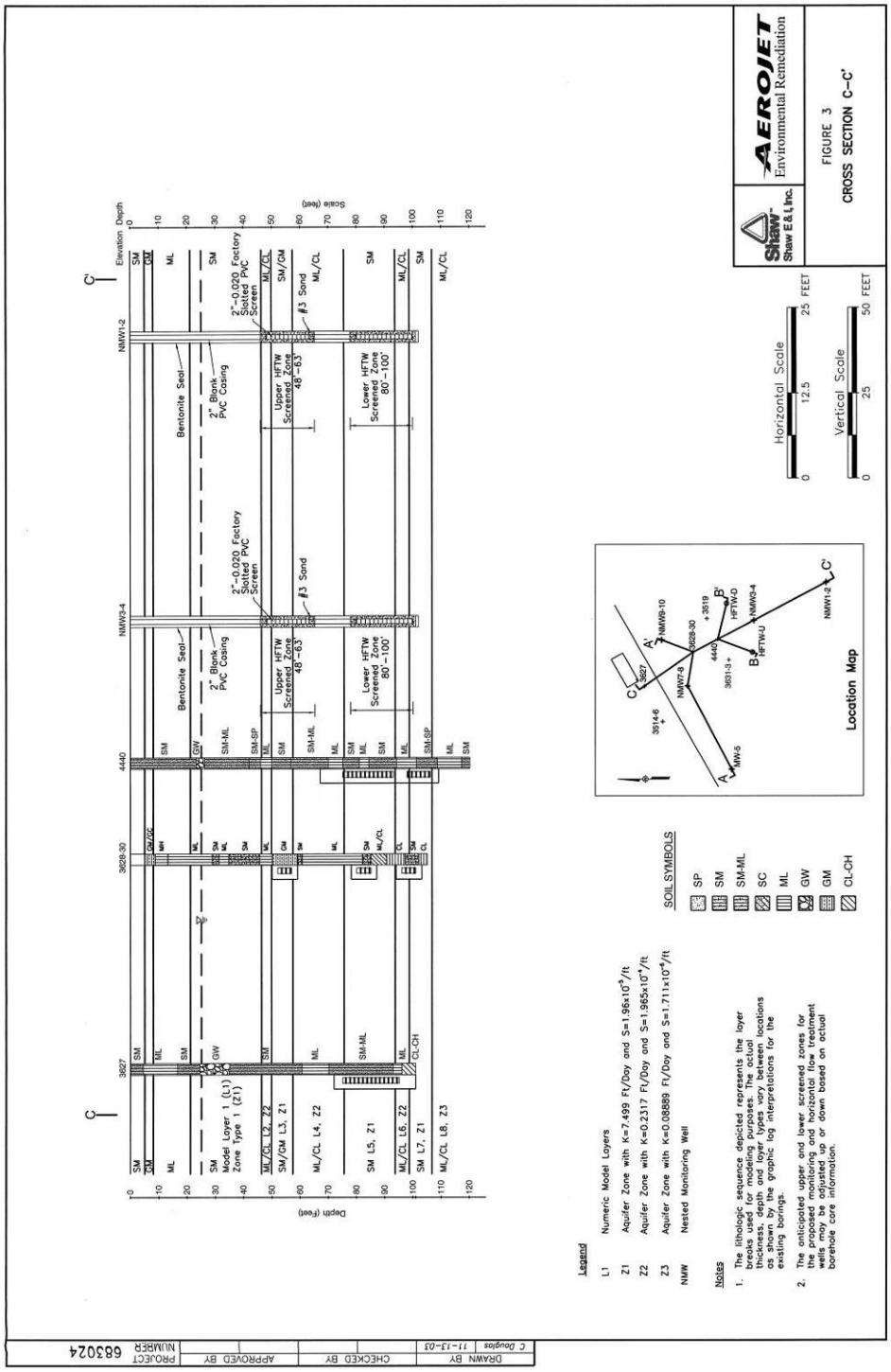


Figure 3.27. Cross-Sectional View (C-C') of Test Plot Wells Detailing Screen Intervals and Interpreted Geologic Units.



3.5.1.2 HFTW and Monitoring Well Installation

A California licensed driller (WDC Exploration and Wells, Woodlawn, CA) was contracted to install the HFTWs and remaining monitoring wells. All necessary permits were obtained prior to well installation and development. During installation, representative soil samples were collected for visual classification in order to verify the geologic data collected during previous investigative work at the site.

For the two HFTW completions, a dual-drilling technique was implemented. A rotosonic rig was initially used to drill down to ~ 100 ft bgs and to collect intact cores for geological assessment. The cores were characterized to ensure consistency with previous investigative work. The rotosonic pilot hole (~ 8 in) was then over-drilled and enlarged to 13-in diameter using an air-rotary casing hammer drilling method. Each well was then completed with 8-in I.D. PVC well casing and slotted screen sections (0.020 factory slot). Each HFTW had dual screen intervals. A 20 ft section of screen was installed at 80 – 100 ft bls and a 15 ft section was installed at 46 – 61 ft bls. The annular space was filled with a sequence of sand pack and bentonite seal. The sand pack consisted of coarse sand (#3) installed across each screened interval. A 12-in thick layer of fine sand (#30) was installed above and below the coarse sand pack. An additional 12-in thick layer of very fine sand (#60) was installed above and below the #30 sand (i.e., sand layers below the well screen consisted of 12 in of #60 sand, then 12 in of #30 sand, then #3 sand in the region of the screen). A mixture of bentonite chips and #30 sand was tremied into place to seal the annular space between the sand pack for the lower and upper screened sections for each HFTW. This material was also placed above the upper screen sand to within 24-in bls. Above that material, a concrete grout was poured. The casings for the HFTWs were extended to approximately 24-in above grade and were not covered with a protective casing to permit easy access to the wells during the system installation and operating period. The HFTWs were thoroughly developed by pumping at high flow rates in order to remove all fines prior to start-up. This development phase was critical to avoid clogging during water reinjection. All development water was collected in a Baker Tank, then treated for perchlorate by Aerojet using an existing biological treatment plant (passing through fluidized bed bioreactor system).

The remaining monitoring wells were constructed using 2-in inside diameter (I.D.) polyvinyl chloride (PVC) well casings and screens. The screens were 0.020 factory slotted. The basic installation protocol was as described in Section 3.4.5. In short, filter pack sand (#3) was used to fill the annular space around the screen in each well and 24-in above and below the screen. Bentonite chips were then added via gravity to 24-in below the upper screen interval (for nested completions). The filter pack sand as then be applied again from 24-in below to 24-in above the upper

screen. The annulus above the upper screen filter pack was then filled with bentonite to within 24-in of the ground surface. Above that, a concrete grout was poured. Depths of all fill materials were confirmed using a weighted tape measure once the outer casing was withdrawn past the area of interest. Each of the well casings was extended to approximately 24 to 30-in above grade.

After development, all monitoring wells were fitted with dedicated Waterra Inertial Pumps (Waterra USA Inc., Bellingham. WA). Each Waterra pump consists of dedicated tubing and a weighted one-way foot valve. The foot valves were lowered to the mid-screen level in each monitoring well. During sample collection, an electric jack pump was connected to the tubing in each well. The pump effectively moves the tubing up and down within the well such that the foot valve opens when the tubing is lowered and closes when the tubing is pushed downward. This action results in a slow, continuous flow of groundwater through the tubing. The technique is well suited to low-flow sampling, and was approved by the Regional Water Quality Control Board in Sacramento prior to use for the demonstration. This technology was recommended by personnel at Aerojet based on past field experience with the equipment.

3.5.1.3 System Design and Installation

A P&ID diagram showing the design of the two treatment wells and the associated equipment is provided in Figure 3.28. 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, 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 an 180^{o} angle to push water downward upon release, and to enhance mixing of water with amendments. In the downflow well, 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 (w/v) which equates to a 609 g citric acid/L) was injected directly into the re-circulation water piping (prior to the piping bend) within the well to blend the chemicals into the extracted groundwater.

A metering pump was used to supply citric acid to each well from the surface (P-103 A/B in Figure 3.28). 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 Figures 2.1 & 2.2). 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 system (SCADA) designed by Calcon Systems, San Ramon, CA. The SCADA, which was operated through a desktop computer at the site, allowed remote monitoring and control of the system through 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 onsite. 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 1,000-gal 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 a biofouling control agent (see Section 2.1.3). 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% 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-gallon holding tank (Figure 3.29). 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 programmable logic control system (PLC).

Figure 3.28 Piping and Instrumentation Diagram (P&ID) of the HFTW System.

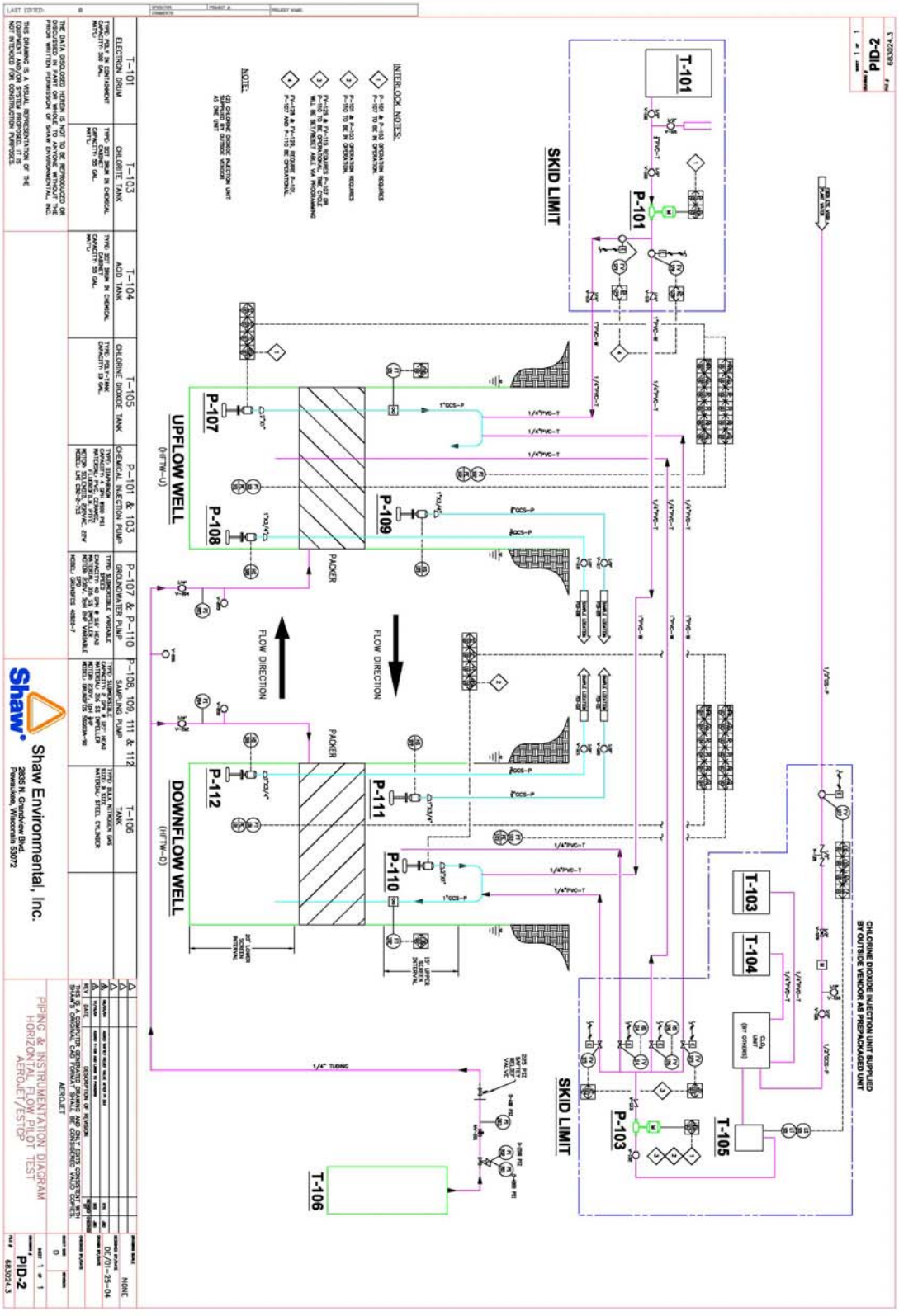
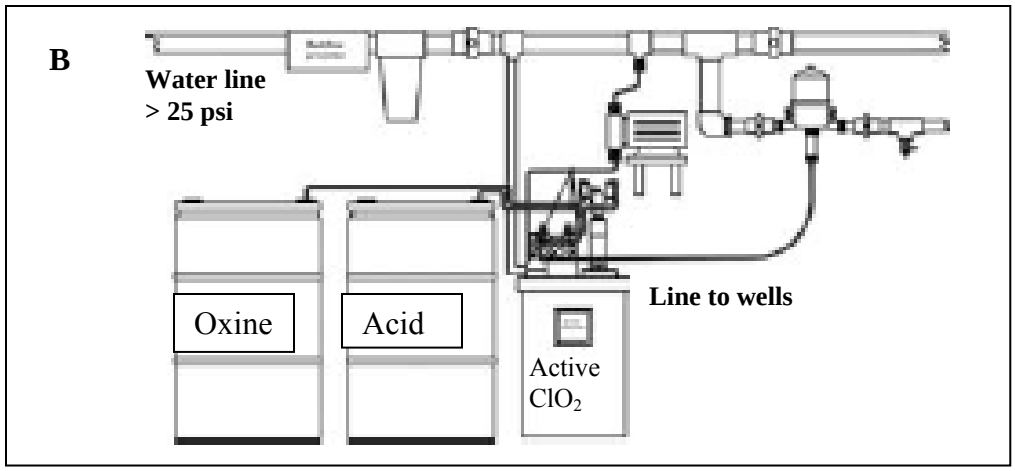


Figure 3.29. (A) Photograph of Bio-Cide AANE System and (B) Generalized Layout of AANE System with Acid Activator and Oxine Drums.



3.5.1.4 System Testing and Tracer Test Design

Once installed, the HFTW system was tested to insure proper operation of pumps and controls. During this process, steps were taken to simulate various operating and alarm conditions and all equipment and sensors were checked for proper calibration. The communication between the PLC and the various pieces of equipment and sensors were monitored to insure that all data was being communicated and logged accurately. Additionally, brief testing of the electron donor injection system was performed.

Initial operation of the upflow and downflow HFTWs was initiated on August 12, 2004. The pumps were initially started at a flow rate of 7 gpm each and continued to operate at these flow rates until August 30, 2004. Water levels were measured in several centerline wells screened within the upper and lower aquifer zones following approximately three hours of pumping. These measurements were compared to baseline levels collected on August 11, 2004. Based on these head responses, it was determined that some vertical leakage was occurring in the vicinity of the downflow HFTW (i.e., water moving from the upper to the lower screen). A similar condition was experienced during a previous demonstration of HFTW's at Edwards Air Force Base (Mark Goltz, *pers. comm*.). After running a series of tests to determine that the packer within the HFTW was fully inflated and free of obstructions, it was determined that the most likely source of leakage was the filter pack external to the well. The flow model developed by the Air Force Institute of Technology (AFIT) was used in conjunction with the hydraulic data to estimate the amount of vertical leakage. Based on the model scenarios, the flow within the two HFTWs was adjusted to account for the leakage. The target flow rates were initially established as 11 gpm and 7 gpm for the downflow and upflow HFTWs, respectively. This initial adjustment improved the system flow balance based on the reduction in the observed drawdown or mounding within the centerline wells. However, due to excessive drawdown in the upper region of the downflow HFTW, the pumping rates were decreased slightly to 9.3 and 6 gpm in the downflow and upflow HFTWs, respectively. This modification reduced the observed drawdown while providing a good flow balance between the two HFTWs. The wells were subsequently run for 6 weeks at these flow rates to allow mixing and the establishment of stable baseline conditions within the demonstration area prior to commencing electron donor addition. Tracer testing was also performed during this period (*see next section*).

As part of this initial task, a tracer test was performed in the test plot area to evaluate/verify local hydrogeologic characteristics, including seepage velocities, vertical distribution of groundwater flow, and dispersivity. The tracer test employed both bromide and chloride as conservative tracers. Separate solutions of sodium bromide (~ 20 g/L as bromide ion) and sodium chloride (~ 80 g/L as

chloride ion) were prepared in Neptune tanks supplied by Aerojet. The injection of the two tracer solutions was initiated on August 24, 2004. Chloride solution was injected into the downflow HFTW and bromide solution was injected into the upflow HFTW. Approximately 100 gallons of each solution was injected during a 30-day period in daily pulses in order to achieve the target dosing rate of approximately 1 kg chloride per day and 250 mg bromide per day (this value was reduced from 1 kg per day in order to minimize the quantity of bromide added to the aquifer to the extent possible). The injection of the tracer solutions was completed on September 28, 2004. During the tracer tests, a limited number of wells near the HFTWs were sampled several times during the first week. After that, all 19 monitoring wells were sampled at weekly intervals for bromide, chloride, nitrate, and perchlorate. During two of these events, VOCs, iron and manganese, and baseline fatty acid analysis was also performed. A field meter was used during each event to measure the conductivity, pH, dissolved oxygen, and redox in each well.

3.5.2 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 in Table 3.4. Phase I of system operation occurred from 10/28/2004 until 8/01/2005 (~ 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 assessment of 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 10/28/2004 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., 1 X stoichiometry). The equations and assumptions are provided in Section 4.4.1.7. 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 12/04/2004 (i.e., 3.0 L/well/day or 58 mg/L). The dosing in the downflow HFTW was increased further to 4X stoichiometry on 2/11/2005 (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 (8/01/2005; 275 Days) while various biofouling treatment strategies were tested (See Section 3.5.3). Thirteen groundwater sampling events were performed during the 9 months of Phase I operation (10/28/2004 – 8/01/2005).

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 of the HFTWs 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 2/15 – 2/17/2006, 45L 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 4/12/2006, and then this dosing was doubled between 4/17/2006 to 6/20/2006, by adding 15 L to each HFTW two times per week. Chlorine dioxide was added to each well on a daily basis (4 – 8 X per day) from 2/15 – 4/12/2006, then reduced to one dose only after citric acid injection from 4/12 – 6/20/2006.

A final mode of HFTW system operation (Phase III) was implemented from 9/11/2006 – 12/11/2006. 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-h pulses (followed by chlorine dioxide as a biocide), resulting in the addition of approximately 60 L of electron donor per 12-h 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 (9/6/2006) to provide a baseline, and a final round was performed on 1/15/2007. The system was shut-down at the end of 12/2006 after the final round of citric acid injection.

Table 3.4. Phases of System Operation

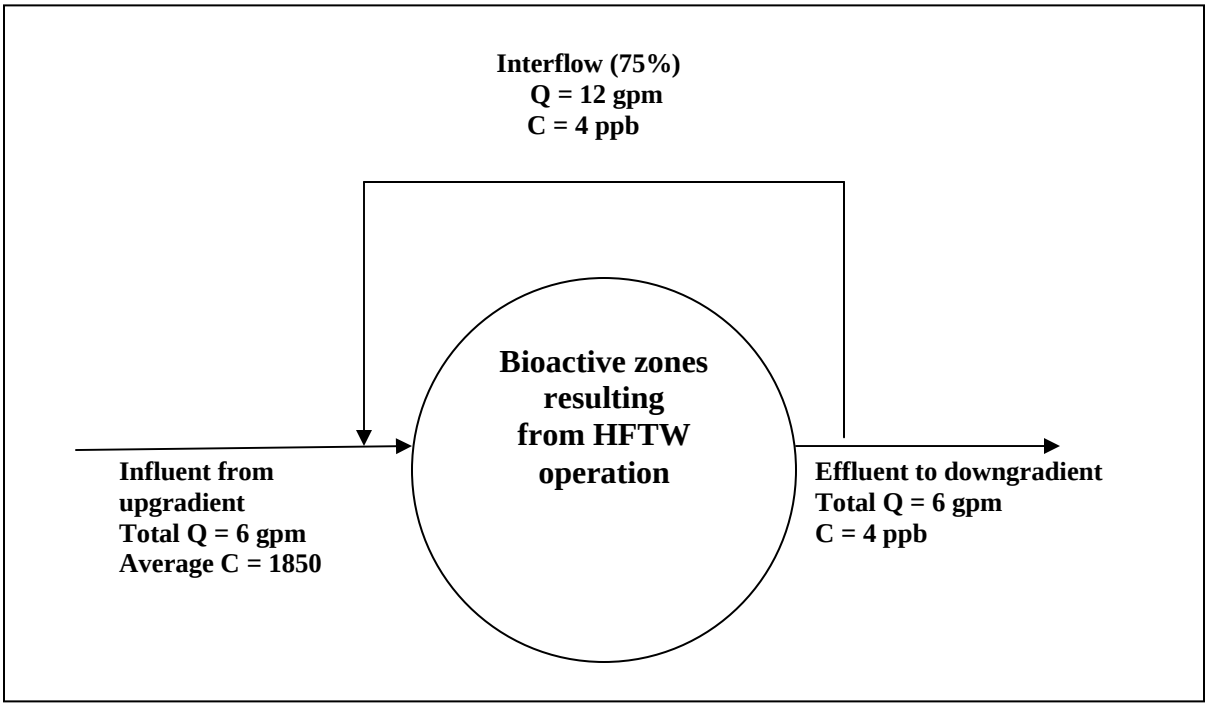
Testing Phases	2004		2005						2006					
	S/O	N/D	J/F	M/A	M/J	J/A	S/O	N/D	J/F	M/A	M/J	J/A	S/O	N/D
1) Tracer Testing														
2) Phase I Operation														
3) Biofouling Control Tests														
4) Rebound Period														
5) Well Develop/System Mod.														
6) Phase II Testing														
7) Phase III Testing														

3.5.3 Treatment Rate

A site hydrological model was formulated by inverse modeling of the data that were obtained from aquifer pump tests conducted in February and August 2003 (see Figure 3.21 and 3.22). Based on the model, flow simulations were used to estimate treatment rates for the two HFTWs. The simulated wells were screened at 46-61 and 80-100 ft bls, separated by 34 ft and each pumping at 10 gpm. The model simulations revealed that this design would result in ~ 75% interflow of water (55% horizontal, 20% vertical) between the two treatment wells (Figure 3.23). For the given design parameters, and assuming approximately 200 ppb perchlorate entering the upper screen of the downflow treatment well from upgradient, and about 3500 ppb entering the lower screen of the upflow treatment well from upgradient (see Table 3.3), approximately 0.111 pounds perchlorate would enter the system daily for treatment from upgradient, and over a year, approximately 40 pounds will have

entered the HFTW system for treatment. Figure 3.30 shows a conceptual model of the HFTW system as a recycle reactor.

Figure 3.30. Conceptual Model of the HFTW System as a Recycle Reactor.



3.5.4 Residuals Handling

All contaminated and treated groundwater remains in the subsurface with a HFTW system (i.e., no water is pumped above ground), so there was no residual water to treat during the demonstration. Water removed from the ground during pump tests was collected in a Baker tank, then sent to an onsite *ex situ* treatment facility consisting of fluidized bed reactors (for removal of perchlorate and nitrate) and an air-stripper for TCE. The treated water from this 5,000 GPM system is presently discharged to land surface.

3.5.5 Operating Parameters for the Technology

The HFTW system was designed for remote or onsite operation. Remote access was conducted via personal computer through a modem. For remote operation, a Supervisory Control and Data Acquisition (SCADA) system was accessed using PC Anywhere (Symantec Corporation) software. This program allowed remote monitoring and adjustment of system groundwater pumping rates, and the timing and length of citric acid and chlorine dioxide injection cycles. Pressures at each of the different well screens (4 total) were also monitored through this system. The

system controls were also accessible via a personal computer located within the utility trailer onsite.

The details of system operation (e.g., groundwater flow rates, citric acid quantities, biofouling control measures) were described in Section 3.5.2, and general phases of operation are outlined in Section 3.5.6 and Table 3.6. The system parameters that were measured included primarily groundwater flow rates in the upflow and downflow HFTWs, pressures at each well screen (4 screens total), length and duration of citric acid injection and length and duration of chlorine dioxide injection. Groundwater sampling events were conducted periodically during the various demonstration phases as detailed in Table 3.5. Groundwater was collected via low-flow sampling using dedicated Waterra Inertial sampling pumps (Waterra USA Inc., Bellingham, WA). When stable field parameters were obtained, groundwater samples were collected for analysis of the compounds described in Section 3.5.7, and detailed in Table 3.5. The analytical methods and Shaw E&I Analytical Laboratory SOPs for analysis of perchlorate (EPA 314.0), nitrate (EPA 300.0), VOCs (EPA 8260B), and VFAs (no standard EPA method) are provided in Appendix A.

3.5.6 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. As previously noted, Table 3.5 contains a list of contaminants that were measured during the demonstration. Analytical method details for perchlorate (EPA 314.0), nitrate (EPA 300.0), VOCs (EPA 8260B), and VFAs are provided in Appendix A. A complete "Control Plot" was installed during a previous demonstration performed at the Indian Head Naval Surface Warfare Center to compare perchlorate levels and overall geochemistry in monitoring wells receiving electron donor and those receiving no amendment (Hatzinger et al., 2006). In the case of this demonstration, the cost of installing two plots (including two sets of HFTWs) was determined to be too high due to drilling and material costs. To evaluate system performance in this demonstration, levels 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 3.24 – 3.27). For experimental purposes, the levels of perchlorate and co-contaminants in the monitoring wells are 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.

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). This document is provided as Appendix F to this report. 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. The presence of competing electron acceptors (oxygen and nitrate) serves to decrease the rate of perchlorate reduction. This is modeled using an inhibition coefficient that slows the rate of nitrate reduction if oxygen is present and slows the rate of perchlorate reduction if either oxygen or nitrate is present. The rate of microbial growth is a result of the consumption of the growth substrate (the electron donor) less biomass decay, which is modeled as a first-order decay process. Kinetic parameters for the model were estimated based on laboratory batch and column studies conducted during SERDP Project ER-1163 and published by Farhan and Hatzinger, (2009).

Table 3.5. Parameters Measured During Groundwater Sampling

Parameter	Method/Procedure	Preservative	Bottle Size
Nitrate	EPA 300.0	4°C	100 mL[1]
Sulfate	EPA 300.0	4°C	100 mL[1]
Chloride	EPA 300.0	4°C	100 mL[1]
Bromide	EPA 300.0	4°C	100 mL[1]
Dissolved Manganese	EPA 200.7	0.45-µm cartridge filter; Nitric Acid	250 mL[2,4]
Dissolved Iron	EPA 200.7	0.45-µm cartridge filter; Nitric Acid	250 mL[2,4]
Volatile Organic Hydrocarbons	EPA 8260	Hydrochloric Acid	40 mL VOA
Perchlorate	EPA 314.0	Sterile 0.22-µ m syringe filter	50 mL sterile[3] screw-cap tube
Volatile Fatty Acids	EPA 300.0m	Sterile 0.22-µ m syringe filter	50 mL sterile[3] screw-cap tube
Redox Potential	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.

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. The details and objectives of these three phases were provided in Section 3.5.2, and outlined in Table 3.4. Sampling events are provided in Table 3.6. A summary of the experimental goals of each phase of testing are provided below

1. Background sampling & tracer testing: All wells were sampled 5 times after the HFTW operation commenced on 8/12/2004 but prior to the initial injection of electron donor on 10/28/2008 (See Table 3.6). 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

8/30/2004) to evaluate and verify local hydrogeologic 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 samples for these salts during the reminder of the background testing phase (5 more sampling events) .

2. Phase I of system operation occurred from 10/28/2004 until 8/01/2005 (~ 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 9 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 4/24/2005 (Table 3.6). The latter period in Phase I was used to test various enzymatic and chemical treatment strategies to move biomass from the HFTW well screens.

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 (enzyme treatment, citric acid treatment, and physical rehabilitation) 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 2/28/2006. 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 (4 – 8 X per day) from 2/15 – 4/12/2006, then reduced to one dose only after citric acid injection from 4/12 – 6/20/2006.

4. Phase III of system operation was implemented from 9/11/2006 – 12/11/2006. 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-h pulses during the active period resulting in the addition of approximately 60 L of electron donor per 12-h 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 (9/6/2006) to provide a baseline, and a final round was performed on January 15, 2007.

Table 3.6. 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 and Cl 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
Phase III	9/6/2006	677
	10/11/2006	712
	11/28/2006	760
	1/8/2007	801

3.5.7 Sampling Plan

A comprehensive and accurate performance evaluation of the biostimulation pilot test depends on obtaining a complete, representative, and consistent data set chronicling the results of the demonstration. The data must characterize the original contaminant concentrations and distribution, the amount and rates of contaminant removal, and any residual contamination. The Sampling Plan presented in this section specifies the sampling location, procedures for collecting samples, the sample chain of custody procedures, and the packaging, labeling and shipping procedures that were used during the demonstration.

Sampling activities supporting the demonstration included two primary phases: pre-demonstration sampling, which included site characterization and background sampling, and demonstration sampling, which included start-up testing, performance optimization and long-term monitoring and sampling. Field methods and procedures include sample collection methods, disposal methods, equipment decontamination, sample labeling, sample preservation, sample packaging and shipment and sample documentation. This section describes the data collection and analysis methods that were performed during the HFTW electron donor technology demonstration. The Sampling Plan provides a discussion of the selection of the laboratory and analytical methods, sample collection, and experimental controls. The Sampling Plan was carried out in general accordance with the Quality Assurance Project Plan (QAPP) (Appendix C).

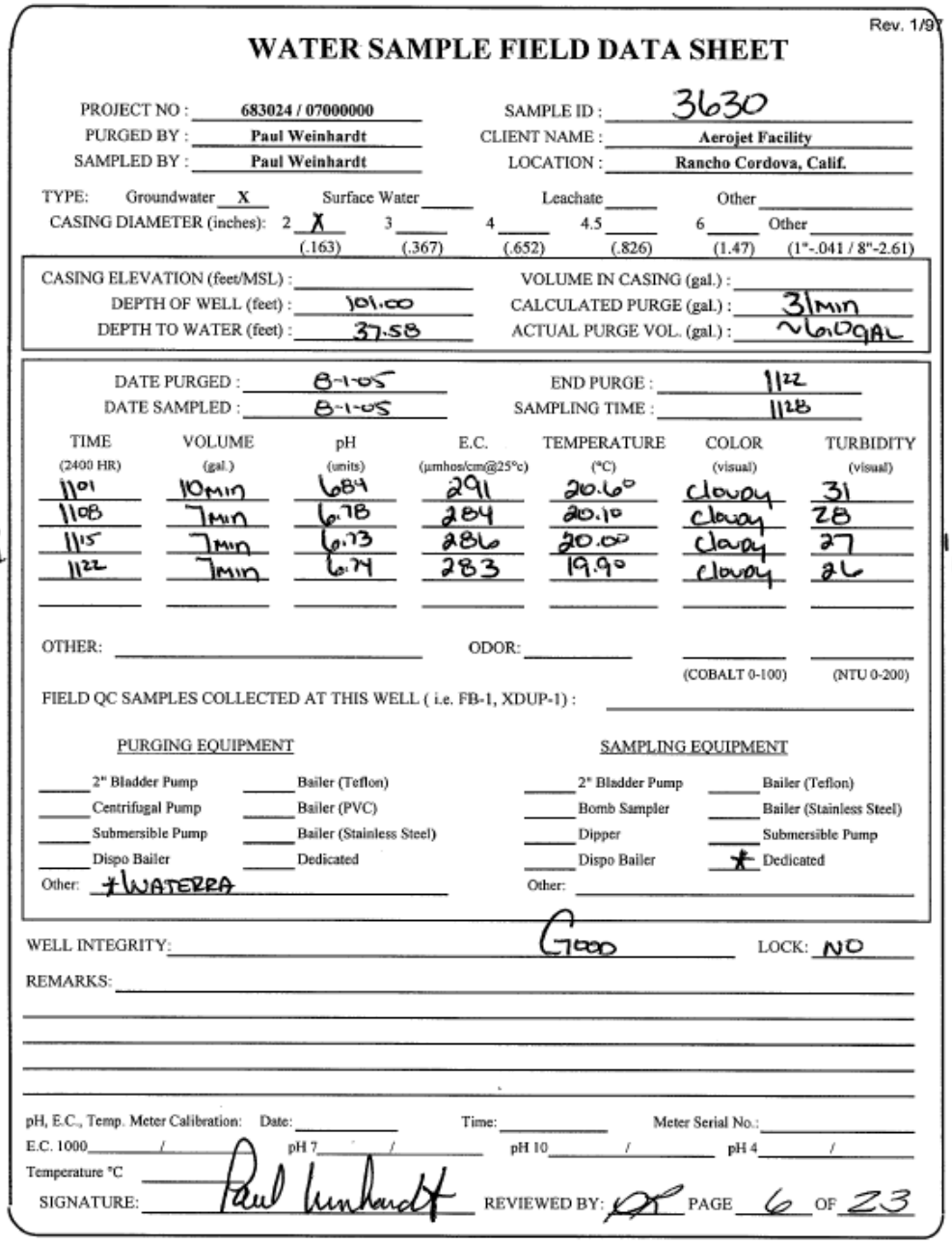
3.5.7.1 Well Purging and Field Geochemical Parameters

A total of 24 sampling events were conducted during the nearly 30-month demonstration (background monitoring, Phases I-III), including 5 baseline events, 2 additional sampling rounds for bromide and chloride, 9 Phase I events, 4 Phase II events and 4 Phase III events (Table 3.6).

Groundwater samples were collected from the Test Plot monitoring wells in general accordance with USEPA Region 9's "Standard Operating Procedure for Low Stress (Low Flow) / Minimal Draw-down Ground-Water Sample Collection" (Appendix B). Groundwater samples were collected using Waterra Inertial Pumps as detailed in Section 3.5.1.2. Groundwater pumped with the Waterra system was collected in a cell for field measurement of geochemical parameters, including pH, Eh, temperature, turbidity, oxidation-reduction potential (ORP) and dissolved oxygen (DO). YSI or equivalent field meters were used to analyze parameters. All field meters were calibrated once at the beginning of the day and checked periodically throughout the day to determine if re-calibration was required. Groundwater samples were submitted to the Shaw Environmental and Infastructure's Analytical Laboratory in Lawrenceville, NJ for analysis of VOCs (EPA Method 8260), fatty acids (by in-house IC method), anions (EPA Method 300.0), and perchlorate (EPA Method 314.0). Total iron and manganese analysis (EPA Method 200.7) were performed by ChemTech, Mountainside, NJ as a subcontract to Shaw. Key analytical methods/SOPs are described as Appendix A to this document.

During groundwater sampling, the field technician was required to maintain accurate records. A "Water Sample Field Data Sheet" was completed for each well during each sampling event, as exemplified in Figure 3.31. This sheet includes all pertinent information regarding the sampling of each well, including the Well ID, the sampler name and date, the general well characteristics, the depth to water prior to pumping, the purge time and total purge volume, the geochemical parameters at several times during well purging, and any general comments concerning the sampling event. The final set of field parameter measurements on each field sheet are the stabilized values that are entered into the data spreadsheet for the project. Groundwater sampling was conducted at each well immediately after the final set of stabilized measurements was recorded. The field technician is required to review and sign all field sheets at the end of the sampling event to ensure accuracy.

Figure 3.31. Example of a Completed Field Sheet Used to Record Well Sampling Data.



Rev. 1/97

WATER SAMPLE FIELD DATA SHEET

PROJECT NO : 683024 / 07000000 — SAMPLE ID : 3630
PURGED BY : Paul Weinhardt — CLIENT NAME : Aerojet Facility
SAMPLED BY : Paul Weinhardt — LOCATION : Rancho Cordova, Calif.

TYPE: Groundwater X Surface Water ____ Leachate ____ Other ____
CASING DIAMETER (inches): 2 X (.163) 3 ____ (.367) 4 ____ (.652) 4.5 ____ (.826) 6 ____ (1.47) Other ____ (1"-.041 / 8"-2.61)

CASING ELEVATION (feet/MSL) : ____ — VOLUME IN CASING (gal.) : ____
DEPTH OF WELL (feet) : 101.00 — CALCULATED PURGE (gal.) : 3 Min
DEPTH TO WATER (feet) : 37.58 — ACTUAL PURGE VOL. (gal.) : ~6.0 GAL

DATE PURGED : 8-1-05 — END PURGE : 1122
DATE SAMPLED : 8-1-05 — SAMPLING TIME : 1128

TIME (2400 HR)	VOLUME (gal.)	pH (units)	E.C. (µmhos/cm@25°c)	TEMPERATURE (°C)	COLOR (visual)	TURBIDITY (visual)
1101	10 Min	6.84	291	20.60°	cloudy	31
1108	7 Min	6.78	284	20.10	cloudy	28
1115	7 Min	6.73	286	20.00	cloudy	27
1122	7 Min	6.74	283	19.90	cloudy	26

0.0 / .48 .44 .43 .42

ORP: 113 109 106 105

OTHER: ____ ODOR: ____ (COBALT 0-100) ____ (NTU 0-200) ____

FIELD QC SAMPLES COLLECTED AT THIS WELL (i.e. FB-1, XDUP-1) : ____

PURGING EQUIPMENT		SAMPLING EQUIPMENT	
____ 2" Bladder Pump	____ Bailer (Teflon)	____ 2" Bladder Pump	____ Bailer (Teflon)
____ Centrifugal Pump	____ Bailer (PVC)	____ Bomb Sampler	____ Bailer (Stainless Steel)
____ Submersible Pump	____ Bailer (Stainless Steel)	____ Dipper	____ Submersible Pump
____ Dispo Bailer	____ Dedicated	____ Dispo Bailer	X Dedicated
Other: #1 WATERRA		Other: ____	

WELL INTEGRITY: Good — LOCK: NO

REMARKS: ____

pH, E.C., Temp. Meter Calibration: Date: ____ Time: ____ Meter Serial No.: ____
E.C. 1000 ____ / ____ pH 7 ____ / ____ pH 10 ____ / ____ pH 4 ____ / ____
Temperature °C ____
SIGNATURE: Paul Weinhardt REVIEWED BY: ____ PAGE 6 OF 23

3.5.7.2 Sample Containers

The type and size of the sample container(s) for each analyte are listed in Table 3.5. All glass bottles have Teflon® caps. New certified-clean VOA vials (40-mL) were used for VOC collection. Clean polyethylene bottles (100 mL and 250 mL, respectively, were used for analysis of anions (nitrate, bromide, sulfate, chloride) and metals (iron and manganese, respectively). Sterile 50-mL conical tubes were used for perchlorate and fatty acids.

3.5.7.3 Sample Collection for Laboratory Analysis

The methods and procedures to be used in collecting groundwater samples from the Test Plot are described below. The sample bottles and preservation methods were summarized previously in Table 3.5. After each well was purged according to previously documented guidelines and field parameters were measured as detailed in Section 3.5.7.1, several different groundwater samples were collected. For analysis of VOCs by EPA Method 8260, two 40-mL amber glass VOA vials containing HCl for sample preservation were filled directly from the groundwater stream at low flow from each well. Each vial was filled with a zero headspace to avoid loss of volatiles from the water, then tightly capped and placed on ice. The HCl was added in the analytical laboratory prior to shipping of the bottles. For analysis of anions by EPA Method 300.0 (nitrate, sulfate, chloride, bromide), a 100-mL polyethylene sample bottle was filled with water. Zero headspace is not required. The bottle was then capped and placed on ice for shipment. For analysis of perchlorate (EPA Method 314.0) and volatile fatty acids (EPA Method 300.0m), sterile-filtered samples are required. For collection, groundwater (~ 25 – 35 mL) was initially pumped into a 60-mL disposable syringe fitted with a sterile 0.2-µM cellulose acetate filter (Nalgene). The syringe plunger was removed prior to groundwater collection. The water in the syringe was then filtered into a sterile 50-mL polycarbonate centrifuge tube (Corning) and tightly capped. Finally, at selected sampling points (see Table 3.5), a 250-mL polyethylene jar preserved with nitric acid was filled for analysis of dissolved iron and manganese (EPA Method 200.7). The water used for this analysis was initially passed through a 0.45-µM pore size cartridge filter designed for analysis of metals. All sample bottles were prepared at the Shaw Laboratory in Lawrenceville, NJ and shipped to the Aerojet Site in an insulated cooler prior to the scheduled sampling event.

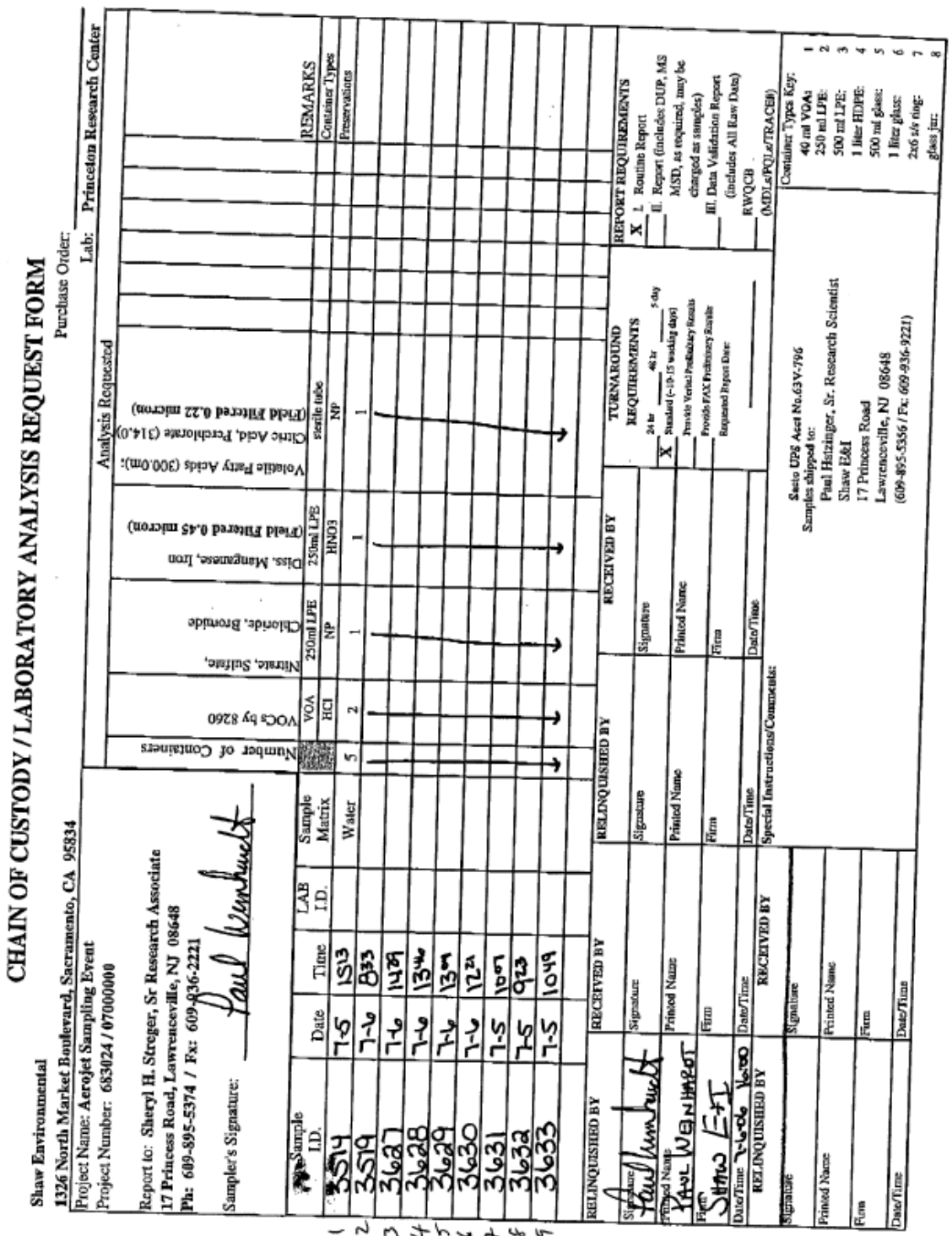
3.5.7.4 Sample Packaging and Shipment

During or immediately after groundwater sampling, the field technician completed a chain-of-custody (COC) form supplied by the Shaw analytical laboratory. The COC includes a detailed description of each sample (sample identification, bottle size, bottle preservation, sampling time). An example of a completed COC form for the project is provided in Figure 3.32. Samples for laboratory analysis were packed in coolers with ice packs. Shock absorbent packing was added to the coolers to prevent breakage or damage

of the sample containers. After review for accuracy, the COC form was signed, sealed in a plastic bag to protect it from water, and then securely taped to the inside lid of the cooler prior to closure. The COC form is removed from the cooler upon arrival and used by the analytical laboratory for sample identification and processing.,

All samples were shipped on the day of collection whenever possible. If shipping was not possible on the collection day, samples were stored at 4^{o}C and shipped on the next business day. Coolers were packed with sufficient ice to maintain sample temperatures at 4°C during shipment. To insure safe transport of the samples, all coolers were securely taped all the way around, and a custody seal was placed over the cooler opening. The field technician relinquished custody of the coolers to an express carrier for overnight delivery. Upon receipt of each sample shipment, the coolers were inspected and any problems were noted on the COC record and reported to the QA staff person responsible.

Figure 3.32. Example of a Completed Chain-of-Custody (COC) Form Used for the Project.



CHAIN OF CUSTODY / LABORATORY ANALYSIS REQUEST FORM

Shaw Environmental
1326 North Market Boulevard, Sacramento, CA 95834

Purchase Order:

Project Name: Aerojet Sampling Event
Project Number: 683024 / 07000000

Lab: Princeton Research Center

Report to: Sheryl H. Streger, Sr Research Associate
17 Princess Road, Lawrenceville, NJ 08648
Ph: 609-895-5374 / Fx: 609-936-2221

Sampler's Signature: Paul Weinhardt

Analysis Requested

	Sample I.D.	Date	Time	LAB I.D.	Sample Matrix	Number of Containers	VOCs by 8260 VOA HCl 2	Nitrate, Sulfate, Chloride, Bromide 250ml LPE NP 1	Diss. Manganese, Iron (Field Filtered 0.45 micron) 250ml LPE HNO3 1	Volatile Fatty Acids (300.0m): Citric Acid, Perchlorate (314.0) (Field Filtered 0.22 micron) sterile tube NP 1								REMARKS
																		Container Types
																		Preservations
11	3626	7-6	1513		Water	5	2	1	1	1								
12	3627	7-6	833															
13	3628	7-6	1428															
14	3629	7-6	1336															
15	3630	7-6	1307															
16	3631	7-5	1212															
17	3632	7-5	1007															
18	3633	7-5	923															
19		7-5	1049															

RELINQUISHED BY
Signature: Paul Weinhardt
Printed Name: PAUL WEINHARDT
Firm: Shaw E&I
Date/Time: 7-6-06 1630

RECEIVED BY
Signature
Printed Name
Firm
Date/Time

RELINQUISHED BY
Signature
Printed Name
Firm
Date/Time

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Firm
Date/Time

RELINQUISHED BY
Signature
Printed Name
Firm
Date/Time

RECEIVED BY
Signature
Printed Name
Firm
Date/Time

Special Instructions/Comments:

Fedex UPS Acct No.637-796
Samples shipped to:
Paul Heininger, Sr. Research Scientist
Shaw E&I
17 Princess Road
Lawrenceville, NJ 08648
(609-895-5356 / Fx: 609-936-9221)

TURNAROUND REQUIREMENTS
24 hr ___ 48 hr ___ 5-day ___
X Standard (~10-15 working days)
Provide Verbal Preliminary Results
Provide FAX Preliminary Results
Requested Report Date: _____

REPORT REQUIREMENTS
X I. Routine Report
II. Report (includes DUP, MS MSD, as required, may be charged as samples)
III. Data Validation Report (includes All Raw Data)
RWQCB
(MDLs/PQLs/TRACER)

Container Types Key:
40 ml VOAs: 1
250 ml LPE: 2
500 ml LPE: 3
1 liter HDPE: 4
500 ml glass: 5
1 liter glass: 6
2x6 x4 ring-glass jar: 7
8

3.5.7.5 Equipment Decontamination

All pumps (Waterra foot valves) and tubing were dedicated in the monitoring wells, so decontamination between wells was not necessary. The jack pump (used at all wells) did not contact the water.

3.5.7.6 Sample Documentation

Groundwater samples were labeled and maintained under COC procedures from the time of collection to analysis. The QAPP provides a more in-depth discussion of sample documentation procedures.

3.5.7.7 Quality Control Sampling

This section describes the field quality control program that will be used to measure and evaluate data quality associated with site characterization sampling. The program involves the collection of duplicate samples and trip blanks. Equipment blanks were not taken because dedicated pumps were used. Collection duplicates are used to assess the homogeneity of contaminants in a given matrix. Trip blanks are artificial samples designed to detect the introduction of contamination or other artifacts into the sampling, handling, and analytical process. For more information detailing the Quality Control Sampling Program, please reference the Quality Assurance Plan (QAPP) in Appendix C.

3.5.8 Demobilization

At the completion of this study all equipment was disconnected and removed from the site. The decommissioning efforts included removing the computer and other temporary equipment from the utility trailer, removing outside equipment from the site, including the chlorine dioxide system, pumps, and the citric acid tank, pulling all pumps and downhole components from the HFTWs using a crane, and disconnecting and removing all piping runs between the HFTWs and the utility trailer. The utility trailer was the property of Aerojet, and will be moved by them to another location based on need. The HFTWs, monitoring wells, and piezometers installed for this study will become the property and responsibility of Aerojet for use in future monitoring, demonstration, or remedial efforts.

3.6 Selection of Analytical Methods

The selected methods represent standard EPA procedures or modifications of these protocols. Perchlorate analysis was conducted using a modification of the original EPA Method 314.0 (Appendix A) and anion analysis for chlorate, nitrate (as N), sulfate, bromide, and chloride was conducted using EPA method 300.0 (Appendix A). The modification to EPA 314.0 was field filtration of groundwater samples through 0.22-um cellulose acetate filters to remove bacteria prior to shipping and analysis. Sterile 50-mL conical tubes were used to preserve sterility. This preservation method was approved by

EPA in 2005 (after the initiation of this ESTCP project) and was incorporated into EPA Method 314.1 (USEPA, 2005). Analysis for fatty acids (citrate, lactate, acetate, formate, and propionate) was conducted using a modification of EPA Method 300.0 developed at Shaw specifically for organic acids. For all aforementioned ion chromatography methods, a Dionex DX-100, DX-120, or ICS-2000 ion chromatograph was used. For this project, the practical quantitation limit (PQL; reporting limit) for perchlorate using EPA Method 314.0 was approximately 2.5 micrograms per liter (2.5 μg/L or 2 ppb), and the PQL for the anions of interest using EPA Method 300.0 is 0.2 milligrams per liter (0.2 mg/L or ppm). The MDL for perchlorate in the Shaw Analytical Laboratory was 0.8 μg/L. Values for perchlorate between 0.8 and 2.5 μg/L were reported with a *J* designation on data reports. The PQL for organic acids is approximately 1 mg/L. VOC analysis was performed using EPA Method 8260B (Appendix A) utilizing a Hewlett Packard 5973 gas chromatograph/mass selective detector. The PQL for TCE and other volatile compounds using this method is 5 micrograms per liter (5 ppb) and the MDL is ~ 0.5 ppb. Detectable values below 5 ppb but greater than the MDL were designated with *J* values on data reports. Analysis of iron and manganese was performed using EPA Method 200.7 or equivalent. The PQL for iron and manganese is 100 μg/L and 15 μg/L, respectively, and the MDL is 5 μg and 0.1 μg/L, respectively. Detectable values below the PQL but greater than the MDL were designated with *J* values on data reports. Field measurements were conducted using hand-held instruments (i.e. an Orion or YSI meter or equivalent) and conventional methods.

3.7 Selection of Analytical/Testing Laboratory

Shaw Environmental's Analytical and Testing Laboratory in Lawrenceville, New Jersey performed laboratory testing for the demonstration. This laboratory has significant experience in implementing EPA-approved methods for the detection of perchlorate, anions, fatty acids, and TCE in groundwater. Total iron and manganese analysis was performed by ChemTech, Mountainside, NJ, a contract laboratory used frequently by Shaw for these analyses.

3.8 Project Personnel

Dr. Paul Hatzinger, with Shaw, was the Principal Investigator for the demonstration, and had overall project management responsibility. Dr. Hatzinger worked closely with each of the demonstration partners to insure all efforts were fully coordinated.

Mr. Jay Diebold, P.E., P.G., with Shaw, served as the Project Field Manager for the demonstration. He was responsible for overseeing system installation, and for day-to-day system operation. Jay also coordinated efforts between the demonstration site personnel and the three Shaw offices that were involved.

Dr. Randi Rothmel, with Shaw, is the Shaw Environmental Laboratory Manager. She had overall QA/QC responsibility for analytical data generated during the project.

Ms. Sue Kraemer, located in Shaw's Sacramento office, assisted with the coordination of local staff and subcontract resources.

Mr. Paul Weinhardt, located in Shaw's Sacramento office, perfomed most of the groundwater sampling and system O&M for the project.

Ms. Sheila Richgels, located in Shaw's Sacramento office, was the QA officer for groundwater sampling. She ensured that all field data sheets and COC forms were correct and that samples were properly shipped to the laboratory for analysis.

Mr. Scott Neville served as the site project manager for Aerojet and coordinated all on-site activities and support services provided by Aerojet personnel. Mr. Neville also supported efforts to maintain local regulatory compliance throughout the execution of the demonstration.

Mr. Darren Engbring, formerly with Shaw, provided system design, installation, and operations support including coordinating with all vendors and subcontractors to insure proper installation, operation, and maintenance of all system components.

Dr. Mark Goltz, with AFIT, is a Co-PI on the project. He and his students at AFIT provided hydrogeologic and contaminant fate and transport modeling support throughout the project, including operational model refinements and comparison of model results to actual field observations.

Dr. Eric Nuttall, with UNM, is a Co-PI on the project. He provided well fouling control support. These efforts included laboratory studies to assess the most practical and cost effective means of preventing or controlling well fouling associated with biomass growth and assisting with the field implementation and assessment of the most promising remedies.

4.0 PERFORMANCE ASSESSMENT

4.1 Performance Criteria

See Table 4.1 for performance criteria.

Table 4.1. Performance Criteria.

Performance Criteria	Description	Primary or Secondary
Contaminant Reduction	The destruction of perchlorate, nitrate and TCE in groundwater.	Primary
Mixing	Assess the mixing of groundwater and delivery of groundwater with electron donor via tracer testing and electron donor measurement.	Primary
Factors Affecting Technology Performance	Hydrogeologic characteristics, biogeochemical characteristics and contaminant concentration may affect biostimulation treatment performance. Hydrogeologic characteristics of the treatment zone including the presence of low-permeability lenses or layers may affect the vertical and lateral distribution of injected substrates. Irregular distribution of electron donor caused by heterogeneities may result in zones where little or no treatment can occur.	Primary
Reliability	Application of the treatment system may involve empirical optimization of the electron donor injection rates to achieve optimal performance. Therefore, initial operations will involve close monitoring of electron donor concentrations in groundwater to ensure adequate distribution in the treatment zone. Once stable performance is achieved, the system is designed to allow automated operation with minimal intervention and maintenance.	Primary
Ease of Use	Tasks associated with operations and maintenance (O&M) of the system include routine flow and pressure measurements at the injection point well heads and monitoring electron donor use. Limited technical expertise or training will be required of personnel involved in	Secondary

	the O&M of the system.	
Versatility	A horizontal flow treatment well (HFTW) system has previously been field tested for the addition of co-substrate (toluene) and oxygen for aerobic remediation of TCE. With this test, the technology will be examined for in situ anaerobic treatment of perchlorate and nitrate, as well as TCE. These two demonstrations will attest to the potential versatility of the HFTW technology for remediation purposes.	Secondary
Maintenance	The operation of the system is designed to be fully automated once initial testing is completed. O&M tasks include routine flow and pressure measurements and monitoring electron donor use. O&M activities will be performed by Shaw and GenCorp Aerojet personnel in conjunction with sampling activities.	Secondary
Scale-Up Constraints	The demonstration system was designed to treat a relatively small area, consistent with pilot-scale systems that may be installed prior to full-scale application. Scale-up to meet the requirements of full-scale site remediation would involve pilot-scale testing and full-scale design and installation. Based on these factors and the site-specific remediation requirements, the installation of a full-scale system may require construction of a new substrate delivery network or modification of existing remediation systems. A variety of methods can be used to match the substrate delivery process with the remediation requirements.	Secondary
Process Waste	Application of the biostimulation technology does not generate any process waste. Limited soil cuttings and groundwater derived from sampling were be generated during the demonstration.	Secondary

4.2 Performance Confirmation Methods

The effectiveness of the electron donor addition with HFTWs for perchlorate treatment depends on the stimulation and growth of indigenous degradative microorganisms, the distribution of electron donor, and the hydraulics of groundwater flow in the test site. A successful demonstration is based primarily on the levels of reduction of contaminant and the even, adequate, and steady dispersion of the electron donor throughout the plot area to be treated. Other factors evaluated include the effect of hydrogeologic and biogeochemical factors on system performance, ease of use, versatility, maintenance, and scale-up constraints (Table 4.2).

Field data were analyzed as available throughout the demonstration to determine the efficacy and effectiveness of the *in situ* electron donor biostimulation pilot test. The data were subject to the QA procedures outlined in the QAPP (Appendix C) to ensure a consistent and scientific evaluation of performance.

Table 4.2. Performance Confirmation Methods.

Performance Criteria	Expected Performance Metric	Performance Confirmation Method[1]
PRIMARY CRITERIA (Performance Objectives) **(Quantitative)**		
Perchlorate	*Reduce perchlorate to <4 μg/L*	*EPA Standard Method 314.0 (modified with filtered sample according to EPA Standard Method 314.1)*
Co-contaminants: Nitrate and TCE	*Reduce Nitrate-N to < 1 mg/L and TCE to < 5 ug/L*	*EPA Standard Method 300.0 (for Nitrate-N) and EPA 3260 (for TCE and CVOCs)*
Overall system performance	*Observe the presence of injected electron donor and/or negative oxidation reduction potential (ORP) sampling wells throughout the test plot at appropriate time points (i.e. indicative of a broadly distributed treatment ozone)*	*EPA Standard Method 300.0m for electron donor (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 iron and manganese analysis. Field meter measurements of 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*

4.3 Data Analysis, Interpretation, and Evaluation

The scientific data generated during the project consisted primarily of temporal measurements of perchlorate and co-contaminant concentrations in monitoring wells within and outside of the HFTW treatment zone. In addition, operational data, including well pumping rates, well pressures, and electron donor usage was recorded. In the subsequent section (Section 4.4), the concentrations of perchlorate and co-contaminants in the monitoring wells are plotted with time and compared to baseline perchlorate and co-contaminant levels in each monitoring well prior to electron donor addition and during HFTW operation and to contaminant levels in a nested upgradient monitoring well. In addition, geochemical and operational parameters are plotted and discussed to evaluate system performance. These data generated during the project were modeled using the groundwater flow/biodegradation model developed at AFIT. The modeling data are presented in Appendices E and F.

4.4 Demonstration Results

4.4.1 Phase I Operation

As previously noted, the objectives of the first phase (Phase I) of system operation 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. 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 10/28/2004 after tracer testing was complete.

The HFTW was operated with only a moderate stoichiometric excess of electron donor in Phase I to evaluate what levels of perchlorate bioreduction were possible without major impacts to groundwater geochemistry. The required citric acid dosage was calculated based on average groundwater flow rate, the average concentrations of oxygen, perchlorate and nitrate in existing monitoring wells on 9/24/2004, and the relevant oxidation reaction for electron donor (i.e., citric acid oxidized to carbon dioxide) and reduction reactions for each electron acceptor (i.e., oxygen, nitrate, and perchlorate). The basic equations and assumptions used to calculate stoichiometry are provided below:

1. Total groundwater flow of 65,405 L/day (6 gpm per well x 24 h pumping)
2. Oxygen, nitrate, and perchlorate are present at 9/24/2004 average levels:
    a. Oxygen = 1.87 mg/L (including 0.5 mg/L from Oxine).

b. Perchlorate = 3.31 mg/L.
c. Nitrate–N = 4.63 mg/L.

3. Citric acid concentration is 609 g/L (50 % by weight).
4. Stoichiometric ½ reactions (no biomass growth included):
   a. $NO_3 + 6H^+ + 6e^- \rightarrow 1/2N_2 + 3H_2O$.
   b. $ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$.
   c. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.
   d. $C_6H_8O_6 + 4H_2O \rightarrow 6CO_2 + 18H^+ + 18e^-$.
5. Balancing for electrons donated/consumed results in the following equation :
   $[C_6H_8O_6] = 1.33\ [O_2] + 3.81\ [NO_3\text{-}N] + 0.855[ClO_4^-]$ (values in mg/L).
6. Substituting concentrations of O_2 (1.87), NO_3-N (4.63) and ClO_4^- (3.31) yields a total of 23 mg/L $C_6H_8O_6$ required.
7. 64,405 L/day water x 23 mg/L citric acid required = 1481 g citric acid/day
8. 1481 g / 609 g/L = 2.43 L citric acid/day = **1.22 L citric acid/HFTW/day**

The electron donor dosage was initially set at 1.25X the stoichiometric requirement during Phase I. An electron donor dosage of 1.5 L of 50 % citric acid was added to both the upflow and the downflow HFTW as a daily pulse to achieve the desired dosage. Based on monitoring well data, the citric acid quantity was increased to 2.5X stoichiometry on 12/04/2004 (3.0 L/day). The dosing in the downflow HFTW was increased further to 4X stoichiometry (~ 4.9 L/day) on 2/11/2005. The system was operated intermittently from April, 2005 to the end of Phase I (8/01/2005; 275 Days) while various biofouling treatment strategies were tested.

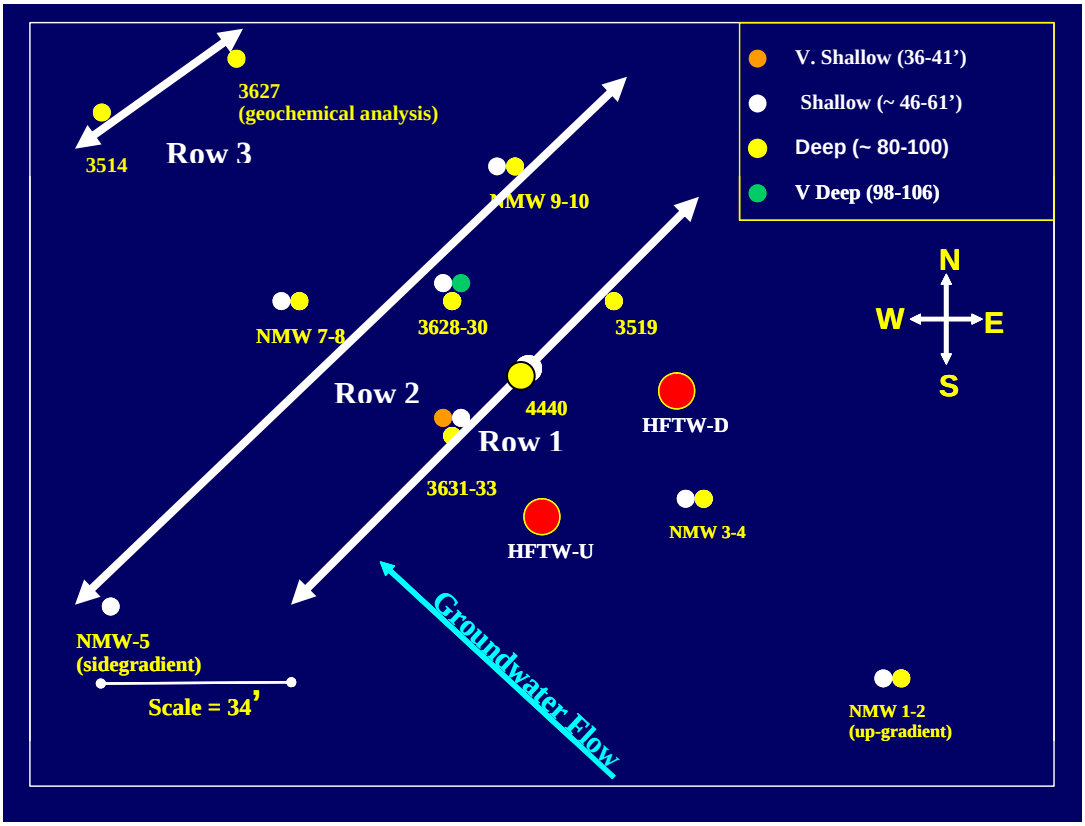
4.4.1.1 Phase I: Tracer Testing Results

A dual tracer test was performed as described in Section 3.5.1.3. Solutions of sodium bromide (~ 20 g/L as bromide ion) and sodium chloride (~ 80 g/L as chloride ion) were injected into the two HFTWs commencing on August 24, 2004. The chloride tracer was injected into the downflow HFTW and the bromide tracer was added to the upflow HFTW. Approximately 100 gallons of each solution was injected during a 30-day period in daily pulses in order to achieve the target dosing rate of approximately 1 kg chloride per day and 250 g bromide per day. The injection of the tracer solutions was completed on September 28, 2004.

For purposes of discussing the tracer results and geochemical data, the monitoring wells are separated into "rows" of shallow (2 rows) and deep (3 rows) based on distance from the HFTWs (see Figure 4.1 for Plot Layout and detail of "Rows"). Row 1 of the shallow wells consists of Well 3631, 3632, and NMW-3, the latter of which is between and slightly upgradient of the two HFTWs. Row 2 consists of Wells NMW-7, NMW-9,

and 3628. The side-gradient well NMW-5 is also included. Bromide was detected in all shallow monitoring wells within the test plot, showing that all were hydraulically connected to the HFTW system (Figures 4.2 & 4.3). Day 0 for the plots is the first day of the 30-day bromide injection. Bromide was detected at a maximum concentration within the Row 1 wells 3631 and 3632 within 3 days of injection, then in Well NMW-3 after ~ 30 days (Figure 4.2). Bromide in the second row of wells reached a maximum concentration at ~ 30 days for Wells 3628 and NMW-7, and ~ 45 days for Wells NMW-5 and NMW-9 (Figure 4.3).

Figure 4.1. General Layout of Demonstration Plot with Generalized Rows of Wells Denoted. Distances between monitoring wells are not to scale. The white arrows represent "rows" of wells used in discussion of tracer and geochemical data.



Bromide was also detected in all of the deeper monitoring wells, although concentrations were generally much lower than in the shallow wells. The majority of the tracer entering the deep wells was probably recycled between the HFTW-U and the HFTW-D. The maximum concentrations in the deep Row 1 wells (Well 3519, Well 3633, Well 4440, and NMW-4) were slightly more than 2 mg/L, compared to 6-10 mg/L in shallow Row 1 wells, and the peak concentrations occurred between ~ 20 and 30 Days (Figure 4.4). Bromide was also detected in each of the wells further downgradient, denoted as Row 2 (Well 3629, 3630, NMW-8, NMW-10) and Row 3 (Well 3627 and Well 3628) (Figure 4.5). The highest concentration was detected in NMW-8, which had nearly 6 mg/L after 30 days. The maximum concentrations in the other wells was near 2 mg/L, with maximum concentrations occurring from 30 days for Well 3630 to greater then 60 days for Wells 3514 and 3627. Bromide was not detected in either of the upgradient monitoring wells NMW-1 and NMW-2 (data not shown).

The data from the chloride tracer study used to evaluate connectivity of the HFTW-D to the monitoring wells was more difficult to interpret than the bromide data, particularly for the deep wells. The background variability in chloride among the wells was greater than initially thought. The background chloride concentrations ranged between ~ 3 and 30 mg/L in the treatment plot (with a few higher values), and with the exception of a few wells, chloride concentrations did not exceed 30 mg/L after the chloride was injected. As a result, it was not possible to conclusively distinguish changes in chloride levels resulting from mixing of background chloride throughout the plot from those due to injection of the chloride tracer. Reasonable data were obtained for several of the shallow wells, but rather than rely on these data, a second bromide tracer test was performed in the HFTW-D later in the project.

This test was conducted beginning on January 30, 2006, and was performed as previously detailed for the chloride tracer test except that bromide was added to the HFTW-D (rather than the HFTW-U), and the test was conducted for 15 rather than 30 days. The injection schedule and daily quantities of bromide added were as described for the previous test (i.e., 250 g pulsed in one time per day). The HFTW flow rates were also as described previously. No tracer was added to the HFTW-U.

Bromide added to the HFTW-D was detected in all shallow monitoring wells, with the highest concentrations occurring in Wells 3628, 3631, 3632, and NMW-7 (Figures 4.6 and 4.7). The first sampling event for the shallow wells was ~ 2 weeks after injection, so the peak may have been earlier in some wells, but for each of the aforementioned wells and Well NMW-3, the highest bromide concentrations occurred at this two week sampling point. The maximum concentrations at the other shallow wells occurred 32 days after the initial injection. Among the deep wells in Row 1, bromide was detected at > 4 mg/L in wells 3519 and NMW-4 after two weeks (Figure 4.8). These wells were also sampled at 1, 8, and 11 days after the injection commenced. Compared

to the first two wells in this group, low concentrations of bromide were detected in wells 4440 and 3633 during the test (< 1.5 mg/L maximum). However, the bromide was present at these levels over several weeks. These data suggest much more dilution of the tracer occurred than in the other wells. Bromide was detected in each of the deep downgradient wells (Rows 2 & 3) although only very low concentrations were observed in Wells 3627 and 3629 (Figure 4.9). The other deep wells showed peak concentrations at 32 days (Well 3514) or 64 days (wells NMW-10, 3514, and 3630). Bromide was detected in upgradient monitoring well NMW-2 at 0.6 mg/L on Day 11 and in NMW-1 at 0.39 mg/L on Day 99, suggesting a slight influence of the HFTW pumping system on the upgradient wells (data not shown).

A comparison of the relevant tracer test data with model simulations for each well is given in Appendix E (Figures E-1 to E-20). In general, the model simulations match the field data reasonably well. Notable exceptions include the following: (1) Well 3629 was predicted to be quickly impacted buy the HFTW-U, with bromide concentrations of ~ 7 mg/L occurring within a few days. During the test, very little bromide was detected in this well, with a maximum concentration of < 2 mg/L occurring after ~ 30 days (Appendix E: Figures E-5 & E-6). (2) For Well NMW-8, the reverse was true. The model predicted bromide reaching a maximum concentration of ~ 2.5 mg/L after > 100 days of travel time, but in reality, the well was impacted maximally 30 days with a peak concentration of > 5 mg/L (Appendix E: Figures E-7 & E-8). (3) Bromide also arrived at wells 3514 and 3627 much more rapidly than predicted by the model simulations (Appendix E: Figures E-9 & E-10). The results of the tracer testing will be discussed further as relevant to the biodegradation data.

Figure 4.2. Tracer Test 1, HFTW-U: Bromide Concentrations in Shallow Monitoring Wells Near the HFTWs – Row 1.

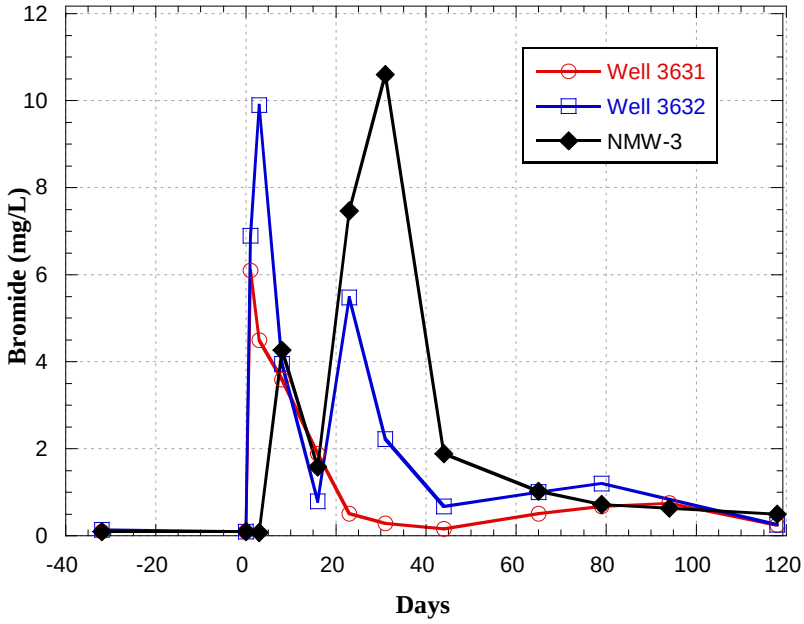


Figure 4.3. Tracer Test 1, HFTW-U: Bromide Concentrations in Shallow Monitoring Wells Distant from the HFTWs – Row 2 and Side-gradient Well NMW-5.

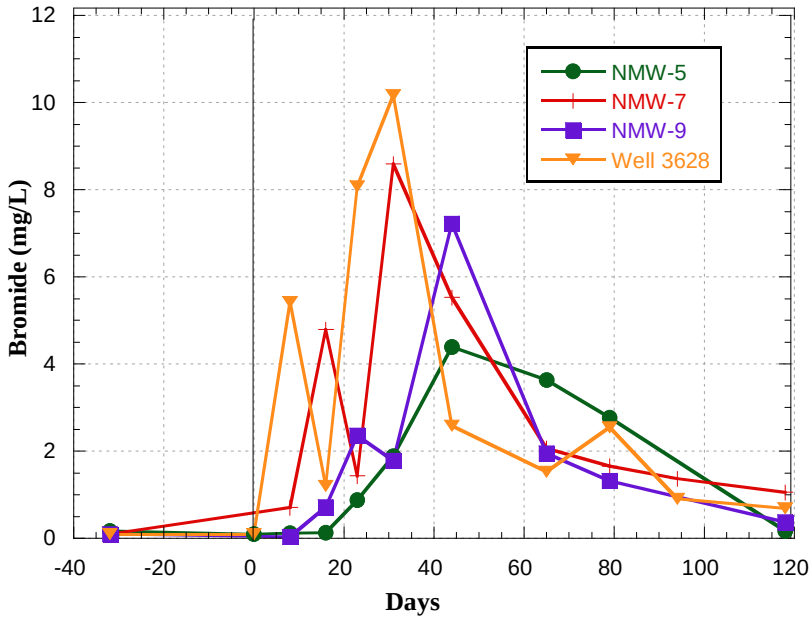


Figure 4.4. Tracer Test 1, HFTW-U: Bromide Concentrations in Deep Monitoring Wells Closest to the HFTWs – Row 1.

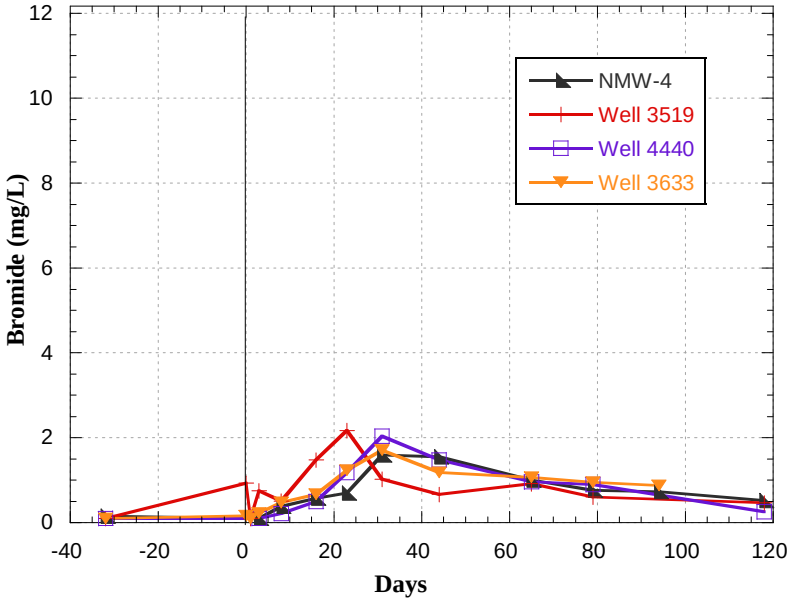


Figure 4.5. Tracer Test 1, HFTW-U: Bromide Concentrations in Deep Monitoring Wells Distant from the HFTWs – Row 2 & Row 3.

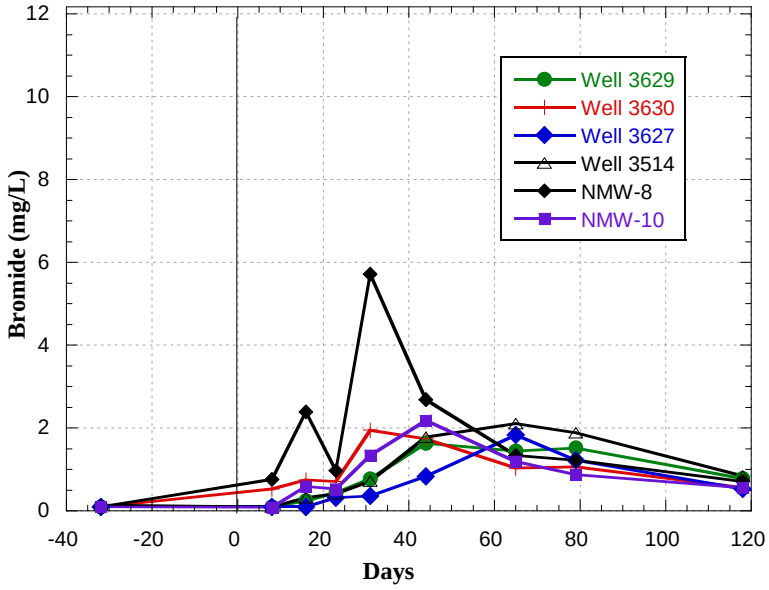


Figure 4.6. Tracer Test 2, HFTW-D: Bromide Concentrations in Shallow Monitoring Wells Near the HFTWs – Row 1.

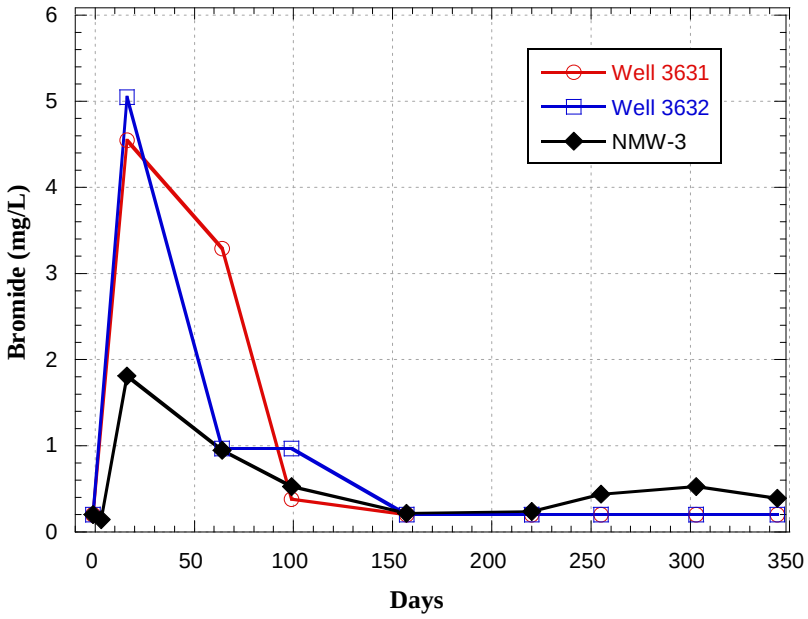


Figure 4.7. Tracer Test 2, HFTW-D: Bromide Concentrations in Shallow Monitoring Wells Distant from the HFTWs – Row 2 and Side-gradient Well NMW-5.

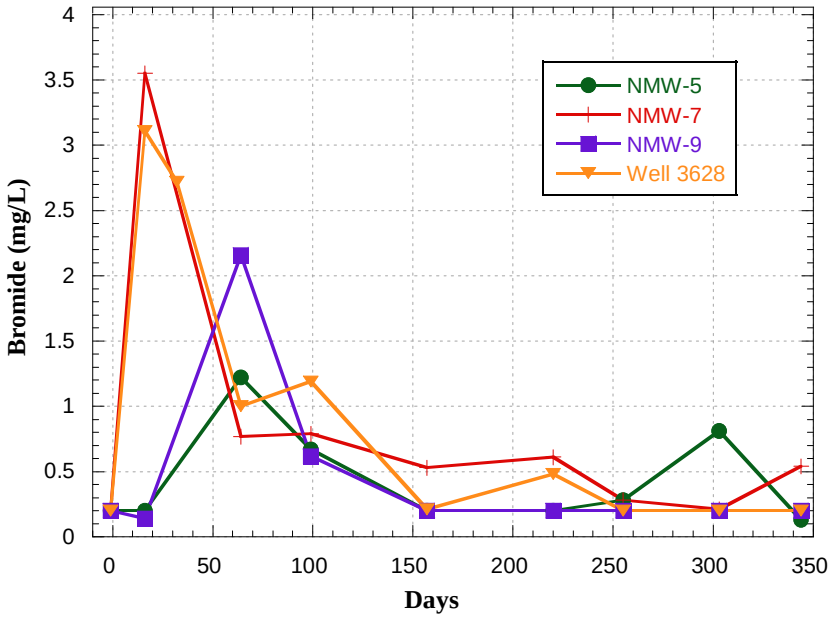


Figure 4.8. Tracer Test 2, HFTW-D: Bromide Concentrations in Deep Monitoring Wells Closest to the HFTWs – Row 1.

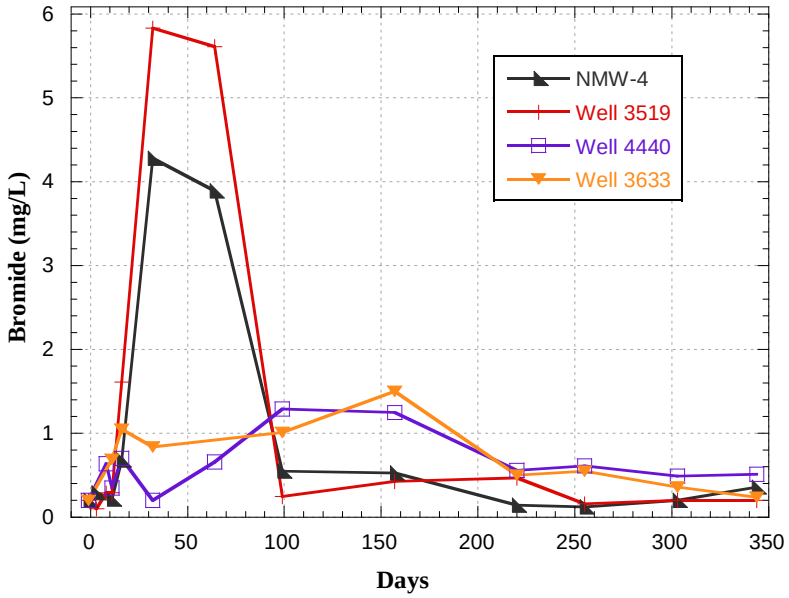
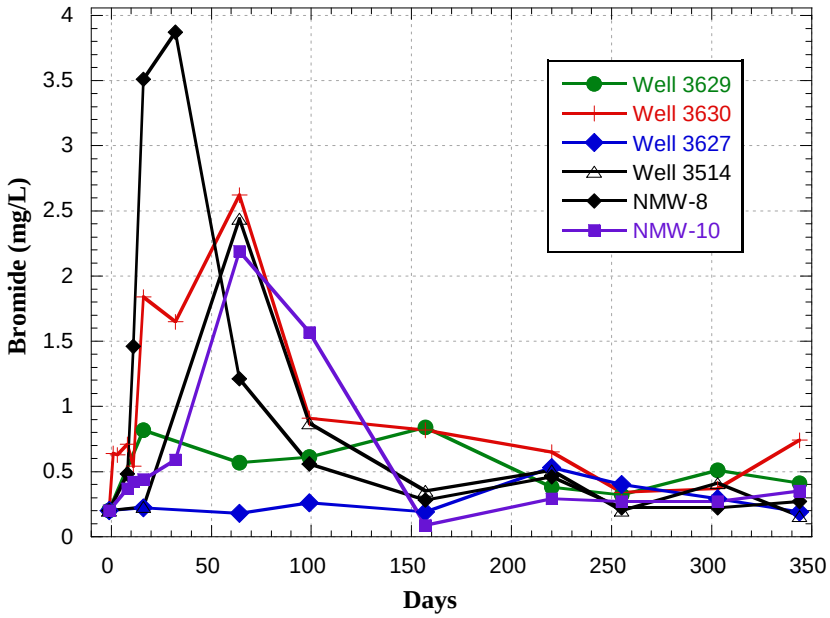


Figure 4.9. Tracer Test 2, HFTW-D: Bromide Concentrations in Deep Monitoring Wells Distant from the HFTWs – Row 2 & Row 3.



4.4.1.2 Phase I: Perchlorate Treatment

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 3.6). Between the final background monitoring event (Day -15; 10/13/2004) and the groundwater sampling conducted on 8/1/2005 (Day 275), perchlorate levels in the 7 shallow monitoring wells (See Figure 3.24 & Figure 4.1 for plot layout) declined by an average of 95 % from the starting average of 2230 μg/L to 90 μg/L (Figure 4.10 and Table 4.3). Well 3632 reached < 5 μg/L (MDL) on Day 67, but most of the other wells showed stable perchlorate levels ranging from ~ 40 – 160 μg/L. These levels remained reasonably consistent with electron donor dosages up to 2.5X stoichiometry added to the HFTW-U.

The consistent decline in perchlorate levels throughout the entire shallow aquifer zone during Phase I showed that the HFTW system provided good mixing and electron donor delivery within this region. Moreover, the rapid and consistent reduction in perchlorate levels in the side-gradient well (NMW-5) suggested that the zone of influence of the HFTW system in the shallow zone met or exceeded initial predictions derived from the site-specific groundwater transport model. The low residual levels 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 one-pass mixing design and flow field of the system. It should also be noted that the system was not operated consistently between April 24, 2005 (Day 177) and the end of Phase 1 in August, 2005 (Day 275) due to biofouling issues with the HFTW-U. Tests were performed during this period to determine if the fouled well could be rehabilitated using acid and enzymatic treatments (See Section 4.4.9). Thus, the low residual perchlorate in the HFTW demonstration well network during the latter months of Phase I may reflect the operational conditions. This topic is addressed further during the discussion of Phase II and Phase III results.

Some decrease in perchlorate concentration was also observed in the shallow upgradient well (NMW-1) (Table 4.3). The perchlorate concentration in this well declined slowly from ~ 5400 μg/L at Day -51 (which was more than 1,400 μg/L higher than any of the other shallow wells) to ~ 3700 μg/L just prior to the beginning of electron donor addition. The perchlorate concentration in this upgradient well declined to ~ 1500 μg/L by Day 53, then remained consistently between ~ 1,200 and 1,600 μg/L through Day 275, when all of the shallow downgradient wells declined to < 100 μg/L. The tracer test data suggest that the well did not receive water from either HFTW (i.e., bromide was below detection during each tracer test). Rather, the declining perchlorate in NMW-1 most likely resulted from impacts to groundwater flow during pumping of the two HFTWs or alterations in mass flux and contaminant transport from the upgradient perchlorate source area. Besides unusually high perchlorate, NMW-1 had significantly lower sulfate (Table 4.13) and TCE (Table 4.9) than the other shallow downgradient

wells, suggesting that water in the well may have originated from a slightly different geologic unit/region than in the downgradient wells (or possibly that the well screen intercepted multiple units), and that pumping impacted the water entering this well. Nitrate concentrations were generally similar to the downgradient wells, and did not decline with time.

Like the shallow downgradient wells, the perchlorate levels 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 4.11 and Table 4.4). Unlike NMW-1, there was no appreciable change in perchlorate concentrations in deep upgradient well NMW-2 during Phase I (Table 4.4). In the 9 deep downgradient wells within the treatment zone, perchlorate levels declined by an average of 60% from a starting concentration of 3722 μg/L on Day 0 to 1780 ug/L on Day 275. However, in the five deep wells furthest downgradient (NMW-8, NMW-10, 3514, 3627, 3630; see Figure 4.1), 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) (Figure 4.12). In addition, perchlorate levels in Well NMW-8 were below detection (<2.5 μg/L) on Day 275 (see Figure 4.11). 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. 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 Figure 4.9 and Appendix E). Appreciable dispersion of the tracer cloud was apparent for these wells suggesting either (1) that the water from the HFTW-D was significantly diluted with untreated water prior to reaching these wells or (2) that the quantity of water (and electron donor) reaching these deep wells was appreciably lower than anticipated due to significant recycling of the injected water from HFTW-D into HFTW-U with subsequent delivery into the shallow aquifer.

As with the shallow zone, the citric acid levels 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 levels 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 levels had rebounded in many of the wells. Phase II and Phase III results are reported in later sections.

Figure 4.10. Perchlorate Levels in Shallow Downgradient Monitoring Wells – Phase I.

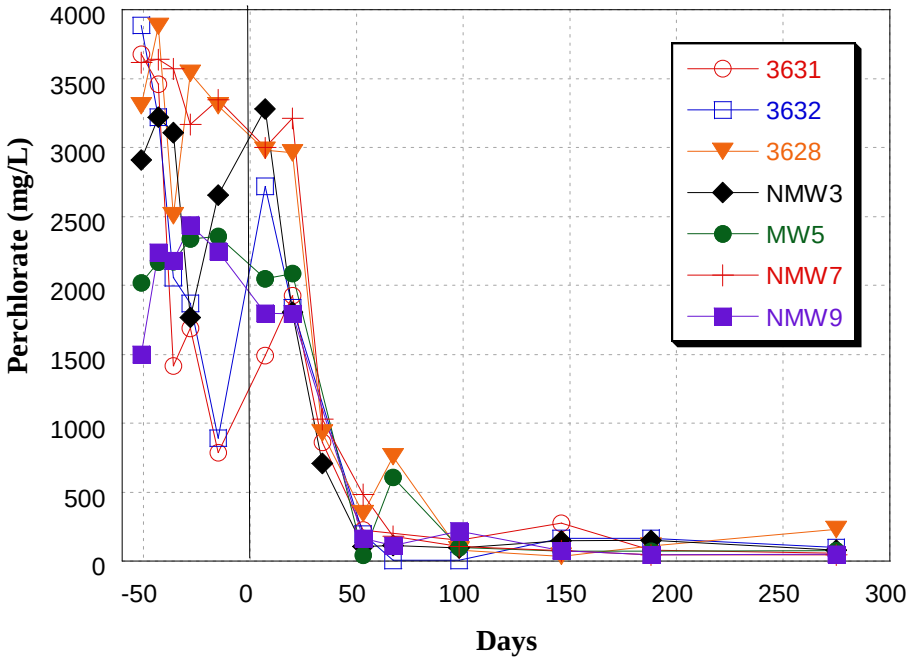


Figure 4.11. Perchlorate Levels in Deep Downgradient Monitoring Wells – Phase I.

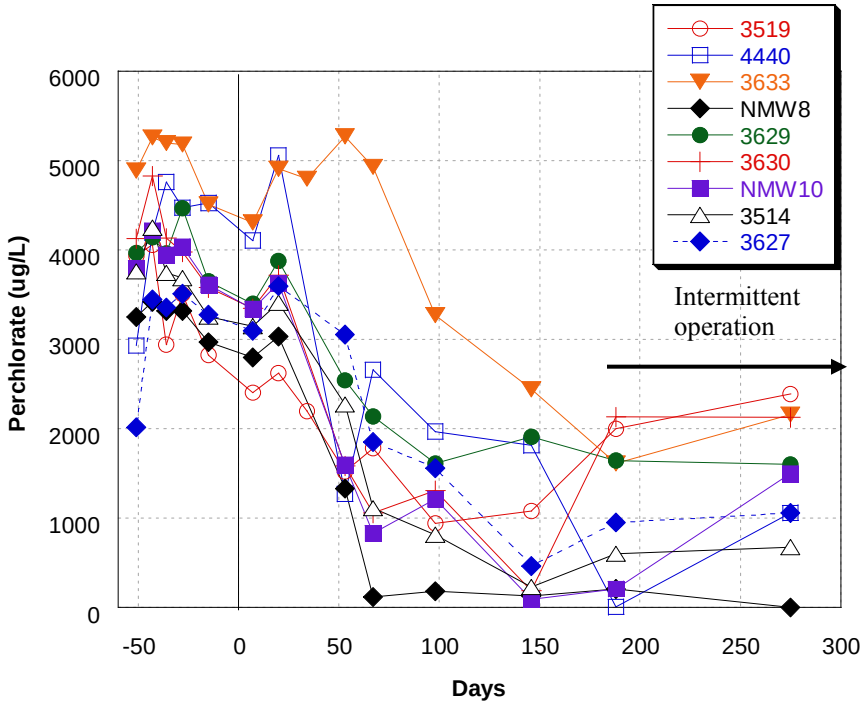


Figure 4.12. Perchlorate Levels in Deep Downgradient Monitoring Wells in Rows 2 & 3 through Day 149 – Phase I.

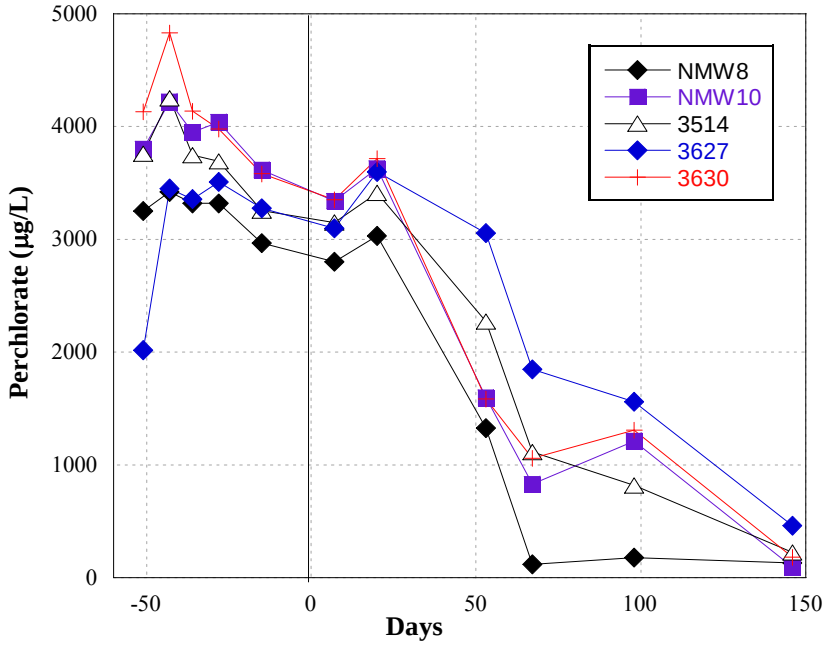


Table 4.3. Perchlorate Concentrations (μg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/7/04	**-51**	3680	3888	3302	5310	2910	2020	3619	1500
9/15/04	**-43**	3460	3220	3883	5440	3220	2170	3640.	2240
9/22/04	**-36**	1418	2058	2506	4665	3109	2175	3572	2182
9/30/04	**-28**	1690	1870	3540	4340	1770	2340	3170	2440
10/13/04	**-15**	789	890	3303	3678	2655	2357	3347	2249
11/4/04	**7**	1490	2720	2980	2820	3280	2050	3000	1800
11/17/04	**20**	1924	1840	2964	2564	1807	2088	3213	1796
12/1/04	**34**	860	NS	93	NS	710	NS	1030	NS
12/20/04	**53**	224	197	344	1572	105	41	485	166
1/3/05	**67**	NS	5	759	1690	112	607	180	112
2/3/05	**98**	150	11	80	1270	94	96	105	217
3/21/05	**146**	273	168	35	1209	148	73	74	77
5/5/05	**188**	78	165	109	1296	150	72	44	45
8/1/05	**275**	56	99	228	1570	80	76	44	49

* NMW-1 is an upgradient control well
NS = Not sampled.

Table 4.4. Perchlorate Concentrations (μg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2	NMW-4	NMW-8	NMW-10
9/7/04	**-51**	2017	2930	3937	3760	3970	4130	4890	1030	4520	3250	3800
9/15/04	**-43**	3450	4200	4060	4250	4147	4830	5260	1160	4850	3420	4220
9/22/04	**-36**	3358	4759	2944	3747	3962	4137	5198	1115	4628	3320	3949
9/30/04	**-28**	3510	4472	3508	3690	4470	3980	5180	1170	4340	3320	4040
10/13/04	**-15**	3276	4529	2827	3257	3650	3582	4511	1366	4095	2969	3614
11/4/04	**7**	3096	4110	2404	3150	3400	3350	4310	1170	3815	2800	3340
11/17/04	**20**	3598	5060	2624	3413	3879	3716	4909	939	4090	303	3630
12/1/04	**34**	NS	NS	2200	NS	NS	NS	4800	NS	3610	NS	NS
12/20/04	**53**	3056	1269	1523	2271	2543	1587	5274	891	2040	1329	1598
1/3/05	**67**	1850	2658	1780	1115	2140	1060	4932	1000	3230	119	833
2/3/05	**98**	1560	1970	945	817	1610	1310	3270	1140	3720	180	1213
3/21/05	**146**	463	1814	1079	228	1908	184	2443	1302	4540	130	93
5/5/05	**188**	952	<5	2000	603	1644	2134	1612	1214	5320	207	210
8/1/05	**275**	1060	1060	2390	677	1600	2130	2160	1480	5000	<2.5	1500

* NMW-2 is an upgradient control well
** NS = Not sampled.

4.4.1.3 Phase I: Mobilization of Iron and Manganese

Overall, mobilization of iron and manganese was minimal during the course of Phase I operation. The soluble iron levels in the monitoring well network through 188 days of operation are presented in Figure 4.13, Tables 4.5 (Shallow Wells) and Table 4.6 (Deep Wells). Samples were not analyzed for these parameters on Day 275, as the system had been operated intermittently for the three month period prior to this event. Iron and manganese levels in wells 4440 and 3514 are not plotted as these wells have artificially high background levels presumably due to the fact that iron well casings were used during installation. The values are provided in Table 4.6. With the exception of two shallow wells closest to the upflow HFTW (Wells 3631 & 3632), soluble iron levels throughout the plot remained well below 500 μg/L. 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 in which iron levels 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 that which came into solution was rapidly removed once the system was shut down.

Among the shallow wells, manganese levels increased most significantly in wells 3631 & 3632, reaching a maximum of 1470 μg/L in Well 3632 at Day 98 (Figure 4.14 and Table 4.7). However, concentrations in both of 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 level observed at this time was 715 μg /L in NMW-8. This well is directly downgradient of the nest with wells 3631 & 3632 (see Figure 4.1). 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 & reinjection design), iron in a some monitoring wells exceeded 2.9 mg/L, and manganese 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. The measured concentrations of acetate (produced from the oxidation of ethanol) exceeded 30 mg/L in downgradient wells after all of the perchlorate and nitrate were degraded. It is this excess donor that serves as the substrate for microbial Fe and Mn reduction. Dissolved Fe and Mn exceeding 70 mg/L and 40 mg/L, respectively, has been observed using slow release substrates for *in situ* perchlorate treatment (ESTCP, 2006).

It should be noted that, during the previous demonstration at Aerojet, perchlorate concentrations were reduced to < 4 μg/L in the three downgradient wells within 30 days of ethanol addition (from ~ 8 mg/L) and remained at this level throughout the initial demonstration. Although dramatic declines in perchlorate were observed during Phase I of the current demonstration, particularly in the shallow wells and deep downgradient

wells, consistent reduction to < 4 ug/L was not achieved throughout the plot. It is unclear whether the low residual perchlorate (50 – 100 µg/L) in many of the wells reflects a limitation in electron donor, or is the result of the complex mixing of groundwater by the HFTW system. A similar low residual of TCE was observed during a previous demonstration with these wells (McCarty et al., 1998). Additional discussion of this topic is provided in Section 4.4.3.6.

Figure 4.13. Soluble Iron Levels in Downgradient Monitoring Wells – Phase I.

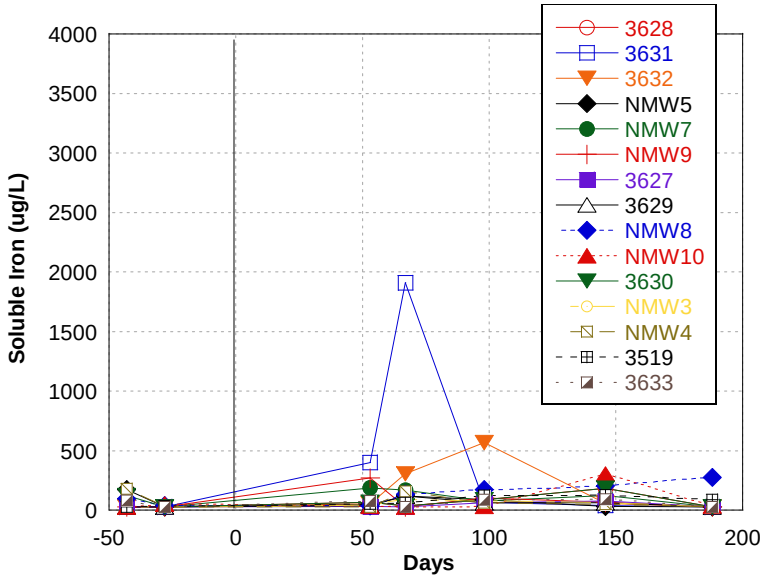


Table 4.5. Iron Concentrations (µg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/15/04	**-43**	<29	<29	<29	85	<29	172	<29	<29
9/30/04	**-28**	<29	<29	<29	<29	<29	<29	<29	<29
12/20/04	**53**	401	54	65	39	42	46	186	270
1/3/05	**67**	1910	305	36	93	90	117	166	<29
2/3/05	**98**	66	567	89	163	76	89	76	104
3/21/05	**146**	39	57	184	161	64	32	123	66
5/5/05	**188**	<27	<27	<27	<27	<27	<27	<27	<27

*NMW-1 is an upgradient control well.

Table 4.6. Iron Concentrations (µg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2	NMW-4	NMW-8	NMW-10
9/15/04	**-43**	<29	11600	<29	154	<29	121	79	<29	180	95	<29
9/30/04	**-28**	<29	3050	34	84	<29	29	<29	89	<29	39	49
12/20/04	**53**	<29	NA	53	783	39	36	76	59	<29	36	30
1/3/05	**67**	33	1510	63	182	119	32	<29	93	157	135	<29
2/3/05	**98**	<29	10600	122	895	60	145	89	63	63	171	31
3/21/05	**146**	78	6650	126	680	60	485	94	<29	51	204	303
5/5/05	**188**	28	41000	88	4700	<27	<27	<27	80	<27	276	34

*NMW-2 is an upgradient control well.

Figure 4.14. Soluble Manganese Levels in Downgradient Monitoring Wells – Phase I

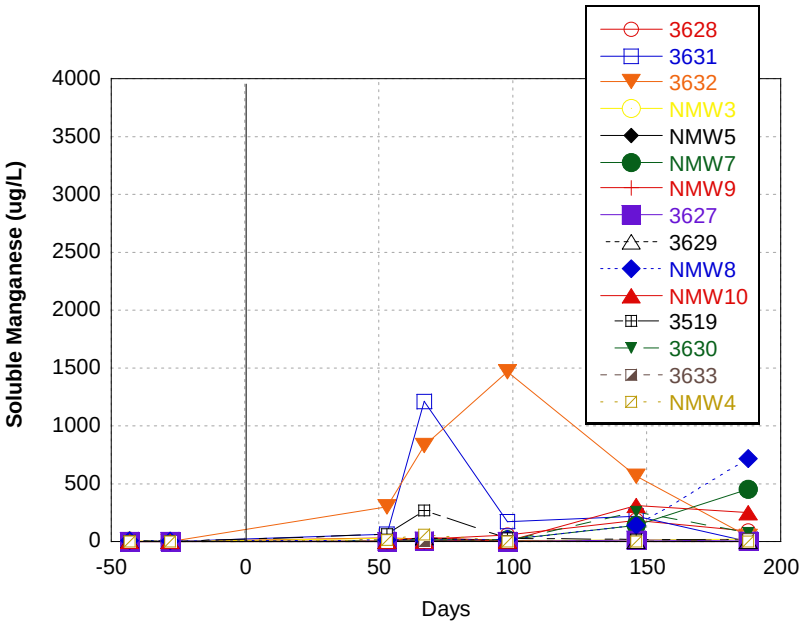


Table 4.7. Manganese Concentrations (µg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/15/04	**-43**	1.1	6.3	1.8	15	3.2	2.0	2.7	1.5
9/30/04	**-28**	0.6	0.6	1.6	0.8	0.9	1.0	1.0	0.3
12/20/04	**53**	64	302	32	2.0	28	2.4	3.0	6.5
1/3/05	**67**	1210	831	20	6.6	14	8.2	19	38
2/3/05	**98**	172	1470	54	6.1	8.9	3.7	17	5.7
3/21/05	**146**	219	566	183	2.9	12	0.6	140	1.3
5/5/05	**188**	0.4	44	88	1.7	23	0.3	452	0.5

*NMW-1 is an upgradient control well.

Table 4.8. Manganese Concentrations (μg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
9/15/04	**-43**	1.5	2500	3.0	30	2.8	3.7	3.4	2.0	2.76	8.0	1.1
9/30/04	**-28**	2.7	636	1.8	35	1.0	1.0	0.4	1.0	0.44	4.4	0.6
12/20/04	**53**	2.2	NA	62	79	2.3	3.2	3.1	2.5	13.7	11	2.0
1/3/05	**67**	4.3	943	269	34	34	3.6	3.3	4.7	57.1	10	6.8
2/3/05	**98**	1.0	1690	26	97	2.6	3.4	6.2	2.8	1.81	18	2.9
3/21/05	**146**	10	969	17	47	2.4	257	1.8	1.9	0.86	140	313
5/5/05	**188**	3.0	1890	15	131	<0.1	72	20	2.2	0.57	715	250

*NMW-2 is an upgradient control well.

4.4.1.4. Phase I: Treatment of Chlorinated Solvents.

The Phase I system operation was designed primarily to determine whether perchlorate reduction was possible without significant mobilization of iron and manganese. To achieve this end, electron donor was added only in moderate stoichiometric excess and as a result, the reduction potentials throughout the test plot rarely fell below 0 mV and usually averaged between + 25 and + 100 mV (Section 4.4.1.6). These redox conditions, while sufficient for perchlorate biodegradation, are not generally considered low enough to promote significant reductive dechlorination. That being said, significant losses of TCE were observed in several of the plot's shallow monitoring toward the end of Phase I operation. The average TCE levels in the downgradient shallow wells declined by approximately 40 % from 1620 μg/L just prior to electron donor addition to 990 μg/L at the end of Phase I (275 days) (Figure 4.15; Table 4.9). However, two of the shallow wells furthest downgradient, NMW-9 and Well 3628, had TCE levels below 50 μg/L at Day 275. Losses of TCE were also observed in a few of the deep downgradient wells, including Wells 3627 and 3629, but TCE concentrations in most of these wells remained reasonably constant (Table 4.10).

A few of the wells had detectable levels of *cis*-1,2-DCE ranging from 22 to 190 μg/L during one of the last two sampling events in Phase I, and this compound was measured in 15 of the 19 wells in the first sampling event performed for Phase II (2/2006). This compound is indicative of reductive dechlorination. However, *cis*-1,2-DCE was also detected in several of the monitoring wells, including the upgradient well NMW-2, prior to the initiation of citric acid injection. This observation suggests that reductive dechlorination is likely to be occurring (or has occurred in the past) at an upgradient location, probably within the landfill that is the source area of the plume. It is unclear how much of the *cis*-1,2-DCE in the downgradient wells is newly formed from dechlorination within the plot, or is present primarily from mixing and redistribution of compound entering the plot from upgradient. Additional discussion concerning TCE degradation intermediates during Phase II and Phase III is provided in Section 4.4.3.5.

Figure 4.15. TCE Levels in Shallow Downgradient Monitoring Wells – Phase I

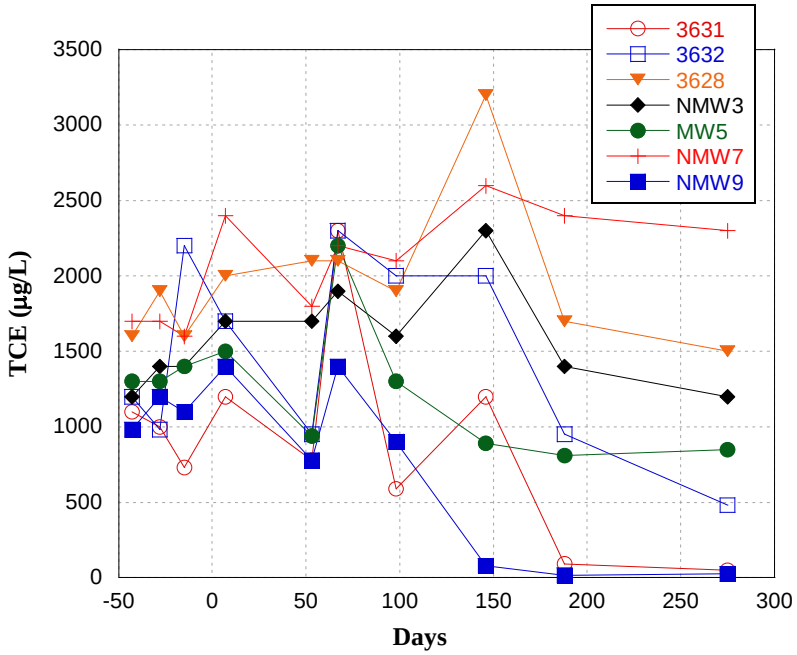


Table 4.9. TCE Concentrations (μg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/15/04	**-43**	1100	1200	1600	450	1200	1300	1700	980
9/30/04	**-28**	1000	980	1900	500	1400	1300	1700	1200
10/13/04	**-15**	730	2200	1600	410	1400	1400	1600	1100
11/3/04	**7**	1200	1700	2000	460	1700	1500	2400	1400
12/20/04	**53**	780	950	2100	320	1700	940	1800	780
1/3/05	**67**	2300	2300	2100	280	1900	2200	2200	1400
2/3/05	**98**	590	2000	1900	200	1600	1300	2100	900
3/23/05	**146**	1200	2000	3200	250	2300	890	2600	78
5/5/05	**188**	92	950	1700	210	1400	810	2400	17
8/1/05	**275**	49	480	1500	170	1200	850	2300	24

* NMW-1 is an upgradient control well

Table 4.10. TCE Concentrations (μg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
9/15/04	**-43**	1500	1100	1400	1500	1500	1400	1100	2700	2300	1300	1700
9/30/04	**-28**	1800	1500	1600	1800	1700	1800	1200	3000	2000	1600	2000
10/13/04	**-15**	1900	1400	1400	1700	1600	1700	1800	2900	2000	1400	1900
11/3/04	**7**	2000	1400	1400	1900	1900	1770	1600	3100	2600	1600	3000
12/20/04	**53**	2200	1400	1700	1800	1900	1700	1700	3200	2800	2200	2200
1/3/05	**67**	2100	1100	1500	1900	2100	1800	1500	3600	2900	1800	2400
2/3/05	**98**	1600	1100	1100	1200	1500	1700	1300	3500	3300	1800	1900
3/21/05	**146**	2300	2000	860	2400	1800	2500	2400	3000	5900	2600	2400
5/5/05	**188**	1200	1400	1800	1900	650	1400	1900	2600	5200	2000	2000
8/1/05	**275**	900	1100	1600	1500	680	1200	1600	1300	2900	1900	2800

* NMW-2 is an upgradient control well

4.4.1.5 Phase I: Nitrate and Sulfate

The nitrate concentration throughout the treatment plot averaged 4.8 ± 0.6 mg/L (nitrate-N) prior to system start-up. Nitrate concentrations declined rapidly in many of the shallow treatment wells after citric acid was added (Figure 4.16; Table 4.11). Nitrate in wells 3631 and 3632 was below detection (< 0.2 mg/L) after 67 days, and that in further downgradient wells NMW-7 and NMW-9 reached *J* values of 0.13 ad 0.10 mg/L, respectively, by Day 146. When system operation became intermittent due to biofouling in the HFTW-U, nitrate concentrations increased rapidly in many of the shallow wells. Interestingly, this increase was much more evident than for perchlorate (See Figure 4.10). A significant reduction in nitrate was also apparent for many of the deep monitoring wells, particularly the downgradient wells (Figure 4.17; Table 4.12). In fact, with the exception of NMW-9, nitrate concentrations in all of the downgradient wells (Row 2 & 3 deep and shallow) declined to < 0.7 mg/L during the initial 146 days of the demonstration (Figure 4.18). Thus, with enough residence time, consistent nitrate treatment appears to have occurred throughout the vertical profile of the Test Plot.

Perchlorate and nitrate biodegraded simultaneously in many of the wells. In some pure culture studies, nitrate has been observed to inhibit perchlorate reduction (Farhan and Hatzinger, 2009; Coates and Achenbach, 2004; Chaudhuri et al., 2002). Based on net energy yield and competitive inhibition, perchlorate is expected to be utilized after oxygen and nitrate, but before sulfate in environments where each of these electron acceptors are present (Hatzinger and Kelsey, 2005; Song and Logan, 2004; Chaudhuri et al., 2002). However, in field studies, the concurrent degradation of nitrate and perchlorate has been observed (e.g., Hatzinger et al., 2009). Thus, laboratory observations, which are primarily gained with pure cultures, may not be particularly relevant in the field, when a variety of denitrifiers and perchlorate-reducing bacteria are present, and where biological processes may be segregated within the structure of an aquifer matrix (see Section 4.4.3.6 for discussion related to aquifer heterogeneity and process segregation).

Unlike perchlorate and nitrate, significant sulfate biodegradation was not apparent in the shallow or deep monitoring wells (Table 4.13 & 4.14). During the final sampling event prior to citric acid injection (Day -7), the average sulfate concentration in all downgradient wells (excluding upgradient wells NMW1 and NMW2) was 13.6 mg/L, and on Day 146, the average concentration was 12.9 mg/L.

Figure 4.16. Nitrate-N Concentrations (mg/L) in Shallow Monitoring Wells during Phase I Evaluation.

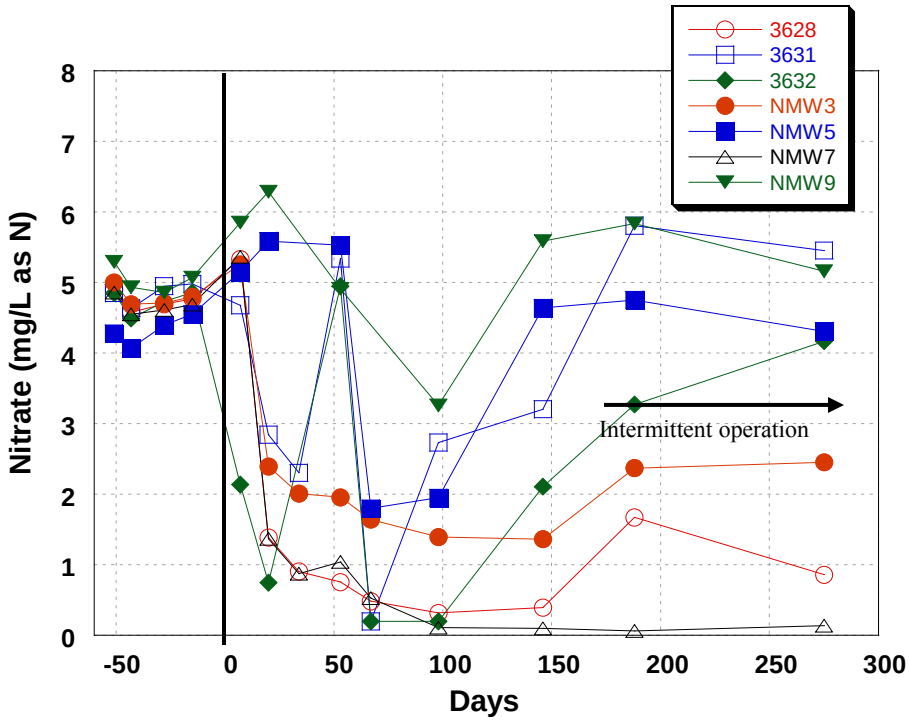


Figure 4.17. Nitrate-N Concentrations (mg/L) in Deep Monitoring Wells during Phase I Evaluation.

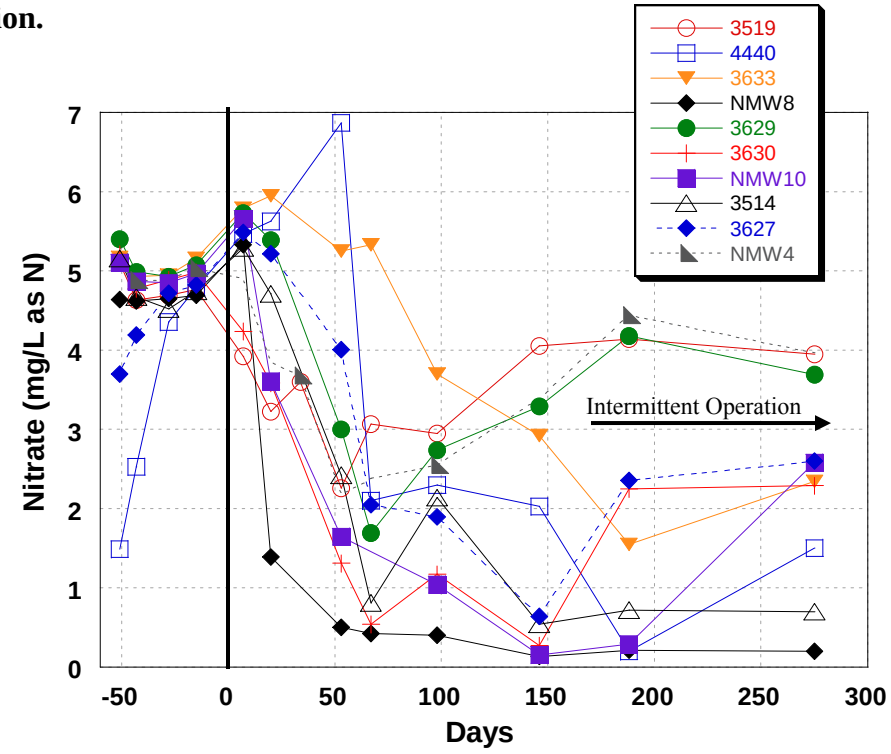


Figure 4.18. Nitrate-N Concentrations (mg/L) in Shallow and Deep Monitoring Wells Distant from the HFTWs – Row 2 & Row 3

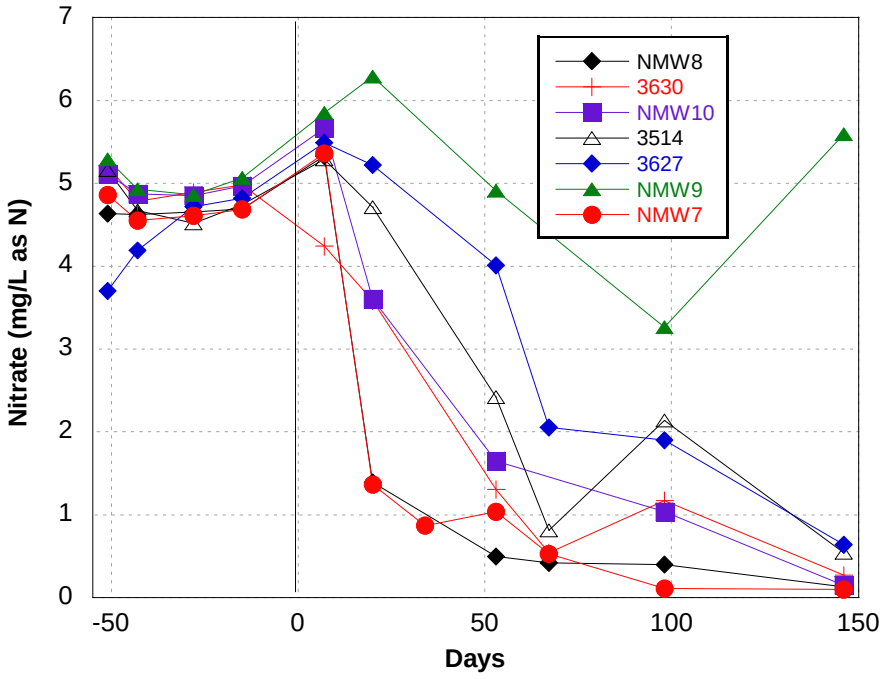


Table 4.11. Nitrate-N Concentrations (mg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/7/04	**-51**	4.85	4.85	4.89	5.62	5.00	4.28	4.86	5.29
9/15/04	**-43**	4.49	4.63	4.58	5.18	4.69	4.07	4.55	4.93
9/30/04	**-28**	4.73	4.95	4.69	5.17	4.71	4.40	4.61	4.86
10/13/04	**-15**	4.98	4.86	4.77	5.24	4.80	4.55	4.68	5.07
11/3/04	**7**	4.68	2.14	5.33	6.02	5.26	5.15	5.36	5.85
11/17/04	**20**	2.84	0.74	1.39	6.50	2.39	5.59	1.37	6.29
12/1/04	**34**	2.30	NS	0.90	NS	2.01	NS	0.87	NS
12/20/04	**53**	5.33	4.95	0.75	6.51	1.96	5.56	1.04	4.91
1/3/05	**67**	0.20	<0.20	0.75	6.50	1.60	1.80	0.53	2.43
2/3/05	**98**	2.73	<0.20	0.32	5.40	1.39	1.95	0.11*J*	3.26
3/21/05	**146**	3.20	2.11	0.39	5.32	1.36	4.64	0.10 *J*	5.59
5/5/05	**188**	5.81	3.27	1.67	5.55	2.37	4.75	0.06 *J*	5.84
8/1/05	**275**	5.45	4.17	0.86	5.15	2.45	4.31	0.14	5.16

* NMW-1 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

Table 4.12. Nitrate-N Concentrations (mg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
9/7/04	**-51**	3.70	1.49	5.10	5.16	5.41	5.21	5.17	2.44	5.31	4.64	5.11
9/15/04	**-43**	4.19	2.53	4.63	4.67	4.99	4.78	4.93	2.22	4.88	4.62	4.87
9/30/04	**-28**	4.72	4.36	4.69	4.52	4.93	4.89	4.95	2.33	4.89	4.65	4.85
10/13/04	**-15**	4.82	4.79	4.77	4.74	5.07	4.98	5.16	2.37	5.03	4.69	4.97
11/3/04	**7**	5.49	5.47	3.92	5.29	5.73	4.24	5.79	2.86	4.90	5.33	5.66
11/17/04	**20**	5.22	5.62	3.23	4.70	5.39	3.59	5.92	2.98	3.85	1.39	3.61
12/1/04	**34**	NS	NS	3.60	NS	NS	NS	5.54	NS	3.68	NS	NS
12/20/04	**53**	4.01	6.84	2.26	2.41	2.99	1.31	5.25	2.85	2.18	0.50	1.65
1/3/05	**67**	2.05	2.10	3.07	0.81	1.69	0.54	5.30	2.90	2.40	0.42	0.52
2/3/05	**98**	1.90	2.30	2.95	2.14	2.74	1.17	3.70	2.35	2.55	0.40	1.04
3/21/05	**146**	0.64	2.03	4.05	0.54	3.29	0.27	2.92	2.61	3.38	0.13 *J*	0.15 *J*
5/5/05	**188**	2.36	<0.20	4.14	0.72	4.18	2.25	1.55	2.67	4.44	0.21	0.29
8/1/05	**275**	2.05	2.10	3.07	0.81	1.69	0.54	5.30	2.90	3.97	0.42	0.52

* NMW-2 is an upgradient control well

NS = Not sampled.

J is an estimated value that was above the MDL but below the PQL

Table 4.13. Sulfate Concentrations (mg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/7/04	**-51**	15.0	15.0	14.4	8.5	13.5	12.9	15.4	11.6
9/15/04	**-43**	13.9	13.8	14.5	9.2	13.4	13.7	14.1	12.4
9/30/04	**-28**	13.1	11.5	13.5	8.2	13.2	13.4	14.1	12.8
10/13/04	**-15**	14.4	13.7	15.7	8.7	14.0	14.4	15.5	13.6
11/3/04	**7**	21.4	17.6	18.7	10.5	17.0	16.3	17.5	15.3
11/17/04	**20**	29.3	18.8	19.7	9.9	17.5	15.8	17.3	15.7
12/1/24	**34**	38.6	NS	19.4	NS	17.4	NS	19.3	NS
12/20/04	**53**	19.4	18.5	17.7	9.1	14.7	10.4	17.0	11.9
1/3/05	**67**	16.3	16.9	16.5	8.8	15.3	15.6	15.6	11.2
2/3/05	**98**	44.1	15.7	14.5	7.8	13.2	11.2	14.7	10.9
3/21/05	**146**	21.5	23.1	14.5	7.9	13.5	9.0	15.1	7.9
5/5/05	**188**	13.8	16.3	12.4	6.7	10.6	7.9	14.5	7.4
8/1/05	**275**	11.4	12.9	14.3	7.1	12.5	8.8	9.9	7.1

* NMW-1 is an upgradient control well
NS = Not sampled.

Table 4.14. Sulfate Concentrations (mg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
9/7/04	**-51**	16.7	11.1	11.1	10.4	10.4	11.3	10.7	40.7	13.3	13.5	13.7
9/15/04	**-43**	13.4	11.6	11.9	12.6	11.2	11.7	11.1	43.1	13.2	13.9	13.1
9/30/04	**-28**	12.4	11.5	11.2	14.2	11.3	11.7	10.6	42.0	12.8	13.3	12.2
10/13/04	**-15**	13.7	12.1	11.9	13.6	12.4	12.5	11.9	46.6	13.7	14.3	13.2
11/3/04	**7**	15.9	13.8	13.1	16.1	15.2	14.5	14.2	50.2	16.0	16.5	15.6
11/17/04	**20**	17.4	13.7	15.4	16.6	15.3	15.6	13.6	53.6	17.0	20.2	14.7
12/20/04	**53**	NS	NS	14.8	NS	NS	NS	14.0	NS	17.1	NS	NS
1/3/05	**67**	12.2	8.8	10.5	11.6	13.5	13.3	11.7	51.3	14.8	16.4	11.6
2/3/05	**98**	12.8	14.2	9.9	10.8	11.1	10.9	10.2	39.0	15.3	13.9	10.7
3/21/05	**146**	12.1	13.3	8.5	11.6	10.3	9.8	10.9	35.3	13.6	14.3	7.6
5/5/05	**188**	15.6	7.2	8.3	10.5	8.8	9.3	11.8	33.4	16.6	10.9	8.5
8/1/05	**275**	15.9	12.9	9.8	9.7	9.2	10.0	11.8	33.1	19.5	8.7	35.1

* NMW-2 is an upgradient control well
NS = Not sampled.

4.4.1.6 Phase I: Oxidation-Reduction Potential

The average ORP in the shallow monitoring wells during the sampling events prior to injection of citric acid was ~ + 250 mV (Figure 4.19; Table 4.15). There was an apparent decline in all wells on Day -15, which was most likely caused by a malfunction in the field meter. The average ORP values in the shallow wells declined to + 92 mV within 20 days, and then to + 25 mV after both 67 and 98 days of operation, respectively. The ORP then increased somewhat to ~ +100 mV. At the end of the 275 days of Phase I, the average ORP in the shallow downgradient wells was + 73 mV. The deep wells (excluding Well 4440, which had a consistently low ORP, perhaps due to the presence of an iron casing), had an average ORP of + 225 during the three events prior to system start-up excluding Day -15 (Days -43, -36, -28) (Figure 4.20; Table 4.16). The ORP values in the deep wells declined to a mean value of + 84 mV within 20 days, and then to + 20 mV after 98 days of operation. At the conclusion of Phase I (275 day), the average ORP in the deep wells was + 65 mV.

4.4.1.7 Phase I: Electron Donor Concentrations

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* (See Figure 3.12). Other possible fatty acid intermediates include lactate, formate and propionate. During the project, fatty acid analysis was conducted to evaluate electron donor concentrations in the wells. The fatty acids measured included citrate, lactate, valerate, acetate, formate, butyrate, and propionate. 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. During some sampling events, the anion chromatographs from EPA Method 300 were reviewed prior to conducting fatty acid analysis, as these compounds elute as a combined peak (i.e., they are not separated during EPA 300.0 but are visible) early in the sample run time. If a peak consistent with combined fatty acids was observed during EPA 300.0, fatty analysis was conducted by IC to separate and quantify the fatty acids.

As expected, citrate was not consistently detected in any of the monitoring wells above the PQL of 2 mg/L during Phase I. The fatty acid was detected at 0.5 mg/L (J value) in NMW-8 and 3.3 mg/L in NMW-10 on Day 135, and in wells 3514, NMW-7, and NMW-8 on Day 275 at 0.5 – 0.7 mg/L. Acetate was observed in several downgradient wells during the demonstration, particularly towards the end of Phase I (Table 4.17 and 4.18). Concentrations ranged from < 1 mg/L (*J* values) to > 20 mg/L. Formate was detected in very low concentration (< 0.5 mg/L *J* values) in a few of the downgradient wells, while lactate and valerate were not detected in any of the wells during Phase I (PQL 1 mg/L). Propionate and butyrate were detected in Well 4440 on Day 188, along with acetate and formate.

Figure 4.19. Oxidation-Reduction Potential (ORP; mV) in Shallow Monitoring Wells during Phase I Evaluation.

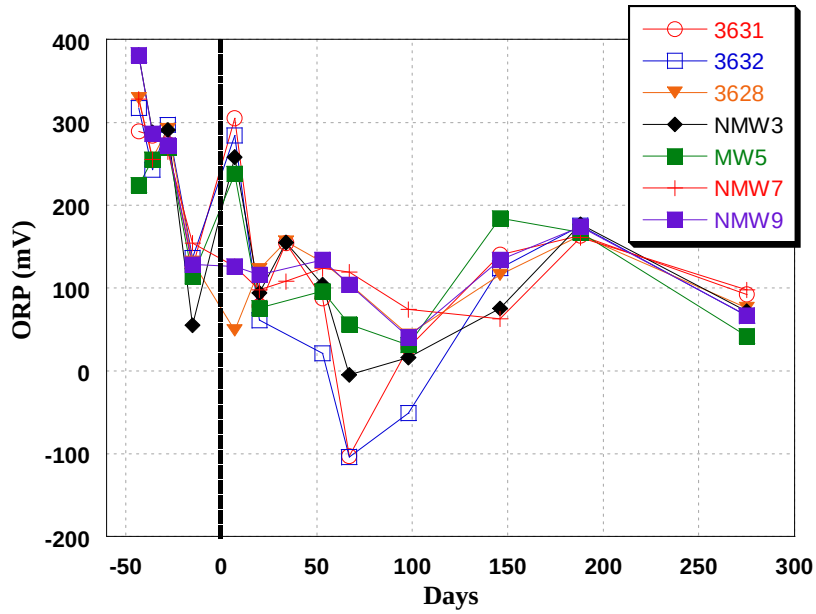


Figure 4.20. Oxidation-Reduction Potential (ORP; mV) in Deep Monitoring Wells during Phase I Evaluation.

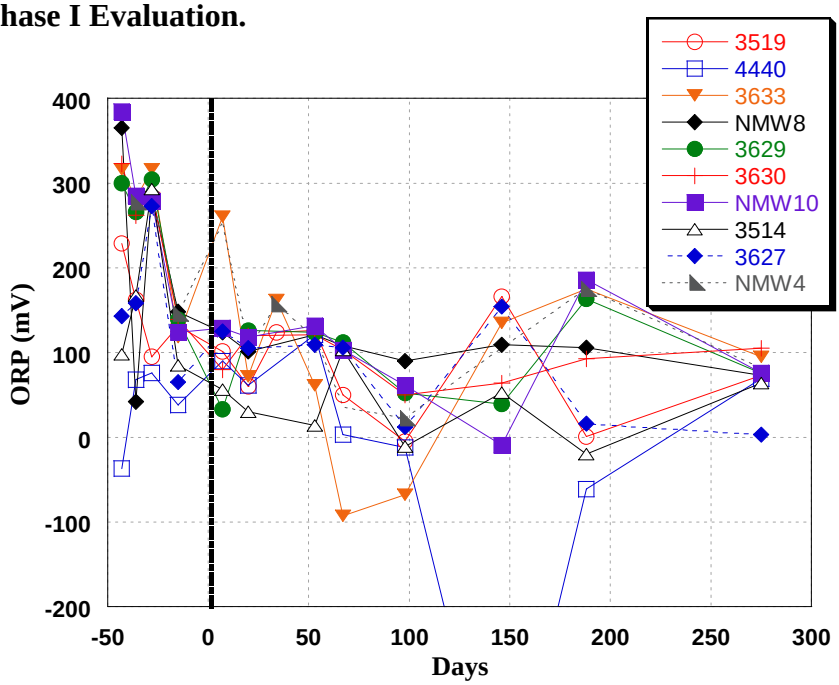


Table 4.15. Oxidation-Reduction Potential (mV) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/15/04	**-43**	289	317	329	48	381	224	328	381
9/22/04	**-36**	284	243	257	280	288	255	255	286
9/30/04	**-28**	274	297	292	283	291	269	265	272
10/13/04	**-15**	125	136	132	24	55	114	154	128
11/3/04	**7**	305	284	49	267	258	238	136	126
11/17/04	**20**	78	61	123	114	94	76	98	116
12/20/04	**53**	88	21	131	111	104	96	124	134
1/3/05	**67**	-103	-104	105	51	-5	56	119	104
2/3/05	**98**	28	-51	44	33	16	31	74	41
3/21/05	**146**	140	124	116	134	75	184	63	134
5/5/05	**188**	163	175	163	96	177	167	161	174
8/2/05	**275**	92	66	76	74	72	42	98	67

* NMW-1 is an upgradient control well

Table 4.16. Oxidation-Reduction Potential (mV) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
9/15/04	**-43**	143	-37	229	98	300	323	316	158	295	365	384
9/22/04	**-36**	158	68	162	167	266	262	281	273	277	42	285
9/30/04	**-28**	273	76	95	293	304	289	316	288	286	288	279
10/13/04	**-15**	65	38	131	85	139	139	118	46	146	148	124
11/3/04	**7**	125	90	101	56	33	80	260	245	254	124	129
11/17/04	**20**	105	61	60	30	126	120	72	108	105	101	118
12/20/04	**53**	109	121	126	14	124	121	61	109	157	121	132
1/3/05	**67**	106	3	50	103	112	103	-93	56	117	108	103
2/3/05	**98**	12	-12	-5	-11	52	50	-68	41	36	90	61
3/21/05	**146**	154	-473	166	53	39	64	135	146	22	109	-9
5/5/05	**188**	16	-61	1	-20	163	93	175	96	105	106	186
8/2/05	**275**	3	69	73	64	75	105	95	72	175	73	76

* NMW-2 is an upgradient control well

Table 4.17. Acetate Concentrations (mg/L) in Shallow Monitoring Wells during Phase I Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
9/15/04	**-43**	< 1	< 1	< 1	<1	< 1	< 1	< 1	< 1
11/3/04	**7**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
12/20/04	**53**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
1/3/05	**67**	8.1	10.1	< 1	< 1	< 1	< 1	< 1	< 1
2/3/05	**98**	< 1	8.2	< 1	< 1	< 1	< 1	< 1	< 1
3/21/05	**146**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
5/5/05	**188**	< 1	< 1	< 1	< 1	< 1	0.16*J*	< 1	0.17 *J*
8/2/05	**275**	< 1	0.65	< 1	< 1	< 1	< 1	16.1	< 1

* NMW-1 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

Table 4.18. Acetate Concentrations (mg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
9/15/04	**-43**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
11/3/04	**7**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
12/20/04	**53**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
1/3/05	**67**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2/3/05	**98**	< 1	0.68	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
3/21/05	**146**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	8.9
5/5/05	**188**	< 1	6.95	< 1	< 1	< 1	< 1	0.38 *J*	0.18 *J*	0.21 *J*	0.80 *J*	0.20 *J*
8/2/05	**275**	< 1	0.94	< 1	0.47	< 1	< 1	< 1	< 1	< 1	20.6	< 1

* NMW-2 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

4.4.2 Biofouling Treatment and Well Redevelopment

4.4.2.1 Biofouling Treatment

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 12/09/2004 (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 (Figure 4.21). The head level increased by approximately 5 ft in the lower screen interval (injection screen) while the chlorine dioxide system was non-functional (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. Interestingly, the pressure in the upper zone (extraction screen) of the downflow well also increased beginning around Day 50. This increase would be inconsistent with biofouling in this zone as water is being pulled in through the screen, rather than pushed out. Thus, biofouling in this area should cause a decline in head levels, and a subsequent pressure drop. The pressure increase in this zone may have actually reflected an increased water table elevation due to the significant rainfall in the area during the winter of 2004-2005 The water table elevation in the shallow monitoring wells increased by approximately 4.2 ft between 12/20/2004 (Day 42) and 2/03/2005 (Day 98). Most of the increase (~ 3.7 ft) occurred after 1/03/2005 (Day 67), which is coincident with the time during which the shallow screen of the HFTW experienced approximately 6 ft of head increase.

An increase in hydraulic head in the upper screen of the upflow well (injection screen) was also observed beginning around Day 50 (Figure 4.21). The pressure in this zone gradually increased through Day 100, at which time the transducer reached it's 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.

The application for biofouling treatment of specialty enzymes capable of dissolving polysaccharides and other polymers was initially investigated in the laboratory in conjunction with the University of New Mexico (see Section 3.4.4). During laboratory testing, a mixed enzyme solution derived from *Aspergillus niger* was observed to be highly effective at removing biomass from sand columns and restoring flow through sand columns at low pressure. Based on these data, an enzymatic approach was tested in the field with the upflow and downflow HFTW. On 6/7/2005, a large dose of citric acid was added to each well to reduce pH below 5.0, then a 55-L solution of commercial enzyme (Pectinex Ultra SL; Novozymes North America, Franklinton, NC) was injected in the upper screen interval of the upflow HFTW. A 20-L solution of laboratory-prepared enzyme was subsequently injected into the downflow HFTW for comparison. This second solution was fermented from *A. niger* at the University of New Mexico. The enzyme solutions were recirculated, and then allowed to incubate for approximately 14 days to reduce microbial biomass and polysaccharides in the wells. Pressure measurements taken before and after the enzyme procedure showed pressure decreases of ~ 40 % due to the enzyme treatment. We believe that with more thorough mixing (i.e., with a well specifically designed to provide good internal mixing), the effectiveness of this treatment could be improved further. However, the data suggest that enzymatic treatment can be useful approach to remove biomass from fouled wells. After the treatment, full system flow was again achieved (~ 6 gpm in the upflow HFTW and 9 gpm in the downflow HFTW) without significant leakage from the upflow well.

Unfortunately, the chlorine dioxide system failed within a week of conducting the enzyme treatment, and pressure again increased in the HFTW screens. Thus, the long-term effectiveness of the enzymatic biomass removal could not be readily determined. At this time, the decision was made to physically redevelop the HFTWs, and to make system modifications to prevent leakage from the upflow well. It should be noted that although biofouling occurred near the lower well screen of the downflow HFTW based on pressure readings, the design of this well (particularly the ability to pump water through a custom packer) allowed continuous operation of this well for more than 7 months. The operation was not significantly affected by the pressure increases in the lower screen zone.

4.4.2.2 Well Redevelopment, System Modification and Restart

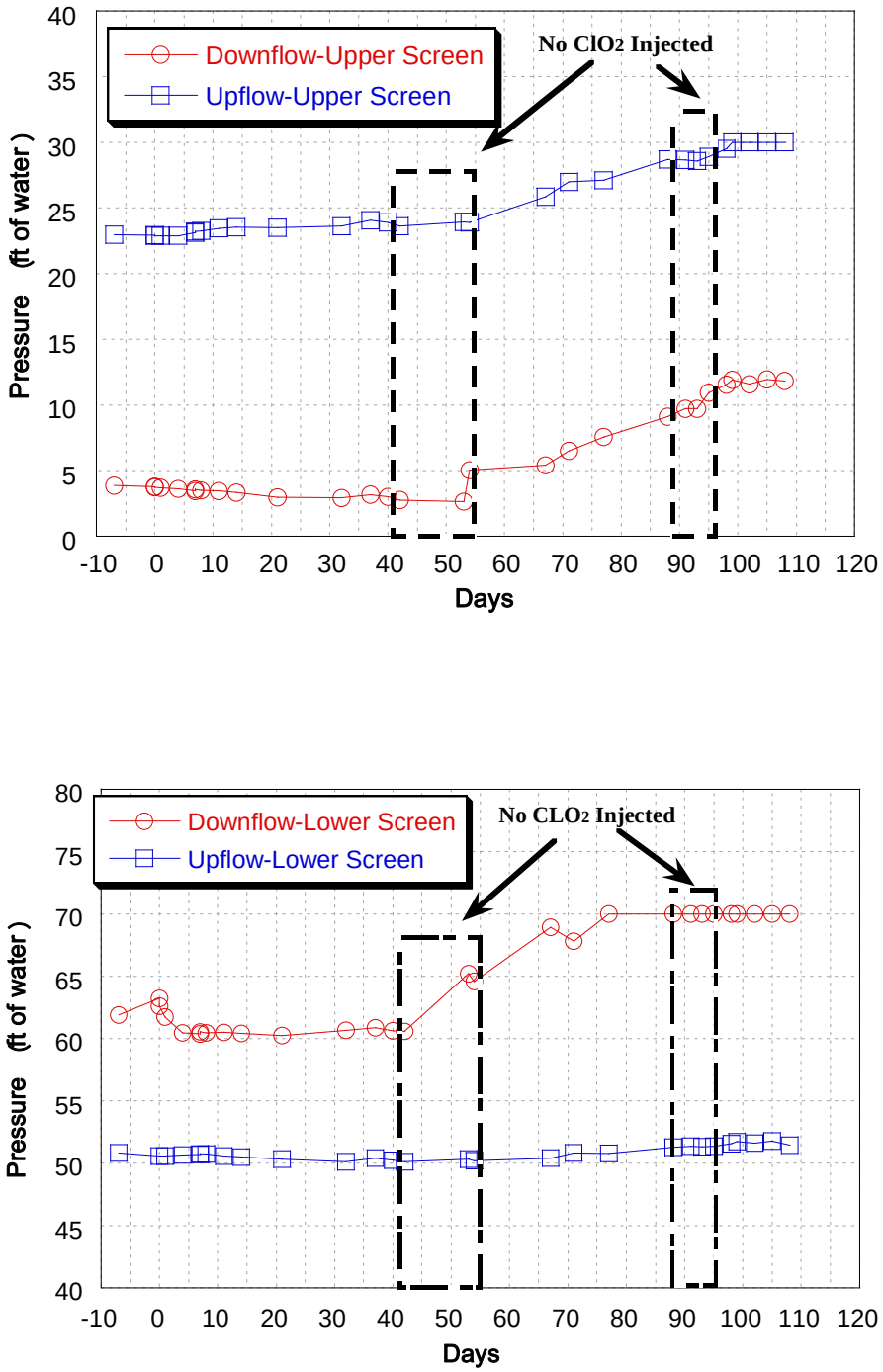
The upflow and downflow HFTWs were physically redeveloped in October, 2005 under Subcontract to Layne Christensen Co., Sacramento, CA. The downflow pumps, packers, and additional equipment in each well were removed by crane and each well was subjected to the following redevelopment procedure to remove biomass, mineral deposits and other materials fouling the well screens:

1. A chemical mixture consisting of QC-21 Well Cleaner (Layne Christensen, Co) and hydrochloric acid mixed with approximately 4,000 liters of water was added to each well.
2. Mechanical swabbing was performed for 4 to 6 hrs following chemical injection.
3. The pH in each HFTW was adjusted to between 4.5 and 5.0 SU and a sodium hypochlorite solution was injected.
4. Steps 2 and 3 were repeated in order.
5. Airlift swabbing and well development were conducted until the total settleable solids in each well were < 0.05 mg/L (via the Imhoff Cone method; US EPA Standard Method 2540F; http://www.epa.gov/region09/lab/sops/sop463.html).

The lines, transducers, pumps, and packers were inspected and cleaned by hand. The transducers in the lower zone of the downflow well and the upper zone of the upflow well were replaced with new units capable of reading higher pressures. In order to prevent subsequent issues with the upflow well, a new well cap capable of holding significant pressure was fitted to the upflow well. The upflow HFTW was also equipped with a bypass line to return groundwater directly to the downflow HFTW during any periods of excessive pressure (> 10 psi). This shunt was designed to ensure that water was not released to the ground surface through the well cap and to maintain safe working pressure levels within this well.

The system rehabilitation was completed in November, 2005 after several back-ordered parts were received and installed. A series of additional system maintenance activities were performed to correct electronic issues associated with the SCADA system. These issues resulted from the replacement and/or recalibration of the transducers. The HFTW system was subsequently restarted in a continuous flow mode in late-November, 2005. The second bromide tracer test described in Section 4.4.1.1 was conducted after all redevelopment work was completed. Phase II of system operation and testing, described in the subsequent sections of this report, was conducted after the redevelopment work was complete.

Figure 4.21 Pressure Levels in Upper (Top Panel) and Lower (Bottom Panel) Screens of the HFTWs.



4.4.3 Phase II & Phase III Operation

4.4.3.1 Phase II Operating Conditions

Once the well rehabilitation was complete, a 15-day bromide tracer test was conducted in HFTW-D (1/30/2006 – 2/13/2006). The results of this test were detailed in Section 4.4.1.1 and Appendix E. Upon the completion of this test, a second phase (Phase II) of treatment was implemented. The key objectives of Phase II, were primarily (1) to determine if the electron donor and chlorine dioxide dosing strategy could be modified to significantly reduce biofouling, which was the major O&M issue during Phase 1; and (2) to evaluate whether the treatment of perchlorate and VOCs could be enhanced from Phase I. Phase II was conducted from 2/15/2006 (Day 473) to 7/05/2006 (Day 614).

Electron donor was not injected from the end of Phase I until the beginning of Phase II operation. During Phase II the HFTWs were operated continuously at a net flow rate of 6 gpm as in Phase I. All 19 monitoring wells were sampled on 2/13 through 2/14, 2006, to provide baseline concentrations of perchlorate, nitrate, and VOCs for Phase II. After this sampling event, citric acid addition was again initiated. The first injection for Phase II occurred on 2/15/2006. 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. Larger, less frequent doses of citric acid are expected to (1) reduce the pH in the vicinity of the injection screens, possibly killing some bacterial biomass; (2) chelate precipitated iron and manganese, and (3) provide a less consistent source of carbon for bacterial growth at the injection screens. On 2/15 – 2/17, 2006, 45L 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 3/16/2006 (~ 2X stoichiometry), then this dosing was doubled between 3/27/2006 to 6/20/2006 (~ 4X stoichiometry), by adding 15 L to each HFTW two times per week (spaced at 3.5-day intervals). Chlorine dioxide was added to each well on a daily basis (4 – 8 X per day) from 2/15/2006 – 4/12/2006, then reduced to one dose only after citric acid injection from 4/12/2006 – 6/20/2006.

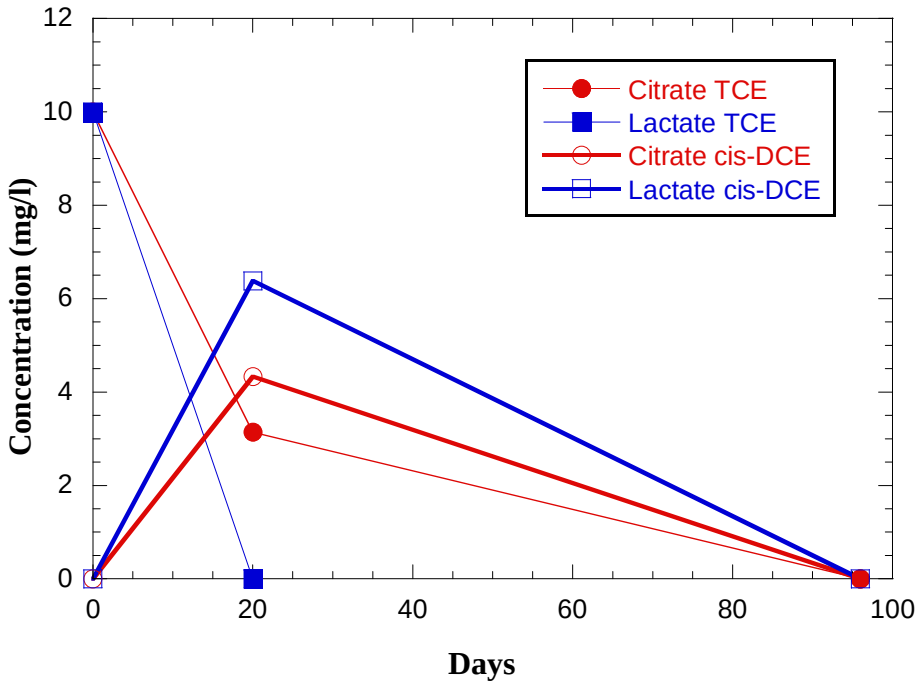
In order to optimize rates and extents of TCE degradation within the plot, both the upflow and downflow HFTW were augmented with bacterial culture SDC-9 on 4/05/2006. Each well received approximately 36L of the concentrated inoculum, which contained 2.7 X 10^8 cells of *Dehalococcoides* per mL based on qPCR analysis. This culture was grown in a 4,000 L fermentor located in the Shaw's Lawrenceville, NJ laboratory, then concentrated approximately 10X prior to shipping to the site. Doses of citric acid (15 L) were added to each well before and after the inoculation in order to lower redox as much as possible (doses added on 4/4/2006; 4/5/2006; 4/7/2006, 4/12/2006). One of the potential issues with *Dehalococcoides* inoculation of the HFTW treatment wells is the constant influx of oxygenated water to the system during active pumping. Inoculation of downgradient monitoring wells (where reduction potential and dissolved oxygen are generally lower) was considered as a secondary option, but the

analytical data from these monitoring wells could then be considered compromised, so this was not performed. Preliminary studies showed that SDC-9 could utilize citric acid as an electron donor during reductive dechlorination (Figure 4.22), and the decision was made to inoculate into the HFTWs despite the expected presence of oxygen in the groundwater.

4.4.3.2 Phase III Operating Conditions

A final mode of HFTW system operation (Phase III) was implemented for three months from 9/11/2006 – 12/01/2006. 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, enhanced reductive dechlorination of TCE, and the potential for significantly 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-h pulses (followed by chlorine dioxide as a biocide), resulting in the addition of approximately 60 L of electron donor per 12-h cycle and 180-L per injection event. 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 (9/6/2006) to provide a baseline, and a final round was performed on 1/08/2007. The system was shut-down at the end of the sixth round of citric acid injection, which was completed on 12/1/2006.

Figure 4.22. Biodegradation of TCE and Resulting cis-DCE by Culture SDC-9 after Growth on either Citrate or Lactate.



4.4.3.3 Phase II & III: Perchlorate Treatment

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 3.6). Perchlorate concentrations rebounded appreciably in most shallow monitoring wells between Day 275, the last day for sampling in Phase I, and Day 472, (the background sampling event conducted just prior to the initiation of Phase II (Table 4.19). Values in most wells increased from < 100 μg/L on Day 275 to > 900 μg/L on Day 472. It is interesting to note however, that perchlorate concentrations in most of the shallow wells on Day 275 were appreciably below their initial concentrations prior to system start-up and electron donor addition, which generally exceeded 2,000 μg/L (Day -51; Table 4.3). As was observed in Phase I, perchlorate concentrations in all of the downgradient shallow wells declined rapidly during Phase II (Figure 4.23; Table 4.19). 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 of ~ 4 X stoichiometry in the HFTW-U through most of the Phase II treatment. This electron donor dosage was increased from a maximum of 2.5X stoichiometry during Phase I.

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 may reflect an increased residence time of water in this region of the aquifer while the HFTWs are not pumping. Both wells are directly downgradient of the HFTW-U (see Figures 3.24 and 4.1), and are likely to receive a significant continuous influx of upgradient groundwater (i.e., with perchlorate, nitrate, and oxygen) during active pumping of the HFTW system. With the system shut down during "passive" treatment, there is a greater potential reaction time in the vicinity of these wells, as upgradient water is not circulated through the plot. This increased reaction time probably resulted in the significantly lower perchlorate concentrations in this region observed during Phase III. The other shallow wells are further downgradient, and thus much less impacted by the pumping system.

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 $\pm$ 4 % reduction in dissolved perchlorate from the starting concentration in each well prior to Phase I (Day -7) and an average 94 $\pm$ 3% reduction from perchlorate concentrations prior to Phase II (Day 472) (Figure 4.24). 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 a 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 non-treated and treated groundwater, potentially within the screen interval of the well (i.e., due to heterogeneities in the aquifer) (see Section 4.4.3.6 for discussion).

Interestingly, in Phase II and particularly Phase III, declines in sulfate concentrations, TCE concentrations, and increases in both soluble iron and manganese were apparent in many wells that still had residual perchlorate. For example, in NMW-7, perchlorate concentrations ranged from 26 – 117 μg/L during operation in Phases II & III (declining from 992 μg/L on Day 472 at the beginning of Phase II). During the same period, sulfate concentrations declined from 22.6 mg/L (Day 472) to as low as 2.6 mg/L (Day 760), soluble Fe increased from 186 to 1810 μg/L, soluble Mn increased from 430 to 2150 μg/L, and TCE concentrations declined from 2500 to 470 μg/L. Moreover, in this well, residual acetate concentrations ranging from 16 to 183 mg/L were present from the end of Phase II (Day 614) to the end of Phase III (Day 801) even though perchlorate never reached < 4 ug/L in the well. This observation, which is discussed further in Section 4.4.6, suggests that appreciable quantities of electron donor were utilized by sulfate-reducing, as well as Fe- and Mn-reducing bacteria, even though low quantities of perchlorate were still present.

Perchlorate concentrations in many of the deep wells declined between Day 275 (the final day of Phase I) and Day 472 (the background sampling event prior to Phase II) (Table 4.20). This is in contrast to data from the shallow wells, most of which showed a significant rebound during this interim period. The data suggest that perchlorate continued to slowly biodegrade in the deep zone throughout the interim period in which well rehabilitation tests and well redevelopment were conducted. Considering only the Phase II and Phase III data, however, the perchlorate concentrations in the deep downgradient monitoring wells showed a much less consistent pattern of decrease than did the shallow wells during the same interval (Figure 4.25; Table 4.19). Perchlorate declined appreciably in wells NMW-8, 3630, and 4440 during the two phases. In addition, the far downgradient wells 3514 and 3627, showed appreciable declines in perchlorate at the end of Phase III. Wells 3633, 3519, and 3629 showed no pattern of consistent decline. However, based on tracer testing, two of these wells (3633 and 3629) were observed to not be well connected to the HFTW system (see Figure 4.9 and Appendix E). Rather, significant dispersion of the tracer cloud was apparent for these wells suggesting that the water from the HFTW was significantly diluted with untreated water. It is also possible that more of the fluid (water with electron donor) injected into the HFTW-D was short-circuiting directly to the HFTW-U than predicted by model simulations (i.e., horizontal flow in Figures 3.22 and 3.23). Thus, the amount of water and electron donor entering the downgradient deep zone may have been less than anticipated based on the flow and transport model predictions. This type of short-circuiting could also account for the low concentrations of tracer reaching some of the deep wells, such as 3633 and 3629.

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 $\pm$ 39 % from the starting perchlorate concentration in each well prior to Phase I (Day -7) (Figure 4.26) and an average 52 $\pm$ 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 4.1), the total perchlorate reduction during the 801 day demonstration was 88 $\pm$ 9%. Thus, reasonable perchlorate treatment occurred in the deep zone, particularly considering results from the far downgradient wells, although the final concentration in this zone was higher than in the shallow wells and the results were clearly not as consistent.

Figure 4.23. Perchlorate Levels in Shallow Downgradient Monitoring Wells – Phase II & III.

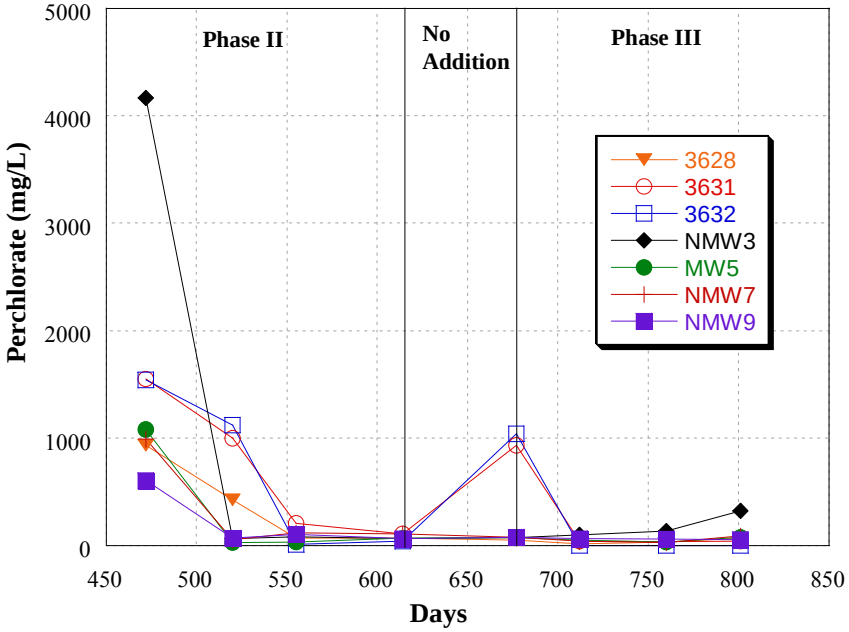


Figure 4.24. Perchlorate Levels in Shallow Downgradient Monitoring Wells during the Entire Demonstration.

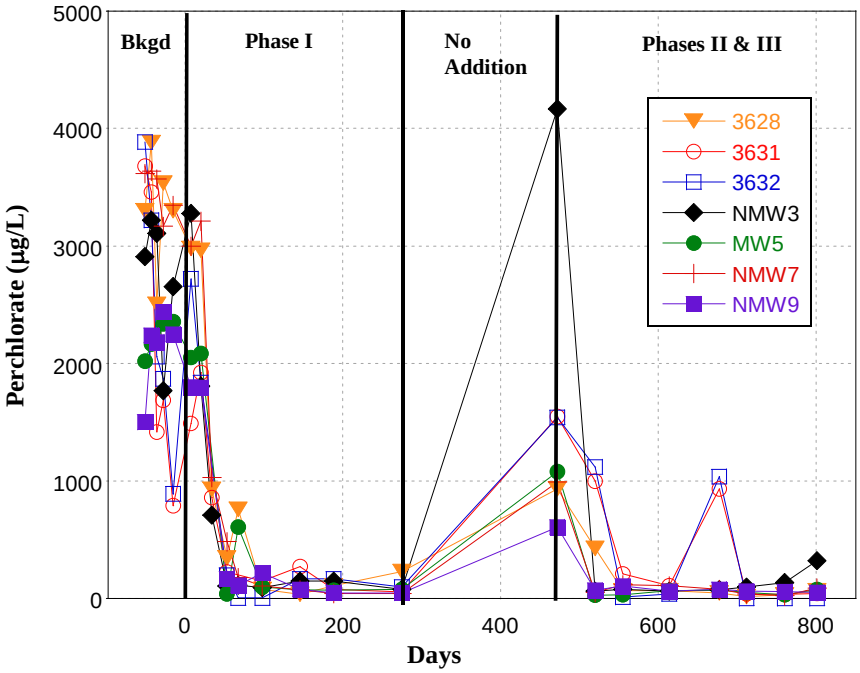


Figure 4.25. Perchlorate Levels in Deep Downgradient Monitoring Wells – Phase II & III.

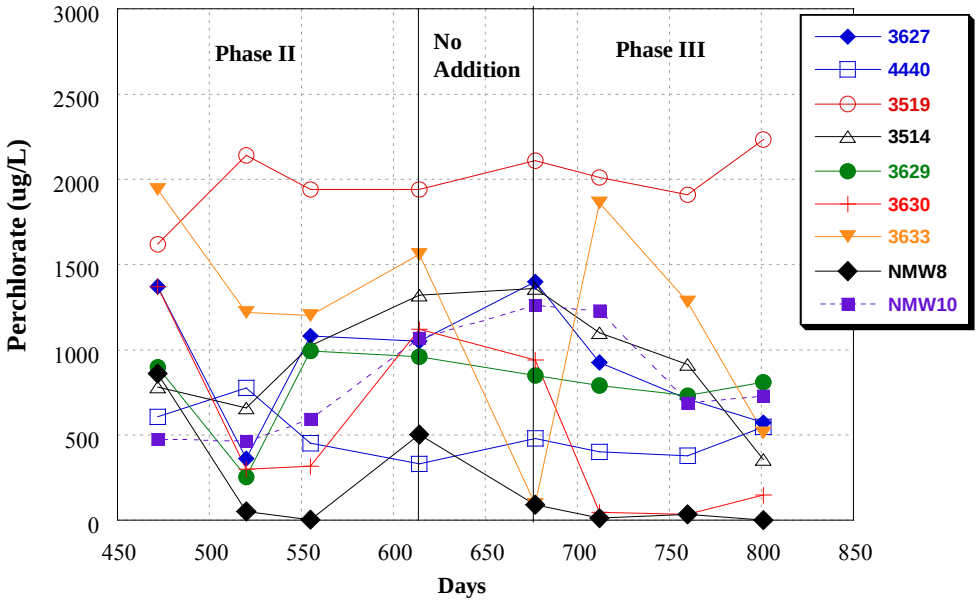


Figure 4.26. Perchlorate Concentrations in Deep Downgradient Monitoring Wells during the Entire Demonstration.

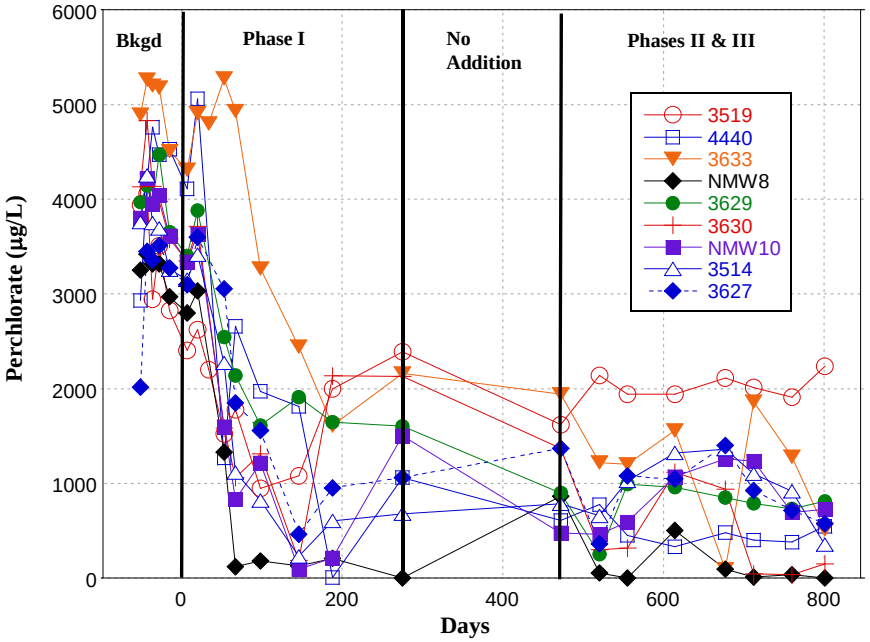


Table 4.19. Perchlorate Concentrations (μg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	275	56	99	228	1570	80	76	44	49
Phase II									
2/14/06	472	1550	1540	932	4880	4170	1080	992	607
4/03/06	520	1000	1120	428	3530	62	28	52	69
5/08/06	555	209	12	68	1460	79	31	117	105
7/05/06	614	110	40	67	1290	62	67	107	64
Phase III									
9/06/06	677	933	1040	49	1080	74	72	76	78
10/11/06	712	40	<2.5	15	861	97	51	41	63
11/28/06	760	36	<2.5	33	755	136	33	26	58
1/08/07	801	42	<2.5	67	710	321	76	90	52

* NMW-1 is an upgradient control well

Table 4.20. Perchlorate Concentrations (μg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
8/01/05	275	1060	1060	2390	677	1600	2130	2160	1480	<2.5	5000	1500
Phase II												
2/14/06	472	1370	607	1620	782	898	1370	1940	700	861	4050	474
4/03/06	520	360	775	2140	658	253	298	1220	1400	53	4450	462
5/08/06	555	1080	450	1940	1025	992	315	1202	1250	3	4720	592
7/05/06	614	1050	330	1940	1320	960	1120	1560	1320	502	4460	1070
Phase III												
9/06/06	677	1400	481	2110	1360	849	939	93	1350	92	4040	1260
10/11/06	712	924	400	2010	1100	790	45	1860	1060	11	3740	1230
11/28/06	760	711	377	1910	915	730	35	1280	1130	36	4320	690
1/08/07	801	574	546	2235	355	809	148	515	1190	< 2.5	5000	727

* NMW-2 is an upgradient control well

4.4.3.4 Phase II & III: Mobilization of Iron and Manganese

Soluble Iron (Fe) and Manganese (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 4.27; Tables 4.21 & 4.22). 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 12/1/2006 (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) (Tables 4.23 & 4.24; Figure 4.28). 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 3,000 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 shown in Figure 4.28. 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 4.27. Soluble Iron Levels in Downgradient Monitoring Wells during the Entire Demonstration.

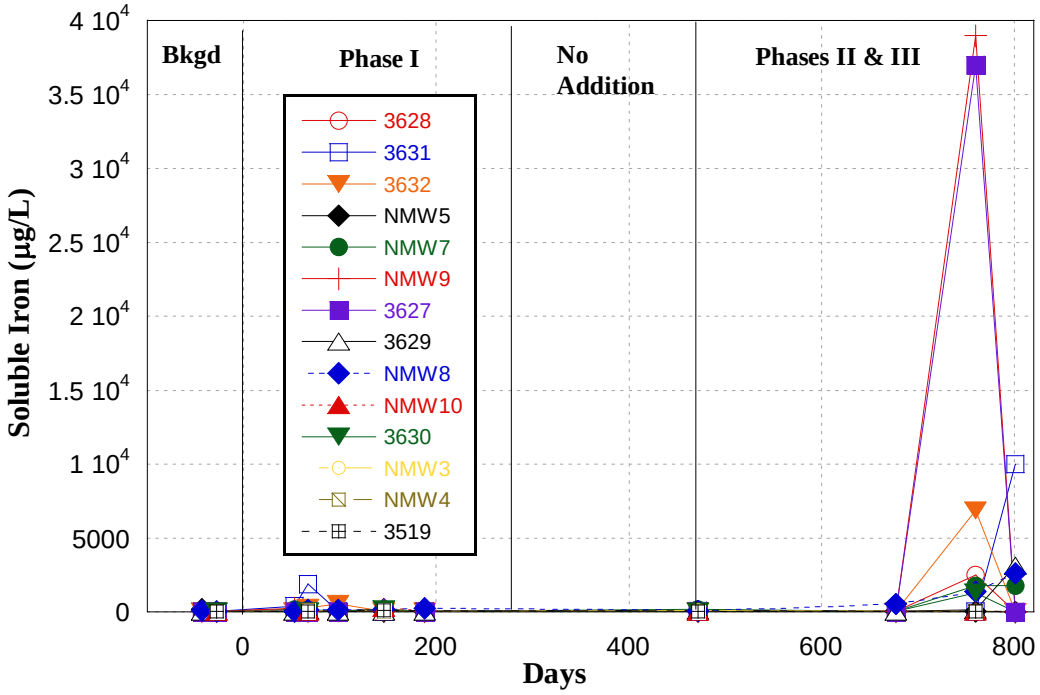


Table 4.21. Iron Concentrations (µg/L) in Shallow Monitoring Wells during Phase II & Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
5/05/05	188	<27	<27	<27	<27	<27	<27	<27	<27
Phase II									
2/14/06	472	<27	<27	<27	33	94	<27	186	<27
Phase III									
9/06/06	677	<30	<30	<30	<30	<30	<30	<30	<30
11/28/06	760	<27	6870	2520	86	29	<27	1810	39000
1/08/07	801	10000	< 14.5	< 14.5	< 14.5	< 14.5	< 14.5	1810	< 14.5

*NMW-1 is an upgradient control well.

Table 4.22. Iron Concentrations (μg/L) in Deep Monitoring Wells during Phase I Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
05/05/05	**188**	28	41000	88	4700	<27	<27	<27	80	276	< 27	34
Phase II												
2/14/06	**472**	<27	841	<27	2120	102	<27	<27	<27	74	50	52
Phase III												
9/06/06	**677**	<30	518	<30	725	<30	<30	<30	<30	556	<30	<30
11/28/06	**760**	37000	5890	<27	268	170	1300	<27	<27	1400	54	<27
1/08/07	**801**	<15	<15	<15	197	3130	<15	<15	<15	2610	<15	<15

*NMW-2 is an upgradient control well

.

Figure 4.28. Soluble Manganese Levels in Downgradient Monitoring Wells during the Entire Demonstration.

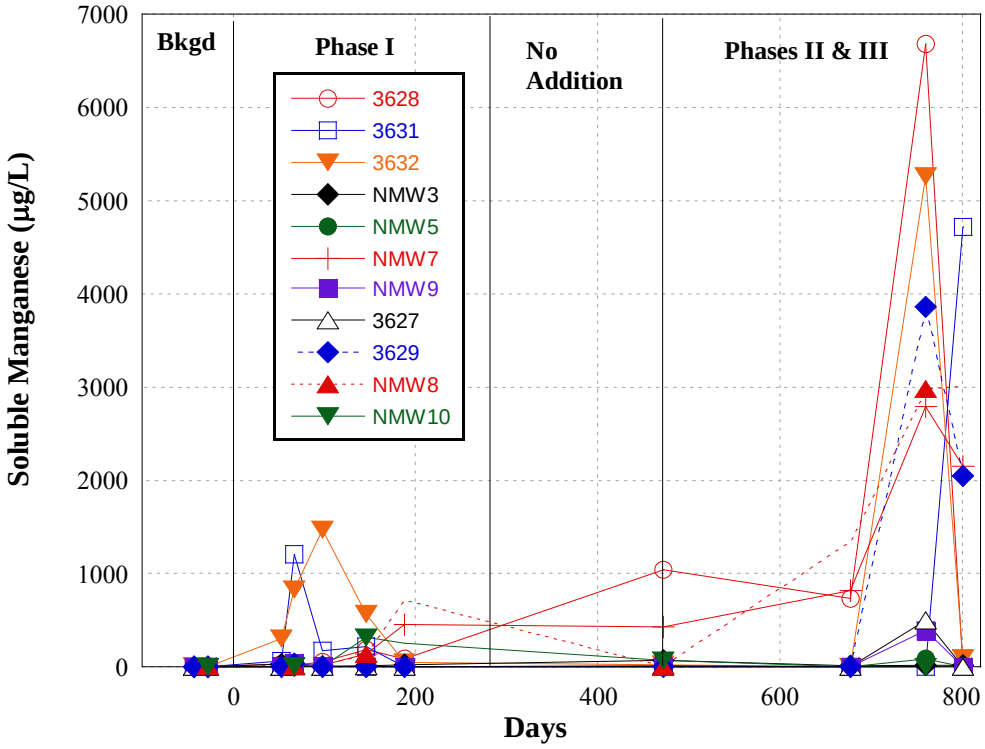


Table 4.23. Manganese Concentrations (μg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
5/05/05	**188**	0.40	44	88	1.7	23	0.3	452	0.50
Phase II									
2/14/06	**472**	4.1	22	1040	0.66	69	<0.11	430	<0.11
Phase III									
9/06/06	**677**	<0.11	0.59	734	<0.11	11	<0.11	818	<0.11
11/28/06	**760**	<0.11	5260	6680	<0.11	16	89	2790	390
1/08/07	**801**	4720	92	<0.50	<0.50	15	<0.50	2150	<0.50

*NMW-1 is an upgradient control well.

Table 4.24. Manganese Concentrations (μg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-4	NMW-8	NMW-10
5/05/05	**188**	3.0	1890	15	131	<0.11	72	20	2.2	0.57	715	250
Phase II												
2/14/06	**472**	12	552	5.5	97	1.18	171	11.20	<0.11	<0.11	<0.11	68
Phase III												
9/06/06	**677**	0.11	205	3.3	25	<0.11	2.25	3.5	<0.11	<0.11	1340	<0.11
11/28/06	**760**	499	522	1850	15	3860	1640	3790	<0.11	0.19	2980	<0.11
1/08/07	**801**	0.50	32	0.50	23	2050	0.50	93	<0.50	<0.50	3010	<0.50

*NMW-2 is an upgradient control well.

4.4.3.5 Phase II & Phase III: 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 4.15; Table 4.9).

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. (SDC-9) was injected into the HFTWs during Phase II in order to enhance reductive dechlorination.

TCE concentrations in many of the shallow wells declined significantly during Phase II and Phase III (Table 4.25, Figure 4.29 & 4.30). There was a 76 $\pm$ 23% reduction in total TCE in all of 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 $\pm$ 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. Unlike Phase I, cis-1,2-DCE (the initial reductive degradation product of TCE) was detected at high concentrations (>1,000 μg/L) in three of the shallow wells (3628, 3632, and NMW-7) (Table 4.27) 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). Vinyl chloride (VC) was only detected during the last sampling event (Day 801) in Well 3632. All other wells were below the RL of 5 μg/L during Phase II and Phase III. It is difficult to accurately determine role of the SDC-9 culture in reducing TCE concentrations throughout the shallow zone without having a control plot in which only electron donor was added. The culture was added primarily to ensure that *Dehalococcoides* spp. were present in the treatment plot, and because TCE dehalogenation has been observed to stall at *cis*-1,2-DCE during reductive dechlorination in this aquifer (Geosyntec, 2003; Hatzinger et al., 2008) However, 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 (e.g., Figure 4.29 & 4.30).

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 (Table 4.26, Figure 4.31 & 4.32). 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 possibility 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.

Interestingly, 1,1-DCE was detected in several of the monitoring wells throughout the demonstration, at levels ranging from 28 to 270 μg/L (Tables 4.29 & 4.30). This compound is not generally considered a common daughter product from reductive dechlorination of TCE. However, one of the *Dehalococcoides* strains that has received extensive study in the laboratory (*D. ethenogenes* 195) has been observed to produce 1,1-

DCE as a transient intermediate during reductive dechlorination of chlorinated ethenes (Mayo-Gattell et al., 1999). It should also be noted, however, that 1,1-DCE can be formed by other mechanisms, including the abiotic dechlorination of both TCE and 1,1,1-TCA. Like *cis*-1,2-DCE, this compound was present at the beginning of the demonstration in several wells, and in upgradient well NMW-2 throughout Phase II and Phase III. Thus, the data suggest that it is likely to have formed upgradient (either from biological dechlorination or via an abiotic mechanism) and to have migrated through the plot.

1,1-DCE was present in 7 of the 9 shallow monitoring wells at the beginning of Phase II (Day 472), although not in shallow upgradient well NMW-1, perhaps because the source of this CVOC was deeper in the formation prior to being redistributed by the HFTW pumping system. 1,1-DCE was present at ~ 200 μg/L in NMW-2 (the deeper upgradient well), for the duration of Phase I and Phase II (Table 4.30). During Phase II and Phase III, 1,1-DCE declined appreciably in concentration in all of the shallow wells downgradient wells, reaching < 5 μg/L in all on Day 760. There was rebound in a few shallow wells by Day 801 (the final sampling event after system shut-down), but the data suggest that 1,1-DCE was biodegraded in the plot, particularly during the "active-passive" regimen implemented in Phase III. The *Dehalococcoides*-containing culture SDC-9 has been observed to degrade this compound along with TCE and *cis*-1,2-DCE (*pers comm. Rob Steffan*). There was no clear pattern of change in 1,1-DCE concentrations among the deep wells in Phase II and Phase III, although the highest concentrations were generally observed in the upgradient wells (NMW-2 and NMW-4), and several deep downgradient wells, including 3514, 3519, 3629, and 3630, concentrations were < 5 μg/L during many of the sampling events. Overall, the data suggest that 1,1-DCE was entering the plot from upgradient, rather than produced as a degradation intermediate, and that, at least in the shallow aquifer, the compound was significantly biodegraded during Phase II and Phase III operation.

Figure 4.29. TCE Levels in Shallow Downgradient Monitoring Wells during Phase II & Phase III.

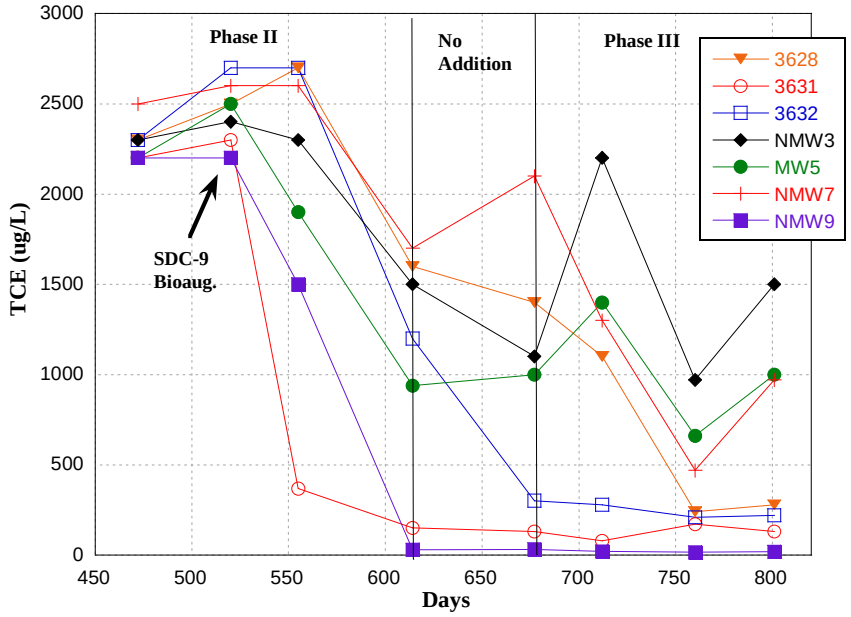


Figure 4.30. TCE Levels in Shallow Downgradient Monitoring Wells during the Entire Demonstration.

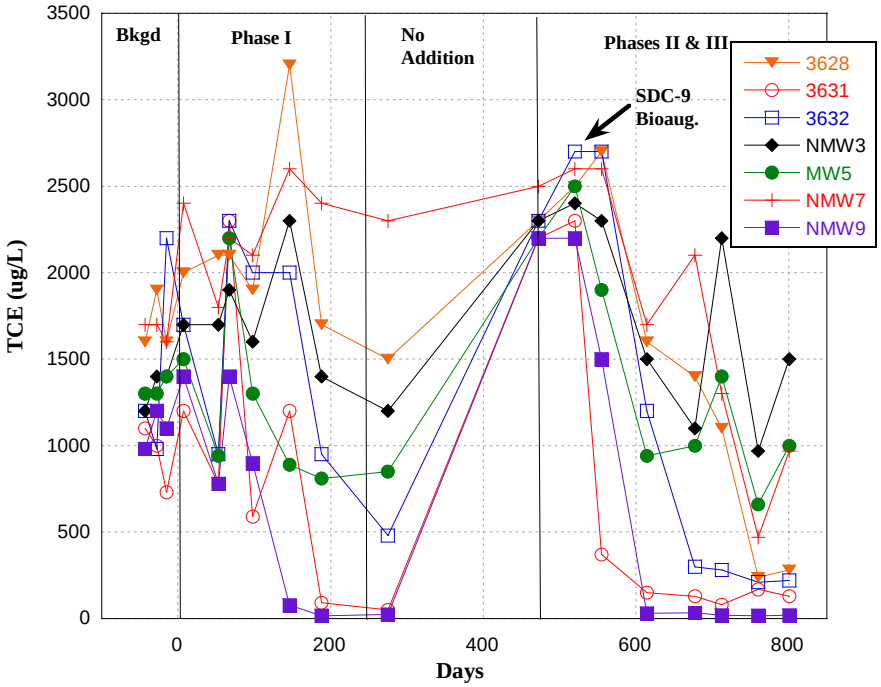


Figure 4.31. TCE Levels in Deep Downgradient Monitoring Wells during the Entire Demonstration.

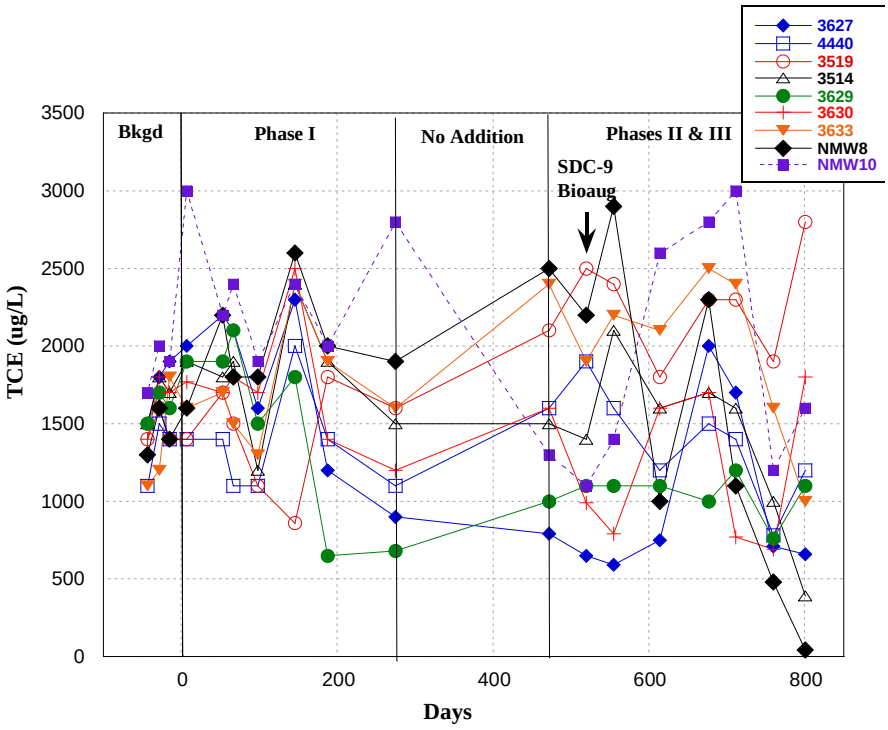


Figure 4.32. TCE Levels in Deep Downgradient Monitoring Wells during Phase II & Phase III.

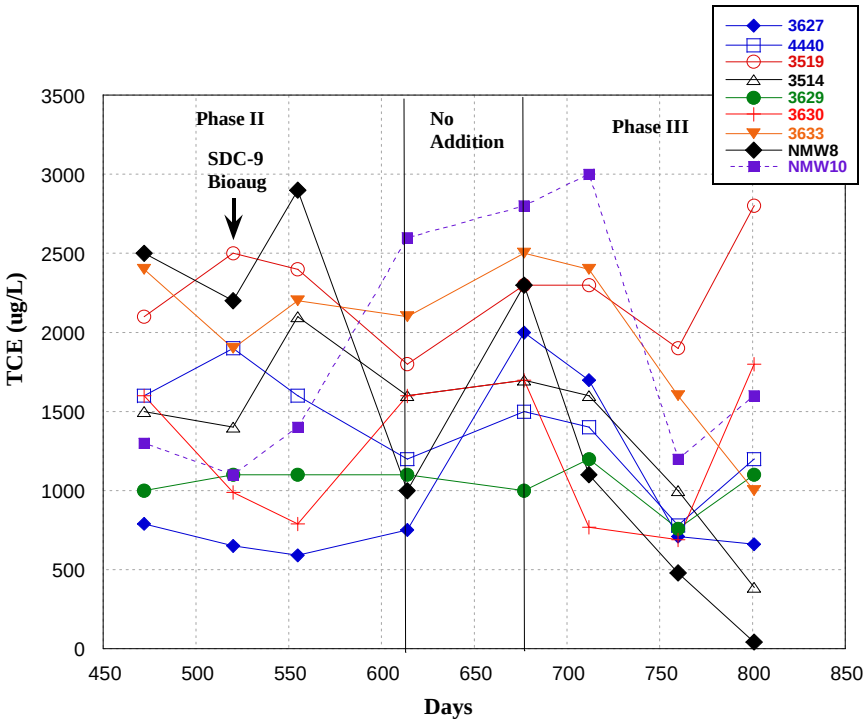


Table 4.25. TCE Concentrations (μg/L) in Shallow Monitoring Wells during Phase II and Phase III Operation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	49	480	1500	170	1200	850	2300	24
Phase II									
2/14/06	**472**	2200	2300	2300	490	2300	2200	2500	2200
4/03/06	**520**	2300	2700	2500	490	2400	2500	2600	2200
5/08/06	**555**	370	2700	2700	240	2300	1900	2600	1500
7/05/06	**614**	150	1200	1600	200	1500	940	1700	30
Phase III									
9/06/06	**677**	130	300	1400	190	1100	1000	2100	33
10/11/06	**712**	79	280	1100	180	2200	1400	1300	20
11/28/06	**760**	170	210	240	130	970	660	470	17
1/08/07	**801**	130	220	280	160	1500	1000	970	19

* NMW-1 is an upgradient control well

Table 4.26. TCE Concentrations (μg/L) in Deep Monitoring Wells during Phase II and Phase III Operation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
8/01/05	**275**	900	1100	1600	1500	680	1200	1600	1300	1900	2900	2800
Phase II												
2/14/06	**472**	790	1600	2100	1500	1000	1600	2400	2800	2500	5000	1300
4/03/06	**520**	650	1900	2500	1400	1100	990	1900	1600	2200	5200	1100
5/08/06	**555**	590	1600	2400	2100	1100	790	2200	3100	2900	5300	1400
7/05/06	**614**	750	1200	1800	1600	1100	1600	2100	2600	1000	2200	2600
Phase III												
9/06/06	**677**	2000	1500	2300	1700	1000	1700	2500	3300	2300	6100	2800
10/11/06	**712**	1700	1400	2300	1600	1200	770	2400	2300	1100	5300	3000
11/28/06	**760**	710	780	1900	1000	760	690	1600	2400	480	4100	1200
1/08/07	**801**	660	1200	2800	390	1100	1800	1000	3100	42	5300	1600

* NMW-2 is an upgradient control well

Table 4.27. Cis-1,2-DCE Concentrations (μg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	ND	ND	30 *J*	ND	ND	ND	58 *J*	ND
2/14/06	**472**	54	ND	57 *J*	ND	61 *J*	67 *J*	59 *J*	72
4/03/06	**520**	ND	ND	<5	ND	ND	ND	56 *J*	ND
5/08/06	**555**	ND	ND	<5	ND	51 *J*	51 *J*	55 *J*	ND
7/05/06	**614**	ND	99 *J*	85 *J*	ND	52 *J*	ND	160	ND
9/06/06	**677**	3*J*	ND	97 *J*	ND	ND	ND	94 *J*	ND
10/11/06	**712**	16	460	1100	ND	53 *J*	ND	190	ND
11/28/06	**760**	23	1700	1000	ND	ND	570	1300	ND
1/08/07	**801**	ND	840	ND	ND	48 *J*	<5	1200	ND

* NMW-1 is an upgradient control well
ND- not detected above MDL
J is an estimated value that was above the MDL but below the PQL

Table 4.28. Cis-1,2-DCE Concentrations (μg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
8/01/05	**275**	22 *J*	75 *J*	ND	43 *J*	ND	ND	ND	ND	ND	50 *J*	ND
2/14/06	**472**	65 *J*	110 *J*	ND	96 *J*	ND	40 *J*	100 *J*	79 *J*	65 *J*	52 *J*	84 *J*
4/03/06	**520**	ND	96 *J*	ND	ND	ND	ND	ND	ND	ND	ND	ND
5/08/06	**555**	ND	180	ND	98 *J*	ND	ND	ND	80 *J*	ND	69 *J*	ND
7/05/06	**614**	ND	140	ND	60 *J*	ND	79 *J*	75 *J*	55 *J*	560	ND	49 *J*
9/06/06	**677**	ND	95 *J*	ND	170 *J*	ND	ND	56 *J*	57 *J*	340	60 *J*	ND
10/11/06	**712**	68 *J*	260	ND	100	ND	770	59 *J*	44 *J*	490	54 *J*	47 *J*
11/28/06	**760**	ND	170	ND	150	ND	370	370	ND	1400	ND	ND
1/08/07	**801**	ND	160	ND	370	ND	250	800	52 *J*	920	79 *J*	ND

* NMW-2 is an upgradient control well
ND- not detected above MDL
J is an estimated value that was above the MDL but below the PQL

Table 4.29. 1,1-DCE Concentrations (μg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	ND	ND	45 *J*	ND	43 *J*	ND	98 *J*	ND
2/14/06	**472**	100 *J*	110 *J*	100 *J*	ND	97 *J*	89 *J*	110 *J*	79 *J*
4/03/06	**520**	99 *J*	120 *J*	110 *J*	ND	89 *J*	100 *J*	110 *J*	86 *J*
5/08/06	**555**	ND	240 *J*	140	ND	120	120	140	ND
7/05/06	**614**	ND	58 *J*	68 *J*	ND	69 *J*	ND	89 *J*	ND
9/06/06	**677**	4 *J*	ND	ND	ND	48 *J*	ND	100 *J*	3 *J*
10/11/06	**712**	ND	ND	140	ND	110 *J*	ND	71 *J*	2 *J*
11/28/06	**760**	ND	ND	ND	ND	ND	ND	ND	ND
1/08/07	**801**	ND	ND	ND	ND	45 *J*	ND	110 *J*	ND

* NMW-1 is an upgradient control well
ND- not detected above MDL
J is an estimated value that was above the MDL but below the PQL

Table 4.30. 1,1-DCE Concentrations (μg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2	NMW-4	NMW-8	NMW-10
8/01/05	**275**	68	ND	26 *J*	52 *J*	ND	ND	36 *J*	45 *J*	110	76 *J*	140
2/14/06	**472**	100 *J*	39 *J*	ND	39 *J*	ND	ND	67 *J*	270	96 *J*	100 *J*	46 *J*
4/03/06	**520**	ND	ND	ND	ND	ND	ND	ND	120 *J*	100 *J*	78 *J*	ND
5/08/06	**555**	ND	ND	ND	ND	ND	ND	ND	260	140	150 *J*	ND
7/05/06	**614**	48 *J*	51 *J*	ND	42 *J*	34 *J*	51 *J*	69 *J*	180	ND	62 *J*	160
9/06/06	**677**	93 *J*	ND	ND	ND	ND	ND	74 *J*	210	130	120 *J*	190 *J*
10/11/06	**712**	89 *J*	68 *J*	ND	32 *J*	ND	62 *J*	ND	180	130	67 *J*	200
11/28/06	**760**	ND	ND	ND	ND	ND	ND	ND	170	ND	ND	ND
1/08/07	**801**	65 *J*	55 *J*	ND	ND	34 *J*	69 *J*	53 *J*	200	100 *J*	36 *J*	110 *J*

* NMW-2 is an upgradient control well
ND- not detected above MDL
J is an estimated value that was above the MDL but below the PQL

4.4.3.6 Phase II & III: Nitrate and Sulfate

The nitrate concentration throughout the treatment plot averaged 4.8 ± 0.6 mg/L (nitrate-N) prior to system start-up in Phase I. Nitrate concentrations declined rapidly in many of the shallow treatment wells after citric acid was added, and then increased slowly during the period of intermittent operation at the end of Phase I (*see* Figure 4.16 and Table 4.11). Interestingly, however, the nitrate concentrations in many of the shallow wells in the treatment plot actually declined from the end of Phase I to the beginning of Phase II (Figure 4.33 & 4.34; Table 4.31). At the conclusion of Phase I (Day 275), the average nitrate-N concentration in all shallow treatment plot wells was 3.2 mg/L. At the beginning of Phase II (Day 472), the average nitrate-N concentration in these wells was only 0.8 mg/L. This average concentration declined further to 0.4 mg/L by Day 520, which was the first sampling event in Phase II after citric acid addition was resumed. The decline in nitrate-N during the "No addition" period when well rehabilitation was conducted runs counter to the trends observed with the other anions of interest, perchlorate and sulfate, as well as with TCE. All of these compounds increased in concentration when the treatment plot was inactive. In addition, a similar decline was not observed in upgradient well NMW-1, which remained > 5 mg/L nitrate-N during all of Phase II and Phase III (Table 4.31). The stable concentrations in the upgradient well appears to rule out dilution of nitrate from rainfall events or other natural aquifer recharge processes, and suggests that the nitrate was biodegrading during the inactive phase, possibly coupled to the re-oxidation of minerals that were reduced in Phase I. After the first several weeks of Phase II, when nitrate-N in the shallow zone reached an average value of 0.4 mg/L, the concentrations of nitrate-N in a number of the shallow wells increased, and then fell significantly again during Phase III (see Figure 4.33).

With the exception of Well 3630, nitrate-N concentrations in the deep wells remained reasonably constant during the period of "No Addition" prior to Phase II. This is in contrast to the shallow wells, as described previously. Nitrate-N declined significantly in several of the wells, particularly Wells 3514, 3630, and 3633, during Phase III. In addition, nitrate-N remained near or below detection in well NMW-8 throughout Phase II and Phase III. However, nitrate-N in several treatment wells, including 3519, 3629, 3627, and NMW-10 did not show a consistent pattern of decline during Phase II or Phase III. Not surprisingly, perchlorate treatment was also generally poor in these wells during Phases II & III (see Figures 4.25 & 4.26). The quantities of electron donor reaching these wells were apparently insufficient to allow biological reduction of nitrate and perchlorate during the latter phases of the study.

During Phase I, significant sulfate degradation was not generally observed in the shallow or deep monitoring wells (Table 4.13 & 4.14). The tight control of electron donor concentration and constant mixing through operation of the HFTW system appeared to limit this process. In contrast, significant sulfate reduction was indicated during Phases II and III when electron donor addition was increased. During the final sampling event prior to citric acid injection (Day -7), the average sulfate concentration in all downgradient wells (excluding upgradient wells NMW1 and NMW2) was 13.6 mg/L

(14.5 mg/L in the shallow wells and 11.8 mg/L in the deep wells). At the end of Phase I testing (Day 275), the mean concentration in the wells was 13.2 mg/L (11.0 mg/L in the shallow wells and 13.4 mg/L in the deep wells). This concentration rose marginally during the period of well rehabilitation (i.e., no addition). At the beginning of Phase II, the concentration of sulfate averaged 18.0 mg/L overall, with 21.8 mg/L in the shallow wells and 14.0 mg/L in the deep wells (Figures 4.37 – 4.40, Tables 4.33 & 4.34). After increasing further to an average of 25 mg/L at Day 420 in Phase II, sulfate concentrations declined consistently in both the shallow and deep wells during the reminder of Phase II and Phase III. At the conclusion of Phase III (Day 801), the mean sulfate concentration in all of the test plot wells was 9.3 mg/L, comprising an average of 7.3 mg/L in the shallow wells and 9.7 mg/L in the deep wells. Even if the increase in sulfate in the beginning of Phase II is not excluded, the data indicate that appreciable sulfate reduction occurred in many of the treatment plot wells during Phase II and Phase III.

The general paradigm for the microbial utilization of common electron acceptors (O_2, NO_3, ClO_4, Fe(III), SO_4, CO_2) is that these compounds will be used in order, based upon potential energy yield (Fig. 4.39; e.g., ITRC, 2008; Hatzinger and Kelsey, 2005). This is often true for single organisms that are capable of using multiple electron acceptors, and for very well mixed systems with microbial communities (e.g., flask studies in laboratories). However, in the field, it is common for some of these processes to appear to occur simultaneously, primarily due to the effects of aquifer heterogeneity. Rather than being a well-mixed system, an aquifer is typically very heterogeneous, and as a result, is characterized by widely variable local reaction conditions when an electron donor is introduced (Fig. 4.41; see Kopinke et al., 2005 for discussion related to aquifer heterogeneity and process segregation). In zones of the aquifer that are highly permeable and well connected to the electron donor injection well, the electron donor may be present in high concentration, and subsequently result in the sequential reduction of each of the electron acceptors shown in Fig 4.41. In other regions however, electron donor may not mix with groundwater during the course of the demonstration due to low permeability, poor connectedness to the injection well, or other factors. As a result, little degradation occurs in these zones. When groundwater is sampled from a broadly screened well, as is typical for most field studies, including this one, zones with varying degrees of local reaction may be represented in the collected sample, as shown in Fig 4.42. 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 demonstration.

During Phase I, when the electron donor concentration was tightly regulated and the system was pumped constantly, NO_3 and ClO_4 appeared to biodegrade simultaneously, but there was only a minor reduction of Fe (III), Mn(IV) or SO_4 throughout the test plot based on analytical data. Simultaneous reduction of NO_3 and ClO_4 in field studies has been reported previously (e.g., Hatzinger et al., 2009). Although some perchlorate

reducing strains are inhibited by NO_3, others are not, so both processes may occur simultaneously in the same local regions of an aquifer (Coates and Achenbach, 2005; Farhan and Hatzinger, 2009). However, it is also possible that local heterogeneity resulted in the apparent simultaneous reduction of these anions. During Phase II, when citric acid was added in large pulses, and in Phase III, when large pulses were added and the system was shut down for the "active-passive" operation, it is likely that the mixing of citric acid within the test plot was not as efficient as in Phase I. As a result, several different electron accepting processes occurred during these phases, resulting in the mobilization of dissolved Fe and Mn, as well as apparent sulfate reduction. In addition, the fact that perchlorate appeared to persist at low concentrations in wells that exhibited significant sulfate reduction as well as excess electron donor (e.g., Wells NMW-8 and 3633) suggests the presence of heterogeneous conditions within the test aquifer, with different electron-accepting reactions occurring, based on electron donor distribution and other factors. In a well mixed system, it would be very unusual for sulfate reduction to occur while significant perchlorate is still present. Thus, it is likely that these processes were segregated.

Figure 4.33. Nitrate-N Concentrations (mg/L) in Shallow Monitoring Wells during Phase II and Phase II Evaluation.

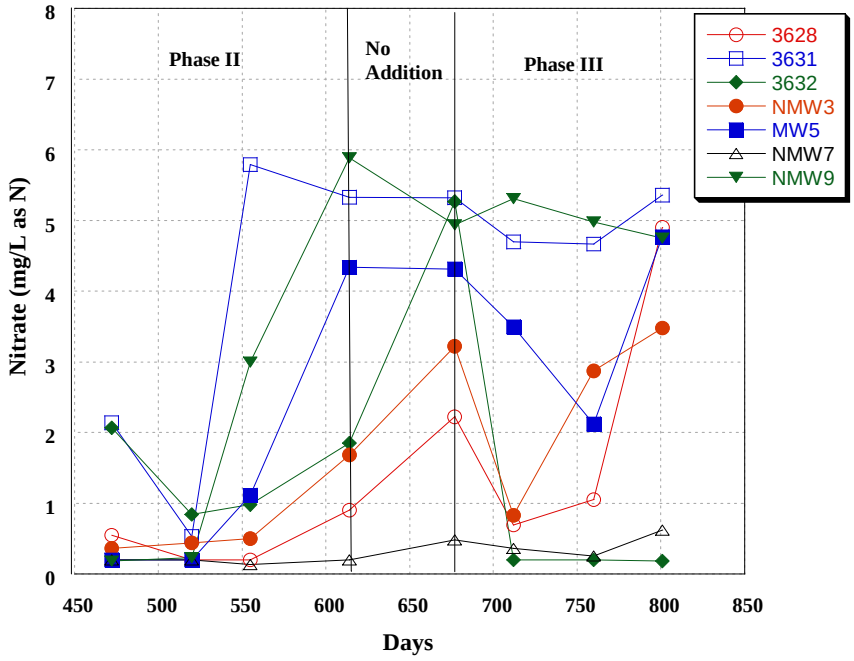


Figure 4.34. Nitrate-N Concentrations (mg/L) in Shallow Monitoring Wells during the Entire Demonstration.

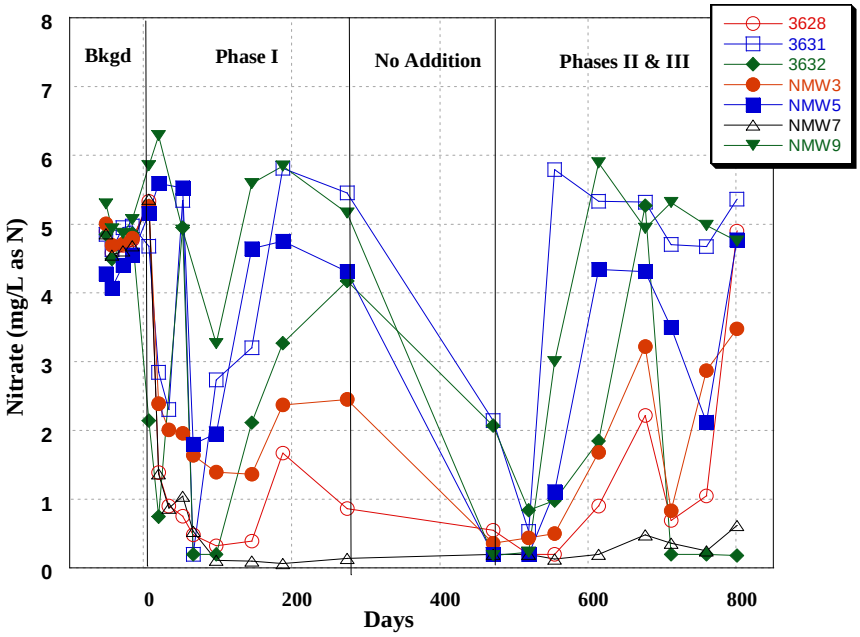


Figure 4.35. Nitrate-N Concentrations (mg/L) in Deep Monitoring Wells during Phase I and Phase II Evaluation.

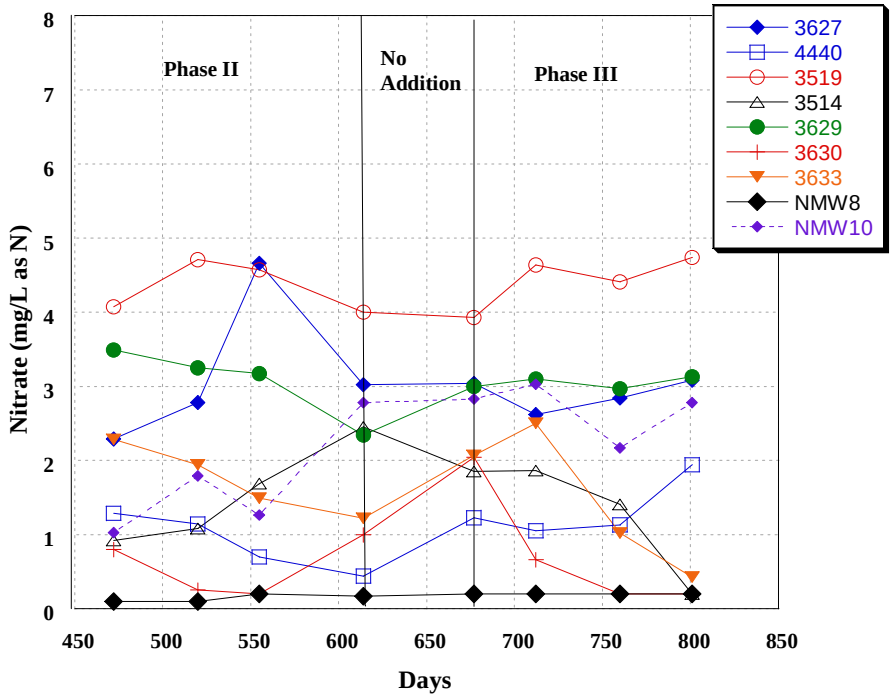


Figure 4.36. Nitrate-N Concentrations (mg/L) in Deep Monitoring Wells during the Entire Demonstration.

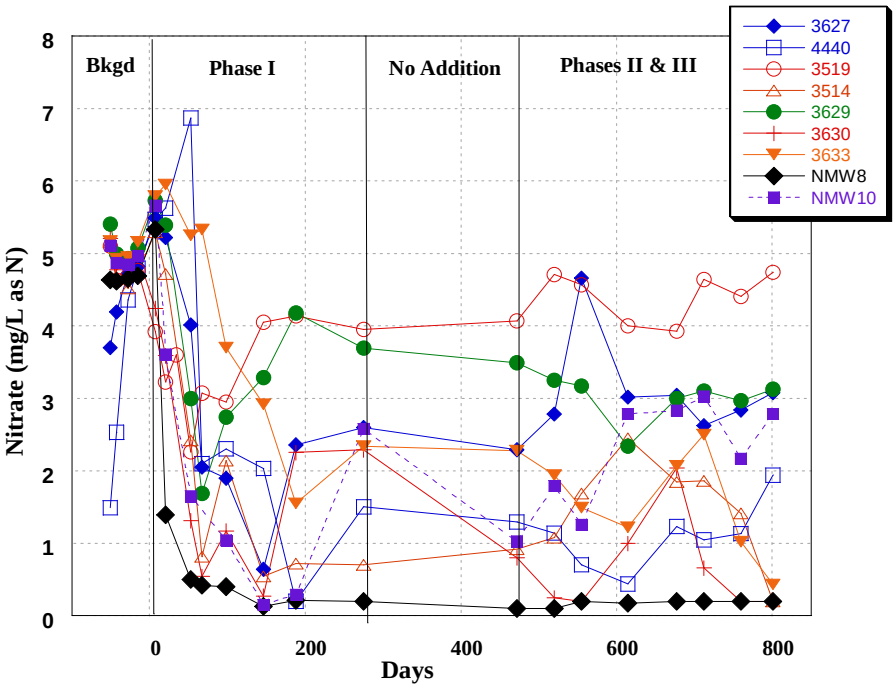


Table 4.31. Nitrate Concentrations (mg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	5.45	4.17	0.86	5.15	2.45	4.31	0.14 *J*	5.16
Phase II									
2/14/06	**472**	2.14	2.07	0.55	5.38	0.36	<0.20	<0.20	0.18 *J*
4/03/06	**520**	0.53	0.84	<0.20	5.85	0.44	<0.20	<0.20	0.23
5/08/06	**555**	5.79	0.98	<0.20	6.25	0.50	1.11	0.13 *J*	3.00
7/05/06	**614**	5.33	1.85	0.90	5.82	1.68	4.34	<0.20	5.89
Phase III									
9/06/06	**677**	5.32	5.27	2.22	5.79	3.22	4.31	0.48	4.94
10/11/06	**712**	4.70	<0.20	0.69	6.17	0.83	3.50	0.36	5.31
11/28/06	**760**	4.67	<0.20	1.05	6.06	2.87	2.12	0.25	4.98
1/08/07	**801**	5.36	0.18 *J*	4.90	6.22	3.48	4.77	0.62	4.75

* NMW-1 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

Table 4.32. Nitrate Concentrations (mg /L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
8/01/05	**275**	2.60	1.50	3.95	0.70	3.69	2.29	2.34	2.60	<0.20	3.97	2.58
Phase II												
2/14/06	**472**	2.29	1.29	4.07	0.92	3.49	0.80	2.28	2.72	0.10 *J*	4.04	1.03
4/03/06	**520**	2.78	1.14	4.71	1.08	3.25	0.25	1.94	2.98	0.10 *J*	4.56	1.79
5/08/06	**555**	4.66	0.70	4.57	1.69	3.17	<0.20	1.49	3.01	<0.20	4.52	1.26
7/05/06	**614**	3.02	0.44	4.00	2.45	2.34	1.00	1.22	2.89	0.17 *J*	4.19	2.78
Phase III												
9/06/06	**677**	3.04	1.23	3.93	1.85	3.00	2.04	2.07	2.84	<0.20	4.23	2.83
10/11/06	**712**	2.62	1.05	4.64	1.86	3.10	0.66	2.50	2.93	<0.20	4.40	3.03
11/28/06	**760**	2.84	1.13	4.41	1.41	2.97	<0.20	1.02	2.69	<0.20	4.34	2.17
1/08/07	**801**	3.08	1.94	4.74	<0.20	3.13	<0.20	0.43	2.88	<0.20	4.56	2.78

* NMW-2 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

Figure 4.37. Sulfate Concentrations (mg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

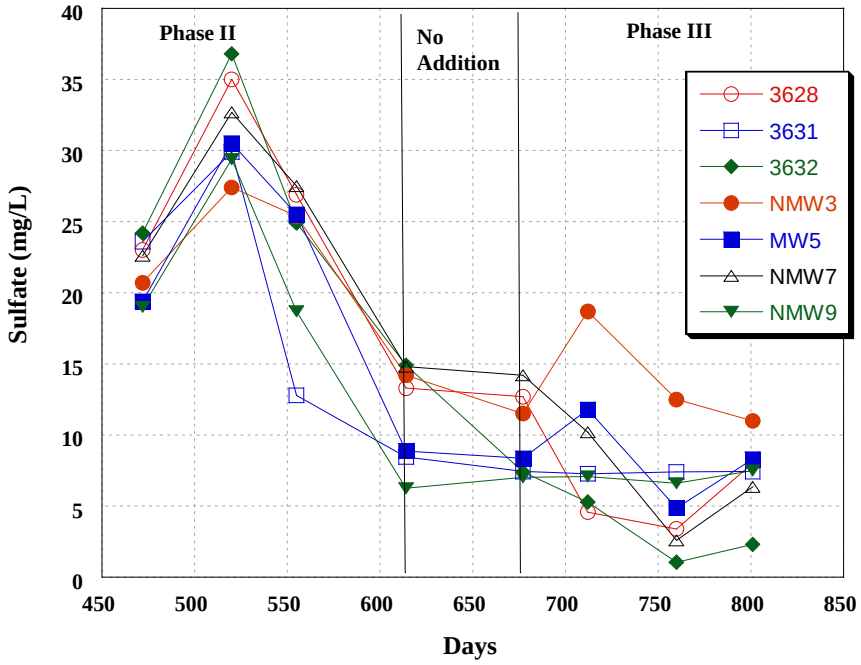


Figure 4.38. Sulfate Concentrations (mg/L) in Shallow Monitoring Wells during the Entire Demonstration.

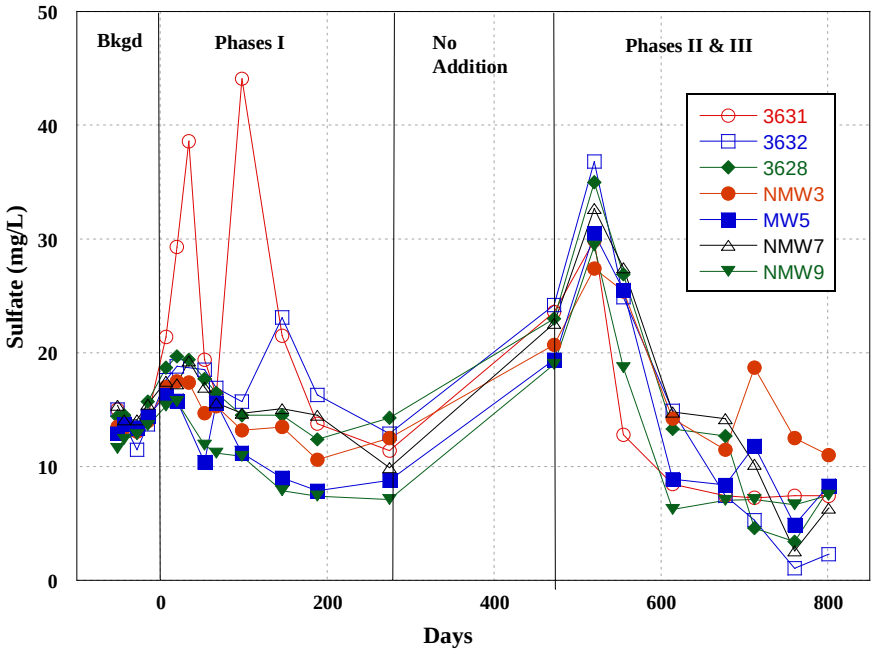


Figure 4.39. Sulfate Concentrations (mg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

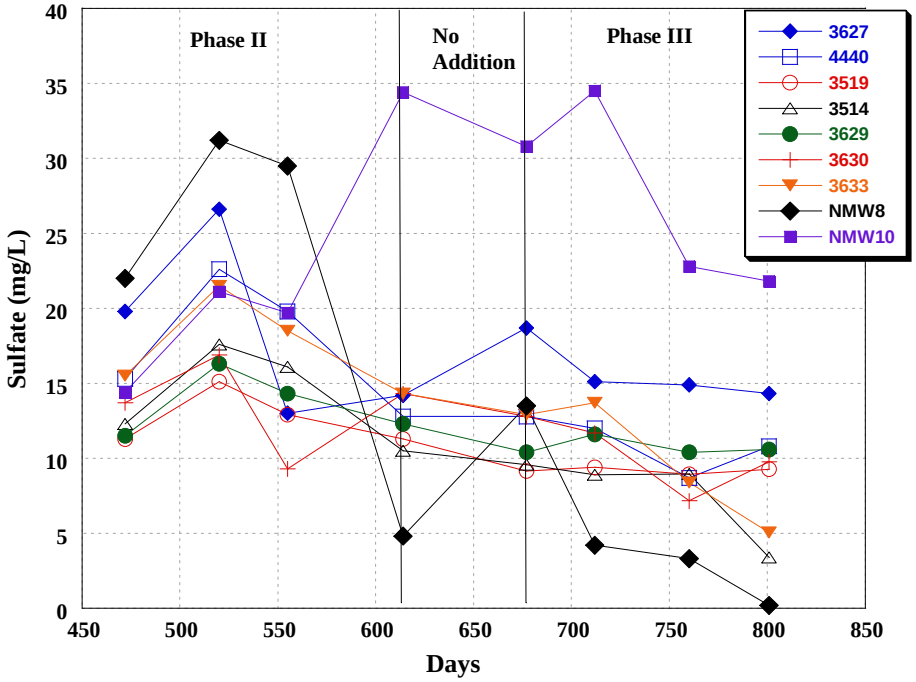


Figure 4.40. Sulfate Concentrations (mg/L) in Deep Monitoring Wells during the Entire Demonstration.

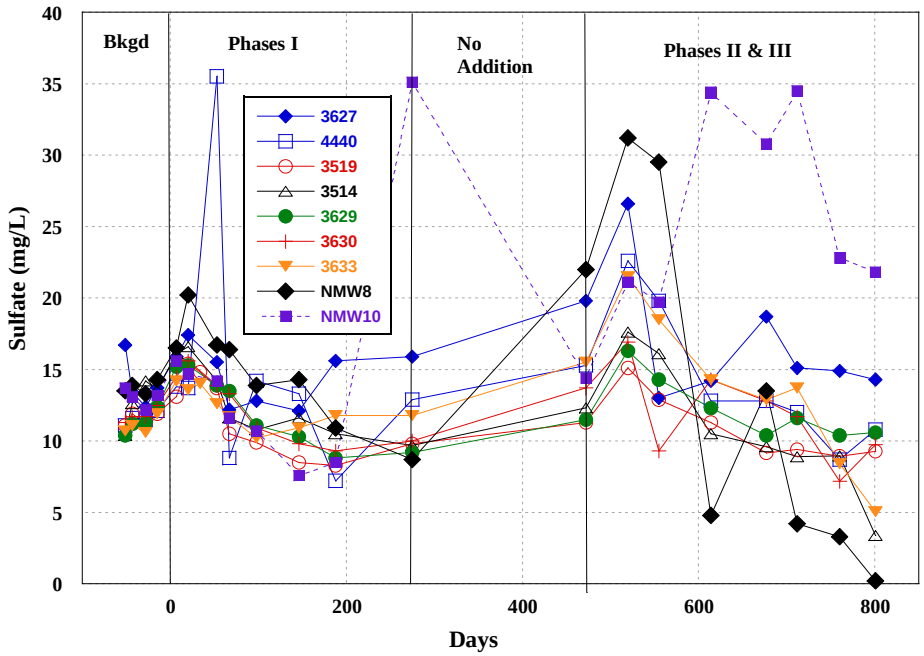


Table 4.33. Sulfate Concentrations (mg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	11.4	12.9	14.3	7.1	12.5	8.8	9.9	7.1
Phase II									
2/14/06	**472**	23.6	24.2	23.0	8.0	20.7	19.4	22.6	19.0
4/03/06	**520**	29.9	36.8	35.0	10.0	27.4	30.5	32.7	29.4
5/08/06	**555**	12.8	24.9	26.9	9.0	25.4	25.5	27.5	18.7
7/05/06	**614**	8.5	14.9	13.3	6.6	14.2	8. 9	14.8	6.3
Phase III									
9/06/06	**677**	7.4	7.4	12.7	5.7	11.5	8.4	14.2	7.0
10/11/06	**712**	7.3	5.3	4.6	5.9	18.7	11.8	10.2	7.1
11/28/06	**760**	7.4	1.1	3.4	5.5	12.5	4. 9	2.6	6.6
1/08/07	**801**	7.5	2.3	8.0	5.0	11.0	8.3	6.4	7.5

* NMW-1 is an upgradient control well

Table 4.34. Sulfate Concentrations (mg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
8/01/05	**275**	15.9	12.9	9.8	9.7	9.2	10.0	11.8	33.1	8.7	24.3	35.1
Phase II												
2/14/06	**472**	19.8	15.3	11.3	12.3	11.5	13.7	15.5	36.0	22.0	18.4	14.4
4/03/06	**520**	26.6	22.6	15.1	17.6	16.3	16.9	21.5	42.2	31.5	28.6	21.1
5/08/06	**555**	13.0	19.8	12.9	16.1	14.3	9.3	18.5	38.7	29.5	27.7	19.7
7/05/06	**614**	14.2	12.8	11.3	10.5	12.3	14.3	14.3	33.3	4.8	23.7	34.4
Phase III												
9/06/06	**677**	18.7	12.8	9.2	9.6	10.4	12.8	12.9	29.8	13.5	21.7	30.8
10/11/06	**712**	15.1	12.0	9.4	8.9	11.6	11.7	13.7	34.1	4.2	24.5	34.5
11/28/06	**760**	14.9	8.7	8.9	9.0	10.4	7.18	8.4	32.7	3.3	21.8	22.8
1/08/07	**801**	14.3	10.8	9.3	3.4	10.6	9.8	5.0	30.9	<0.2	21.6	21.8

* NMW-2 is an upgradient control well

Figure 4.41. General Sequence of Typical Electron-Accepting Reactions (modified from Hatzinger and Kelsey, 2005). Reactions at the top of the chart yield more energy when coupled to the reduction of a typical electron acceptor, and occur at a higher oxidation-reduction potential (ORP).

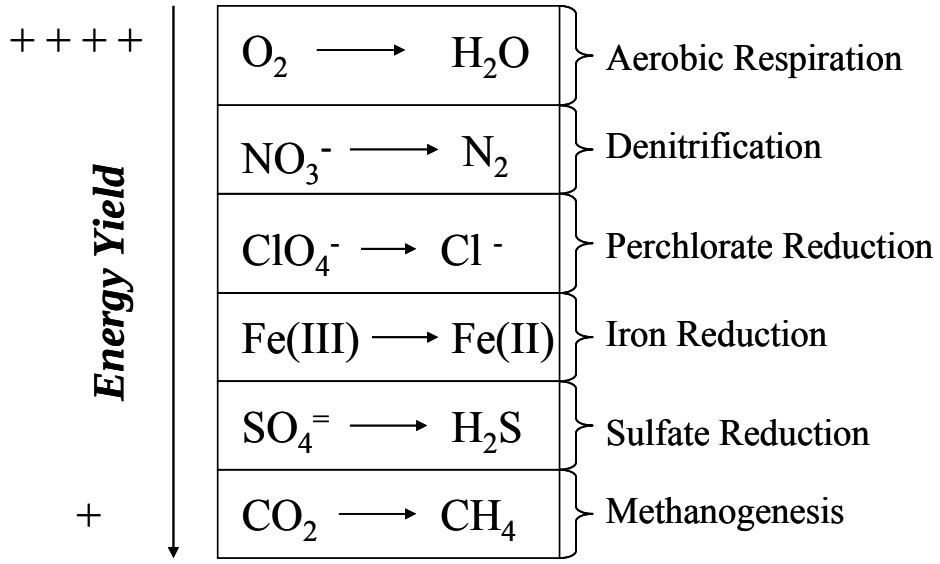
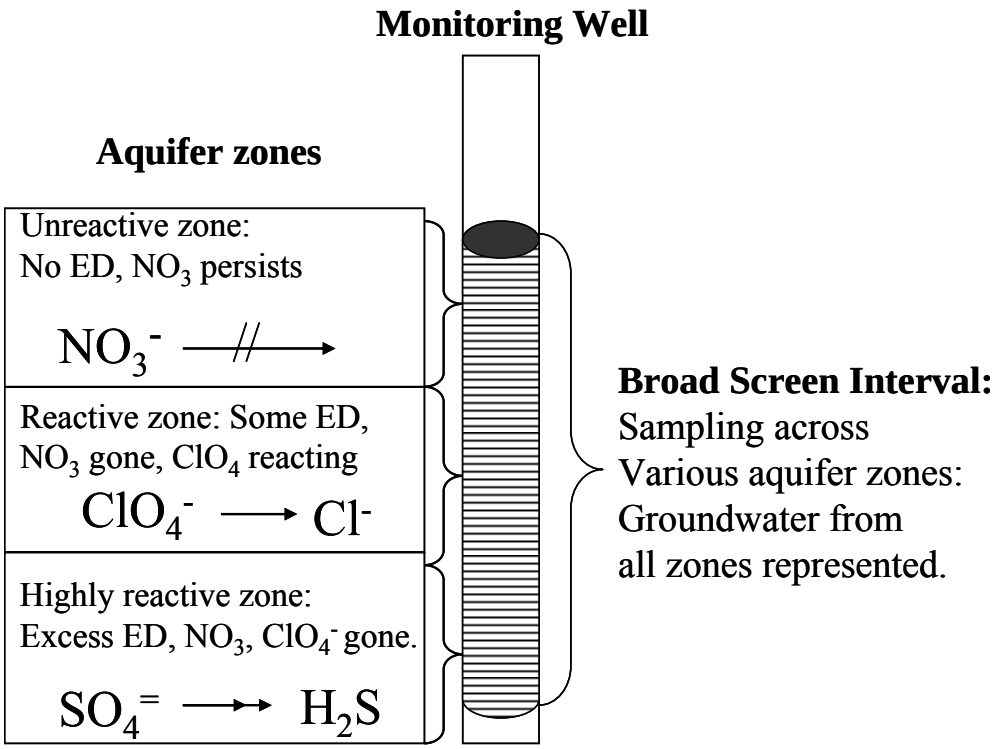


Figure 4.42. Simplified Schematic of an Aquifer with Various Reactive Zones. The monitoring well intercepts multiple zones, resulting in a mixture of groundwater from each zone in varying percentages.



4.4.3.7 Phase II & III:Oxidation-Reduction Potential

The average ORP in the shallow monitoring wells during the sampling events prior to injection of citric acid was ~ + 250 mV (Figure 4.19; Table 4.15). At the end of the 275 days of Phase I, the average ORP in the shallow and deep downgradient wells was averaged + 72 mV. 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) (Figures 4.43 - 4.46; Tables 4.35 & 4.36). 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. 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 4.43. Oxidation-Reduction Potential (ORP; mV) in Shallow Monitoring Wells during Phase I Evaluation.

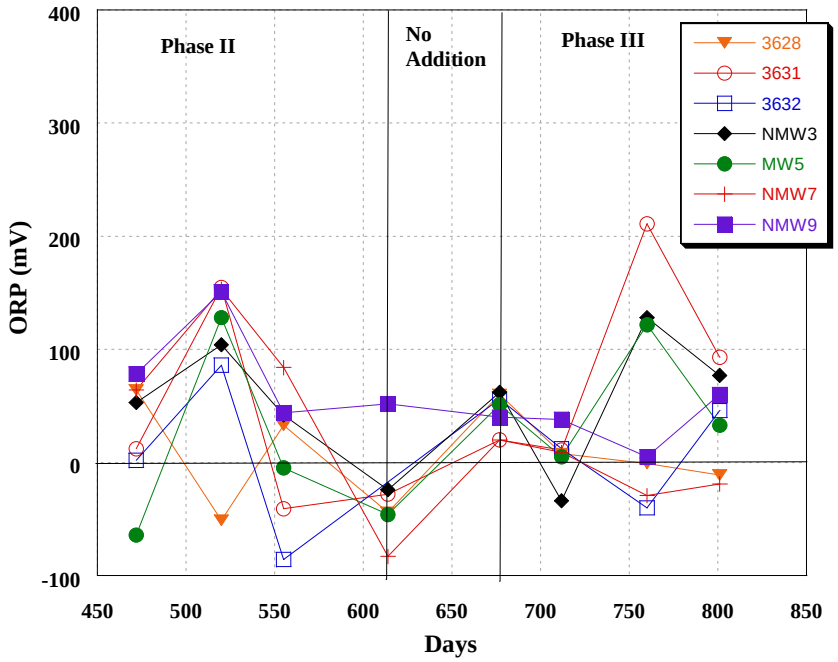


Figure 4.44. Oxidation-Reduction Potential (ORP; mV) in Shallow Monitoring Wells during the Entire Demonstration.

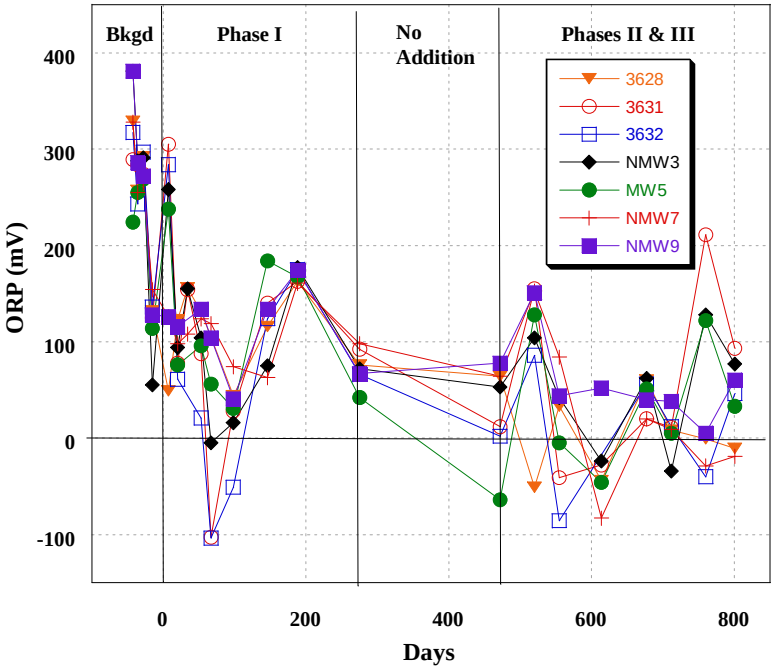


Figure 4.45. Oxidation-Reduction Potential (ORP; mV) in Deep Monitoring Wells during Phase I Evaluation.

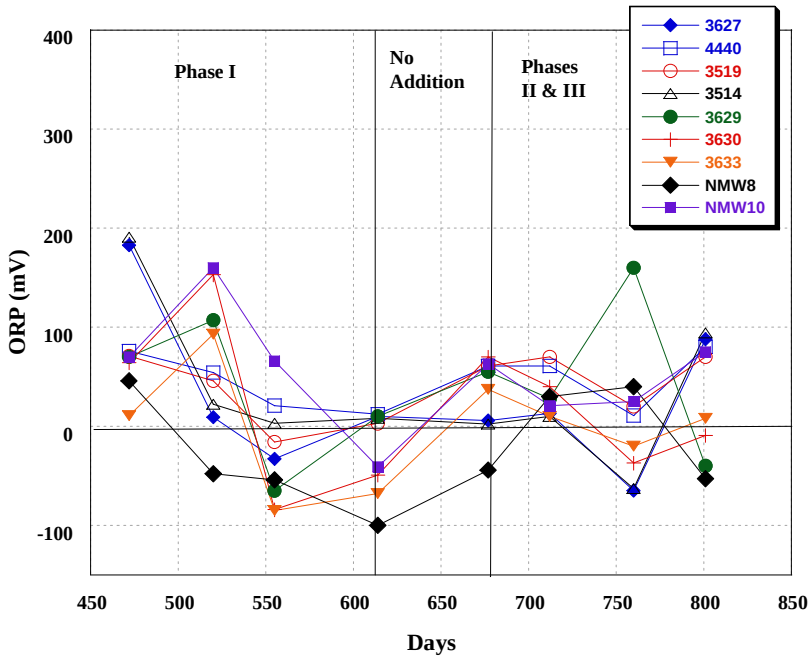


Figure 4.46. Oxidation-Reduction Potential (ORP; mV) in Deep Monitoring Wells during the Entire Demonstration.

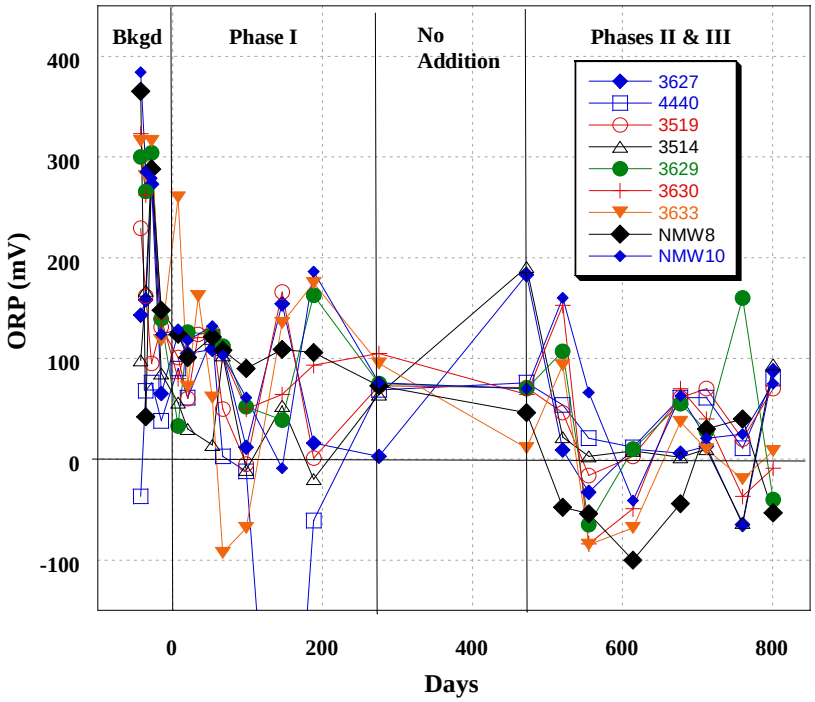


Table 4.35. Oxidation-Reduction Potential (mV) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	92	66	76	74	72	42	98	67
Phase II									
2/14/06	**472**	12	2	64	51	53	-64	64	78
4/03/06	**520**	155	86	-51	158	104	128	153	151
5/08/06	**555**	-41	-86	33	88	42	-5	84	44
7/05/06	**614**	-28		-44	-11	-24	-46	-83	52
Phase III									
9/06/06	**677**	20	56	60	77	62	51	20	40
10/11/06	**712**	11	12	8	35	-34	5	9	38
11/28/06	**760**	211	-40	-1	78	128	122	-29	5
1/08/07	**801**	93	46	-11	92	77	33	-19	60

* NMW-1 is an upgradient control well

Table 4.36. Oxidation-Reduction Potential (mV) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2*	NMW-8	NMW-4	NMW-10
8/01/05	**275**	3	69	73	64	75	105	95	72	73	82	76
Phase II												
2/14/06	**472**	183	76	71	191	70	64	11	60	46	53	70
4/03/06	**520**	9	54	46	22	107	153	93	175	-48	148	160
5/08/06	**555**	-33	21	-16	3	-65	-84	-85	90	-54	85	66
7/05/06	**614**	10	12	3	8	10	-49	-68	-26	-100	-39	-41
Phase III												
9/06/06	**677**	6	61	61	2	55	70	37	87	-44	80	63
10/11/06	**712**	13	61	70	10	28	40	10	14	30	-34	21
11/28/06	**760**	-65	11	20	-63	160	-37	-20	60	40	158	25
1/08/07	**801**	88	80	70	94	-40	-9	8	97	-53	88	75

* NMW-2 is an upgradient control well

4.4.3.8 Phase II & III: Electron Donor Concentrations

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* (See Figure 3.11). Other possible fatty acid intermediates include lactate, formate and propionate. During the project, fatty acid analysis was conducted to evaluate electron donor concentrations in the wells. The fatty acids measured included citrate, lactate, valerate, acetate, formate, butyrate, and propionate. 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. During some sampling events, the anion (EPA 300.0) chromatographs were reviewed prior to conducting fatty acid analysis, as these compounds elute as a combined peak (i.e., they are not separated during EPA 300.0 but are visible) early in the sample run time. If a peak consistent with combined fatty acids was observed during EPA 300.0, fatty analysis was conducted by IC to separate and quantify the fatty acids.

As expected, citrate was not consistently detected in any of the monitoring wells above the PQL of 2 mg/L during Phase I. The fatty acid was detected at 0.5 mg/L (*J* value) in NMW-8 and 3.3 mg/L in NMW-10 at on Day 135, and in wells 3514, NMW-7, and NMW-8 on Day 275 at 0.5 – 0.7 mg/L. Acetate was observed in several downgradient wells during the demonstration, particularly towards the end of Phase I (Table 4.17 and 4.18). Concentrations ranged from < 1 mg/L (*J* values) to > 20 mg/L. Formate was detected in very low concentration (< 0.5 mg/L *J* values) in a few of the downgradient wells, while lactate and valerate were not detected in any of the wells during Phase I (PQL 1 mg/L). Propionate and butyrate were detected in Well 4440 on Day 188, along with acetate and formate.

During Phase II and Phase III, electron donor concentrations were increased, as detailed previously in Section 4.4.3.1. 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 (Table 4.37). For the deep wells, acetate was consistently detected in NMW-8, and was detected on one occasion in both 3514 and 3630.

Table 4.37. Acetate Concentrations (mg/L) in Shallow Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3631	3632	3628	NMW-1*	NMW-3	NMW-5	NMW-7	NMW-9
8/01/05	**275**	<1.0	0.6 *J*	0.9 *J*	<1	<1	<1	16	<1
Phase II									
4/03/06	**520**	<1	<1	<1	<1	<1	<1	<1	<1
5/08/06	**555**	<1	<1	<1	<1	<1	<1	<1	<1
7/05/06	**614**	18.6	<5	13.8	<1	<1	<1	<1	<1
Phase III									
10/11/06	**712**	<5	50	102	<5	<5	<5	16	<5
11/28/06	**760**	<5	164	165	<5	<5	78	183	<5
1/08/07	**801**	<1	175	4.6	<1	<1	<1	83	<1

* NMW-1 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

Table 4.38. Acetate Concentrations (mg/L) in Deep Monitoring Wells during Phase II and Phase III Evaluation.

Date	Days	3627	4440	3519	3514	3629	3630	3633	NMW-2	NMW-4	NMW-8	NMW-10
8/01/05	**275**	<1	0.9 *J*	<1	0.5	<1	<1	<1	<1	<1	21	<1
Phase II												
4/03/06	**520**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
5/08/06	**555**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
7/05/06	**614**	<1	<1	<1	<1	<1	26	<1	<1	<1	<1	<1
Phase III												
10/11/06	**712**	<5	<5	<5	25	<5	<5	<5	<5	<5	58	<5
11/28/06	**760**	<5	<5	<5	<5	<5	1.4 *J*	<5	<5	<5	175	<5
1/08/07	**801**	<1	<1	<1	<1	<1	<1	<1	<1	<1	136	<1

* NMW-2 is an upgradient control well

J is an estimated value that was above the MDL but below the PQL

4.4.4 Biofouling Control - Phase II & III

4.4.4.1 Biofouling Control-Phase II

As described previously, during Phase II operations the HFTWs were operated in continuous flow mode at an average flow rate of 6 gpm. The frequency and amount of electron donor and chlorine dioxide injections were varied to assess the apparent impact of different amendment addition strategies on controlling well biofouling.

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. (SDC-9)), electron donor injections were conducted every seventh day. During this same period (excluding the day of and following the injection of *Dehalococcoides* spp. (SDC-9)) 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.

Figure 4.47 depicts the typical injection zone pressure for each HFTW just prior to and during Phase II operations. On-going 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. 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. Pressures remained fairly stable, although the HFTW-U appeared to experience a steady increase in pressure from the mid-20's to around 40 ft of water at day 56 of Phase II operation. This increase in injection zone pressure was very similar to the head increase measured in the upper zone of the HFTW-D (also shown on Figure 4.47), indicating that some, if not most, of this increase in pressure within the upper zone can be attributed to natural precipitation and increased aquifer saturation within this same zone during this operating period. The winter season in the Rancho Cordova area is the wet season, so this trend appears consistent with normal precipitation patterns. A fairly rapid increase in pressure can be seen in the injection zone of both wells between days 19 and 23 in Phase II, which appears to be related to a period of mechanical problems associated with the chlorine dioxide unit that resulted in reduced or no injection of chlorine dioxide. Pressures in both of the wells declined appreciably after the chlorine dioxide system was repaired and daily chlorine dioxide injections were restored.

System injection pressures became much less stable following the implementation of the reduced chlorine dioxide injection cycles (one injection following the injection of electron donor with no regular injections during the days in between). The pressure in the HFTW-D increased from around 135 ft of water on day 56 of Phase II to 160 ft of water on day 113 of Phase II. The rate of pressure increase in the HFTW-U appeared to be even more rapid with an increase of over 20 ft of water (~40 ft to >60ft) during the first 12 days of modified system operation. Chlorine dioxide was manually injected into the HFTWs and the wells were temporarily shutdown in an effort to reverse the pressure increases. The system operating mode was re-set to restore frequent daily pulses of chlorine dioxide into the HFTW-U. However, upon re-start, the chorine dioxide system malfunctioned resulting in several cycles of electron donor addition with little or no corresponding chlorine dioxide injection. This caused injection pressures to spike to over 95 ft of water by day 75 of Phase II. Following this date, the chlorine dioxide system was repaired and operated normally for several weeks, resulting in regular daily pulses of chlorine dioxide into the HFTW-U and a reduction in injection zone pressures back down into the mid-40 ft of water range by around day 86 of Phase II. Beginning around day 93 of Phase II chlorine dioxide system malfunctions brought on a second rapid increase in pressure within the HFTW-U that ultimately lead to several other system malfunctions and the termination of Phase II operations.

Based on the various pressure trends observed during Phase II operations, it appears that an operating mode which entail 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.

4.4.4.2 Biofouling Control- Phase III

As noted previously, 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-h pulses (followed by chlorine dioxide as a biocide), resulting in the addition of approximately 60 L of electron donor per 12-h 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 6 times during the 3-month test period.

Injection zone pressures were monitored during each active pumping/electron donor injection period to assess system performance trends during Phase III. Figure 4.48 depicts the average injection pressures that were observed within each HFTW. 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 to ft of water in HFTW-D) and were substantially below the pressures that were being observed during the final weeks of Phase II (See Figure 4.47 for Phase II pressure trends). This is believed to be related to the chelating effect created when the large doses of citric acid are being injected.

When comparing the average injection zone pressures during each Phase III event somewhat contradictory trends are noted in the HFTW-U and HFTW-D data. The average injection pressure in the HFTW-U increased over the first 4 events by several feet of water (from ~34 ft of water during event #1 to ~46 ft of water during event #4). During this same period, the pressures in the HFTW-D initially increased (from ~126 ft of water during event #1 to ~143 ft of water during event #2) before returning to the mid-120 ft of water range by event #4. A concentrated pulse of chlorine dioxide was injected into each HFTW between events #4 and #5 in an effort to reverse the increasing injection pressure trend within the HFTW-U. This effort appeared to partially reverse the increasing pressure trend within the HFTW-U, however, the injection pressures remained in the low to mid-140 ft of water range during the final two events. The average pressures within the HFTW-D did decline slightly over the final two events. The pressures did not 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.

Figure 4.47. Well Pressures (ft of H_2O) and ClO_2 Injection Schedule during Phase II Operation. The symbol u-HFTW-UZ refers to the upper screen interval of the upflow HFTW and d-HFTW-UZ and d-HFTW-LZ refer to the upper and lower screen intervals of the downflow HFTW, respectively. Day 0 of Phase II operation is Day 473 of overall system operation.

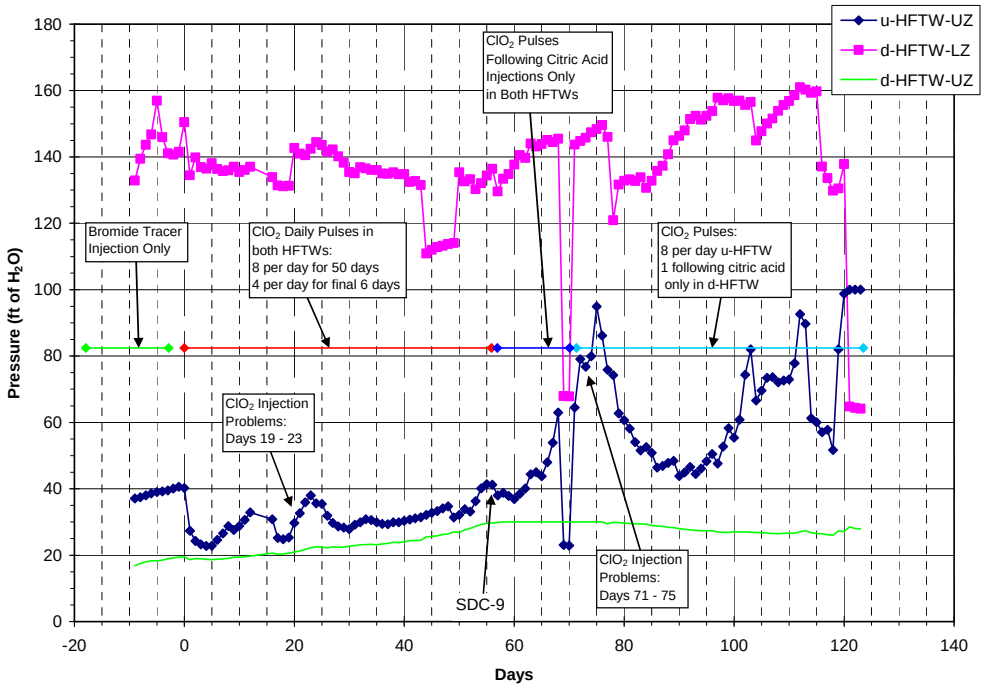
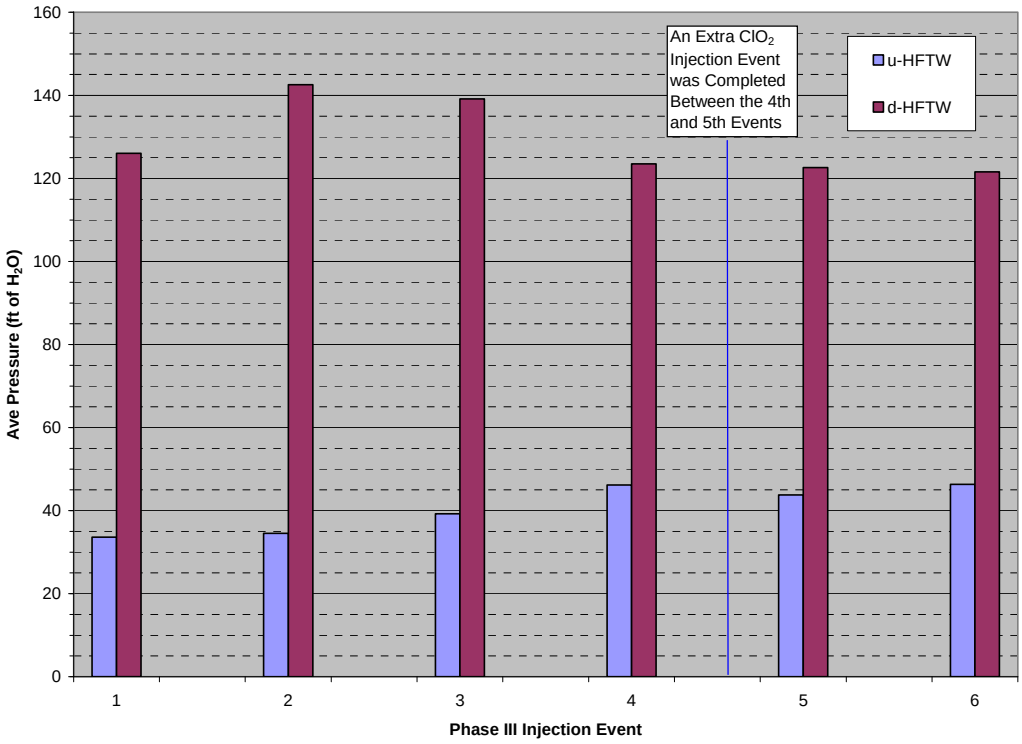


Figure 4.48. Well Pressures (ft of H_2O) and ClO_2 Injection Schedule during Phase III "Active-Passive" Operation.



5.0 COST ASSESSMENT

The horizontal flow treatment well (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 and where re-injection of contaminated water (e.g., extracted groundwater with electron donor added) is either prohibited due to water usage/rights concerns or subject to regulatory injection permits. Longer treatment time frames, high contaminant concentrations, secondary reaction concerns (e.g. 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 then 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/startup, operations, maintenance, monitoring, and reporting were tracked throughout the course of demonstration project. Table 5.1 summarizes the total cost of the demonstration project. The costs have been grouped by categories as recommended in the Federal Remediation Technologies Roundtable Guide to Documenting Cost and Performance for Remediation Project (FRTR, 1998). Many of the costs shown on 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 5.1. 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/Subcomtracts	$ 252,500
4	System Installation - Labor	$ 49,800
5	Travel	$ 5,000
	Sub-Total	$ 515,400
	OPERATION AND MAINTENANCE COSTS	
1	Sampling and System O&M - Labor	$ 90,500
2	Equipment	$ 7,900
3	Consumables	$ 4,900
4	Analytical - In-House Labor	$ 71,600
5	Analytical - Outside Lab	$ 7,300
6	Travel	$ 3,500
7	Reporting	$ 52,600
	Sub-Total	$ 238,300
	OTHER TECHNOLOGY-SPECIFIC COSTS	
1	Site Selection	$ 76,000
2	Site Characterization	$ 119,400
3	Treatability Studies	$ 74,800
	Sub-Total	$ 270,200
	TOTAL COSTS	**$ 1,023,900**

5.1 Cost Model

For purposes of this cost assessment, the costs associated with full-scale implementation of a HFTW barrier are discussed and compared against traditional groundwater extraction, above grade biological treatment using a fluidized bed reactor design (GWET-FBR), and re-injection of the treated water into the subsurface. Only those costs related the post remedial investigation and feasibility study (RI/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 (e.g. 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, operations and maintenance (O&M), and monitoring costs over a projected 30 yr 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.

5.1.1 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.

5.1.2 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 upon 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 (e.g. 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.

5.1.3 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.

5.1.3.1 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, amendment addition dosing patterns and quantities.
- Development of process flow and detailed piping and instrumentation diagrams (P&ID) for both the down-hole and above grade elements of the treatment system. A (P&ID) diagram depicting the common elements of an HFTW system is provided in Figure 3.28.
- Equipment selection based on sizing, compatibility, operational, and system monitoring needs.

5.1.3.2 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 5.1.
- Equipment selection based on sizing, compatibility, operational, and system monitoring needs.

5.1.3.3 HFTW System Installation

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

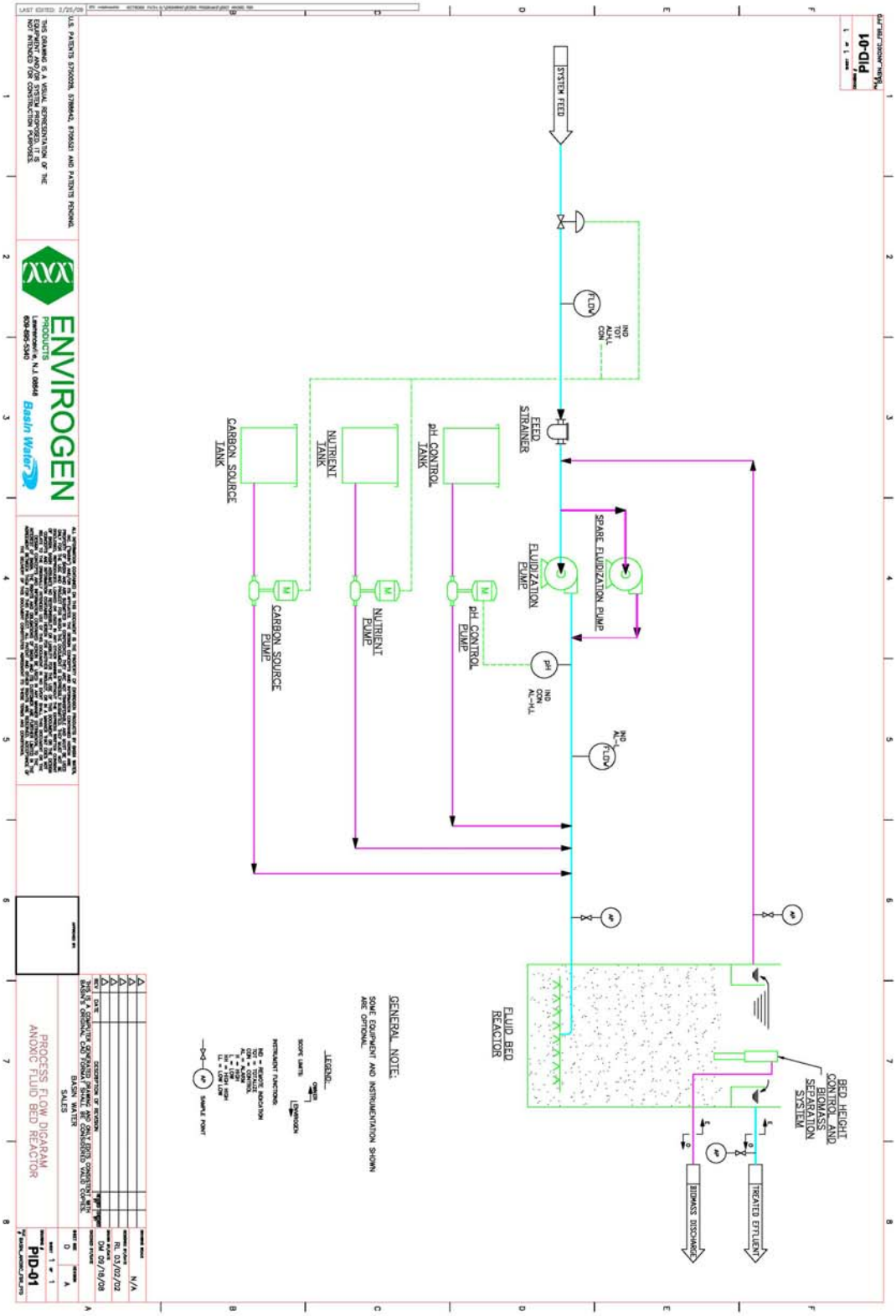
- Two 8" diameter, schedule 80 PVC wells, with dual screened zones.
- Downhole equipment including: 2 pneumatic packers, 2 submersible process pumps (5hp, 10 gpm @ 150 TDH) with variable frequency drives, 4 submersible sampling/mixing pumps, 4 pressure transducers, 2 in-line flow meters, 2 in-line mixing valves, solenoid valves, 2 sealed well caps, 1 pressure gauge, 1 pressure relief valve
- Above grade equipment including: 2 chemical metering pumps, 1 electron donor chemical storage tank, 1 liquid chlorine dioxide generation unit, liquid level sensors for all chemical storage and mixing tanks (total of 3), water supply line, 220 volt, 3 phase, 100 amp power supply, control panel, desktop PC with PLC software, hard wired or wireless modem, climate controlled storage shed.
- Plumbing, mechanical, electrical support to connect all equipment assuming 100 lineal feet of trenching for all piping and wiring runs.

5.1.3.4 GWET-FBR System Installation

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

- Two 6" diameter, schedule 40 PVC wells screened from 40 to 100 ft bgs.
- Downhole equipment including: 1 submersible process pump (5hp, 50 gpm @ 125 TDH), 1 submersible sampling/mixing pump, 2 pressure transducers, 1 sealed well cap, 1 pressure gauge, 1 pressure relief valve
- Above grade equipment including: 1 equalization tank, 1 post-treatment tank, 1 electron donor chemical storage tank, a nutrient tank, and a pH control tank, an integrated FBR system per process flow diagram (Figure 5.2), liquid level sensors for all chemical storage and mixing tanks (total of 5), water supply line, 1 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. A post treatment multi-media filter and aeration system is also included in the cost to remove biomass and aerate water prior to reinjection.
- Plumbing, mechanical, electrical support to connect all equipment assuming 100 lineal feet of trenching for all piping and wiring runs.

Figure 5.1 Process Flow Diagram for Envirogen Anaerobic Fluidized Bed Reactor.



5.1.3.5 HFTW System Startup

For the base case analysis, the HFTW system startup 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 insure flow balance is achieved between the up-flow and down-flow 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 startup process is expected to require a two-person crew and approximately 100 man hours to complete over a period of 1 to 2 weeks.

5.1.3.6 GWET-FBR System Startup

For the base case analysis, the GWET-FBR system startup 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 startup 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 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 startup process is expected to require approximately 250 man hours to complete over a period of 3 to 4 weeks.

5.1.4 System Operations and Maintenance (O&M Costs)

The operations and maintenance (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 on-going 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.

5.1.4.1 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 3yrs
- Chemical/mechanical well rehabilitation for HFTW – every 3 yrs.

Based on the amount of mechanical components and process variables, the HFTW O&M is anticipated to require approximately 120 man hours and $5,000 for other direct costs (ODCs), excluding power and electron donor, per year for routine items and 120 man hours and $25,000 for ODCs every three years for non-routine items and well rehabilitation (to be performed simultaneously).

5.1.4.2 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 yrs
- Chemical/mechanical well rehabilitation for the extraction and injection wells – every 5 yrs.

Based on the amount of mechanical components and process variables, the GWET-FBR O&M is anticipated to require approximately 240 man hours and $5,000 for other direct costs (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 yrs for well rehabilitation.

5.1.4.3 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 yrs
- Semi-annual groundwater measurement and sampling on 4 wells, with 4 additional wells monitored annually for the final 25 yrs

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 8 wells located near and down gradient of the HFTWs during the initial 5 yrs, including 4 screened within the upper and lower target treatment zones and it is assumed each sampling event will require 20 man hours and $2,500 in ODCs per event. From year 6 and beyond, 4 wells will be monitored semi-annually and 4 additional wells will be monitored annually requiring 30 man hours and $4,000 in ODCs per year.

5.1.4.4 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 yrs
- Quarterly system effluent sampling for the final 25 yrs
- Quarterly groundwater measurement and sampling for the first 5 yrs
- Annual groundwater measurement and sampling for the next 25 yrs

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 4 monitoring wells per event and it is assumed each sampling event will require 12 man hours and $1,500 in ODCs per event.

5.2 Cost Drivers

The expected cost drivers for installation and operation of a HFTW system and those that will determine the cost/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/acceptance of groundwater extraction and re-injection
- Regulatory considerations concerning secondary groundwater contaminants
- Length of time for clean-up (e.g., necessity for accelerated clean-up)
- Concentrations of perchlorate and alternate electron acceptor (i.e., NO_3 and 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 et al. (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 others, 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, a 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 a 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.

5.3 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 feet below ground surface (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 below ground surface, 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 $1x10^{-3}$ 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 up-flow mode and the other operated in the down-flow mode, will be sufficient to provide full plume capture and treatment.
- The following 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 inch diameter (ID), schedule 80, polyvinyl chloride (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 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 inch diameter (ID), schedule 40, polyvinyl chloride (PVC) piping.
- Treatment costs are based on the use of a fluidized bed reactor unit (FBR) using published cost factors and/or based on discussion with an FBR vendor.

Tables 5.2 and 5.3 show the estimated capital costs, operations and maintenance (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.

5.3.1 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 COCs. 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 EPA 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 lifecycle cost for the HFTW alternative of $1,459,000 (Table 5.2).

5.3.2 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 multi-media 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 lifecycle cost for the GWET-FBR/reinjection system of $2,117,000 (Table 5.3).

Table 5.2. 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 ($)	403,205	-	-	-	-	-	-	-	-		**403,205**
OPERATION AND MAINTENANCE COSTS											
System Operation and Maintenance	28,172	28,172	61,272	28,172	28,172	61,272	28,172	28,172	61,272	Year 7-9 costs repeat through year 30	784,944
SUBCOST ($)	**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 (Quarterly through 5 years then Annually)	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**	**1,459,492**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 3% discount rate

Table 5.3. 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**
OPERATION AND MAINTENANCE COSTS											
System Operation and Maintenance	34,472	34,472	67,572	34,472	53,872	67,572	34,472	Repeat $34,472 annually through year 30	Add 33,100 for non-routine O&M in each yr listed above	Add 19,400 for well rehab in each yr listed above	977,663
SUBCOST ($)	**34,472**	**34,472**	**67,572**	**34,472**	**53,872**	**67,572**	**34,472**				**977,663**
LONG TERM MONITORING COSTS											
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	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**	**81,952**	**78,502**	**45,402**				**2,117,313**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 3% discount rate

6.0 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 h) 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 suggestions 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 shutdown 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 bio-solids 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 deliver 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, and allowing them to be recovered; and
- 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) (Section 4.4.3.8), yet perchlorate persisted in some of these wells at ~ 30-100 μg/L (Section 4.4.3.3). 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 (Table 4.19 and nitrate-N ranging from 0.2 to 0.7 mg/L (Table 4.31), yet sulfate concentrations declined from 14.2 to 6.4 mg/L (Table 4.33) during Phase III, and both Fe and Mn were present at > 1,000 ug/L (Tables 4.21 and 4.23, respectively). 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 Appendix E). 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. As noted in Section 4.4.3.6, 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 non-detect 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 previously in Fig 4.42. 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 Air Force Base, 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 a 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.

7.0 REFERENCES CITED

Achenbach, L. A., Michaelidou, U., Bruce, R. A., Fryman, J., and Coates, J. D. (2001). *Dechloromonas agitata* gen. nov., sp. nov. and *Dechlorosoma suillum* gen. nov., sp. nov., two novel environmentally dominant (per)chlorate-reducing bacteria and their phylogenetic position. International Journal of Systematic and Evolutionary Microbiology, 51:527-533.

Aziz, C.E. and P.B. Hatzinger. (2008). Perchlorate sources, source identification, and analytical methods. *In* In Situ Bioremediation of Perchlorate. H.F. Stroo and C. H. Ward. (ed.). Springer, New York. pp 55-77.

Aziz, C., R. Borch, P. Nicholson, and E.Cox. (2006). Alternative causes of wide-spread, low concentration perchlorate impacts to groundwater. *In* Perchlorate: Environment Occurrence, Interactions, and Treatment, B. Gu and J. C. Coates (Eds.). Springer, New York.

Betts, K.S. (2000). Accelerating perchlorate detection. Environmental Science and Technology. 34:245A-246A.

Biocide International. (2009). Online: http://www.bio-cide.com/.

Borden, R.C. (2007a). Effective distribution of emulsified edible oil for enhanced *in situ* anaeroic bioremediation. Journal of Contaminant Hydrology, 94:1-12.

Borden, R.C. (2007b). Concurrent bioremediation of perchlorate and 1,1,1-trichloroethane in an emulsified oil barrier. Journal of Contaminant Hydrology, 94:13-21.

Brandhuber, P and S. Clark (2005). Perchlorate Occurrence Mapping. American Water Works Association, Washington, DC. 38 pp. Online: http://www.awwa.org/files /Advocacy/Govtaff/Documents/PerchlorateOccurrenceReportFinalb02092005.pdf

CDHS; California Department of Health Services. (1997). Determination of Perchlorate by Ion Chromatography. Website: http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl /clo4meth.pdf.

CDPH; California Department Public Health. (2009). Perchlorate in Drinking Water: Monitoring Update. Online: http://www.cdph.ca.gov/certlic/drinkingwater/pages/ Perchlorate.aspx.

Chaudhuri, S.K., S.M. O'Conner, R.L. Gustavson, L.A. Achenbach, and J.D. Coates. (2002). Environmental factors that control microbial perchlorate reduction. Applied and Environmental Microbiology, 68:4425-4430.

Chopra G., L. Dutta, E. Nuttall, P. Hatzinger, M.N. Goltz. (2004). Investigation of biomass and their mitigation for in-situ bioremediation, Paper # 4F-02, *In* Remediation of Chlorinated and Recalcitrant Compounds—2004, Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, A.R. Gavaskar and A.S.C. Chen (Eds.), Battelle Press, Columbus, OH, USA (on CD).

Chopra G, L. Dutta, E. Nuttall, W. Anderson, P. Hatzinger, and M.N. Goltz. (2005). Investigation of methods to control biofouling during *in situ* bioremediation, Paper # A-22, *In* In Situ and On-Site Bioremediation—2005, Proceedings of the Eighth International In Situ and On-Site Bioremediation Symposium, B.C. Alleman and M.E. Kelley (Eds.), Battelle Press, Columbus, OH, USA (on CD).

Chosa, P.G. (2004). Modeling a Field Application of In Situ Bioremediation of Perchlorate in Groundwater Using Horizontal Flow Treatment Wells. M.S. Thesis, AFIT/GEM/ENV/04M-05, School of Engineering and Management, Air Force Institute of Technology,(AU), Wright Patterson AFB, OH.

Coates, J. D., U. Michaelidou, R.A. Bruce, S.M. O'Conner, J.N. Crespi, and L.A. Achenbach. (1999). The ubiquity and diversity of dissimilatory (per)chlorate-reducing bacteria. Applied and Environmental Microbiology, 65, 5234-5241.

Coates, J. D. and L. A. Achenbach. (2004). Microbial perchlorate reduction: Rocket-fuelled metabolism. Nature Reviews Microbiology, 2:569-580.

Cox, E.E., M. McMaster, and S.L. Neville. (2001). Perchlorate in Groundwater: Scope of the Problem and Emerging Remedial Solutions. *In* Proceedings of the 36th Annual Engineering Geology and Geotechnical Engineering Symposium, Las Vegas, NV, pp. 27-32.

Cramer, R.J., C.A. Yates, P.B. Hatzinger, and J. Diebold. (2003). Field Demonstration of In Situ Perchlorate Bioremediation at Building 1419. Naval Ordnance Safety and Security Activity, Naval Sea Systems Command Technical Report # NOSSA-TR-2003-002. June 12. 80 pp.

Damian, P., and F.W. Pontius. (1999). From rockets to remediation: the perchlorate problem. Environmental Protection, June, 24-31.

Dasgupta, P.K., J.V. Dyke, A.B. Kirk, W.A. Jackson. (2006). Perchlorate in the United States: Analysis of relative source contributions to the food chain. Environmental Science and Technology, 40:6608-6614.

DoD; Department of Defense. (1995). DoD Instruction 7041.3: Economic Analysis for Decision Making. November 7, 1995. Online: http://www.dtic.mil/whs/directives/corres /pdf/704103p.pdf.

ESTCP; Environmental Technology Certification Program. (2006). Edible Oil Barriers for Treatment of Perchlorate Contaminated Groundwater. Project ER-0221 Final Report, ESTCP, Arlington, VA. Online: http://www.estcp.org/viewfile.cfm?Doc=ER% 2D0221%2DFR%2D01%2Epdf.

ESTCP; Environmental Technology Certification Program. (2007). In Situ Catalytic Groundwater Treatment using Pd-Catalysis and Horizontal Flow Treatment Wells. Final Report. Online: http://wrhsrc.oregonstate.edu/final/ReinhardESTCPFinal07.pdf.

Farhan, Y. and P.B. Hatzinger. (2009). Modeling the biodegradation of perchlorate in the presence of nitrate and oxygen as competing electron acceptors. Bioremediation Journal, 13(2): 1-14.

Fetter, C.W. (1994). Contaminant Hydrogeology, 2nd Ed., Prentice Hall, Upper Saddle River, NJ., 500 pp.

FRTR; Federal Remediation Technologies Roundtable (1998). EPA Publication 542-B-98-007 – Guide to Documenting and Managing Cost and Performance Information for Remediation Projects (Revised Version), October 1998, Online: http://www.frtr.gov/archives.htm.

Gandhi, R.K., G.D. Hopkins, M.N. Goltz, S.M. Gorelick, and P.L. McCarty. (2002a). Full-scale demonstration of in situ cometabolic biodegradation of trichloroethylene in groundwater, 1: dynamics of a recirculating well system, Water Resources Research, 38:11-1 - 11-19

Gandhi, R.K., G.D. Hopkins, M.N. Goltz, S.M. Gorelick, and P.L. McCarty. (2002b). Full-scale demonstration of in situ cometabolic biodegradation of trichloroethylene in groundwater, 2: comprehensive analysis of field data using reactive transport modeling, Water Resources Research, 38:10-1-10-16.

GeoSyntec Consultants Inc. (2002). Pilot Test of In Situ Bioremediation to Treat Perchlorate in GET D Recharge Water, Final Report, GeoSyntec Project Number TR0018.15, Guelph, Ontario, January.

Goltz, M.N., G.C. Mandalas, G.D. Hopkins, and P.L. McCarty. (1998). Technology transfer of an innovative remediation technology from the laboratory to the field: a case study of *in situ* aerobic cometabolic bioremediation, Environmental Engineering and Policy, 1:117-124.

Hackel, O. (1966). Summary of the Geology of the Great Valley. In E.H. Bailey (Ed.), Geology of Northern California, California Division of Mines and Geology Bulletin, 190: 217-238.

Hatzinger, P.B. (2005). Field application of perchlorate biodegradation for water treatment. Environmental Science and Technology, 39:240A-247A.

Hatzinger, P. B. and J. W. Kelsey. 2005. Biodegradation. *In* Encyclopedia of Soils in the Environment, D. Hillel (Ed.). Elsevier Press, Oxford, Volume 3, pp. 250-257.

Hatzinger, P. B., J. Diebold, C. A. Yates and R. J. Cramer. (2006). Field demonstration of *in situ* perchlorate bioremediation in groundwater. *In* Perchlorate: Environment Occurrence, Interactions, and Treatment, B. Gu and J. C. Coates (Eds.). Springer, New York. pp. 311-341.

Hatzinger, P.B., C. E. Schaefer, and E.E. Cox. (2008). Active bioremediation. *In* In Situ Bioremediation of Perchlorate. H Stroo and C.H. Ward. (Ed.). Springer, New York. pp. 91-131.

Hatzinger, P.B., J.K. Bohlke, N.C. Sturchio, L. Heraty, and R.C. Borden. (2009). Fractionation of stable isotopes in perchlorate and nitrate during in situ biodegradation in a sandy aquifer. Environmental Chemistry, 6: 44-52

Hatzinger, P.B. and D. Lippincott. (2009). Technology Demonstration Summary Report: In Situ Bioremediation of Perchlorate in Area 11 Alluvium Groundwater. US Army Corps of Engineers Final Project Report. 121 pp.

Hatzinger, P. B., M.C. Whittier, M.D. Arkins, C.W. Bryan, and W.J. Guarini. (2002). *In-situ* and *ex-situ* bioremediation options for treating perchlorate in groundwater. Remediation, 12, 69-86.

ITRC; Interstate Technology & Regulatory Council. (2008). Remediation Technologies for Perchlorate Contamination in Water and Soil. PERC-2, ITRC, Washington, D.C., 152 pp.

Johansen, C., P. Falholt, and L. Gram. (1997). Enzymatic removal and disinfection of bacterial biofilms. Applied and Environmental Microbiology, 63: 3724-3728.

Kengen, S. W. M., G.B. Rikken, W.R. Hagen, C.G. van Ginkel, and A.J.M. Stams. (1999). Purification and characterization of (per)chlorate reductase from chlorate-respiring strain GR-1. Journal of Bacteriology, 181:6706-6711.

Kopinke, F-D., A. Georgi, M. Voskamp and H.H. Richnow. 2005. Carbon isotope fractionation of organic contaminants due to retardation on humic substances: Implications for natural attenuation studies in aquifers. Environmental Science and Technology, 39:6052-6062.

Knarr, M.R. (2003). Optimizing an In Situ Bioremediation Technology to Manage Perchlorate-Contaminated Groundwater, MS Thesis, AFIT/GEE/ENV/03-14, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March.

Krug, T.A., and E.E. Cox. (2008). Semi-passive In situ bioremediation. *In* In Situ Bioremediation of Perchlorate. H.F. Stroo and C. H. Ward. (Ed.). Springer, New York. pp. 135-154

Logan, B. E. (1998). A review of chlorate- and perchlorate-respiring microorganisms. Bioremediation Journal, 2:69-79.

Logan, B. E. (2001). Assessing the outlook for perchlorate remediation. Environmental Science and Technology, 35:483A-487A.

McCarty, P.L., M.N. Goltz, G.D. Hopkins, M.E. Dolan, J.P. Allan, B. Kawakami, and T.J. Carrothers. (1998). Full-scale evaluation of in situ cometabolic degradation of trichloroethylene in groundwater through toluene injection. Environmental Science and Technology, 32:88-100.

MADEP, Massachusetts Department of Environmental Protection. (2009). Water, Wastewater, and Wetlands. Online: http://www.mass.gov/dep/water/drinking/standards /perchlor.htm.

Miller, J.P., and B.E. Logan. (2000). Sustained perchlorate degradation in an autotrophic, gas-phase, packed-bed bioreactor. Environmental Science and Technology, 34:3018-3022.

Munakata, N., J.A. Cunningham, and M. Reinhard. (2002). Palladium catalysis in horizontal-flow treatment wells: field-scale design and laboratory study. *In* Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Paper 2H-33, Monterey CA, May.

NAS; National Academies of Science. (2005). Health Implications of Perchlorate Ingestion. Committee to Assess the Health Implications of Perchlorate Ingestion, National Research Council, The National Academies Press, 276 pp.

Parr, J.C. (2002). Application of Horizontal Flow Treatment Wells for *In Situ* Treatment of Perchlorate Contaminated Groundwater. M.S. Thesis, AFIT/GEE/ENV/02M-08, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March.

Rajagopalan, S., T.A. Anderson, L. Fahlquist, K.A. Rainwater, M. Ridley, W.A. Jackson. (2006). Widespread presence of naturally occurring perchlorate in high plains of Texas and New Mexico. Environmental Science and Technology. 40:3156-3162.

Rikken, G.B., A.G.M. Kroon, and C.G. van Ginkel. (1996). Transformation of (per)chlorate into chloride by a newly isolated bacterium: reduction and dismutation. Applied Microbiology and Biotechnology, 45:420-426.

Secody, 2007. Modeling In Situ Bioremediation of Perchlorate-Contaminated Groundwater. M.S. Thesis, AFIT/GEM/ENV/07M-13, Graduate School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB OH, March.

SERDP; Strategic Environmental Research and Development Program. (2003). Bioenhanced In-Well Vapor Stripping (BEHIVS) to Treat Trichloroethylene. Final Report, SERDP Project CU-1064. Online: http://www.cluin.org/download/contaminant focus/tce/ BEHIVS2003.pdf.

Shaw Environmental, Inc. 2009. Technology Demonstration Summary Report: In Situ Bioremediation of Perchlorate in Area 11 Alluvium Groundwater, Former Whittaker-Bermite Facility, Santa Clarita, California. Final Project Report, US Army Corps of Engineers Contract DACA42-03-C-0064.

Song, Y, and B.E. Logan, B.E. 2004. Effect of O_2 exposure on perchlorate reduction by *Dechlorosoma* sp. KJ. Water Research, 38:1626-1632.

Stroo, H., and C.H. Ward (Eds). 2008. *In Situ* Bioremediation of Perchlorate in Groundwater. Springer, New York. 248 pp.

Sutton, P.M. (2006). Bioreactor configurations for *ex situ* treatment of perchlorate: A review. Water Environment Research 78:2417-2427.

Tan, K., T.A. Anderson and W.A. Jackson. (2004). Degradation kinetics of perchlorate in sediments and soils. Water, Air, and Soil Pollution, 151: 245-259.

Urbansky, E. T. (1998). Perchlorate chemistry: implications for analysis and remediation. Bioremediation Journal, 2:81-95.

USEPA; U.S. Environmental Protection Agency. (2000). Technical Background Information for the Unregulated Contaminant Monitoring Regulation. EPA 815-R-99-007. Office of Water, Washington, DC.

USEPA; U.S. Environmental Protection Agency. (2001). Perchlorate. Office of Water, Online: http://www.epa.gov/safewater/ccl/perchlor/ perchlo.html.

USEPA; U.S. Environmental Protection Agency. (2002). Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization, External Review Draft, National Center for Environmental Assessment (NCEA), NCEA-1-0503, January 16.

van Ginkel, C. G., G.B. Rikken, A.G.M. Kroon, S.W.M. Kengen. (1996). Purification and characterization of a chlorite dismutase: a novel oxygen-generating enzyme. Archives of Microbiology, 166:321-326.

Waller, A.S., E.E. Cox, and Edwards, E.A. (2004). Perchlorate-reducing microorganisms isolated from contaminated sites. Environmental Microbiology, 6:517-527.

Waterra, Inc. (2009). Waterra Groundwater Monitoring Equipment and Supplies. Online: http://www.waterra.com/pages/Product_Line/inertial_pumps/inertial_pump.html.

Wu, J., R.F. Unz, H. Zhang, and B.E. Logan. (2001). Persistence of perchlorate and the relative numbers of perchlorate- and chlorate-respiring microorganisms in natural waters, soils, and wastewater. Bioremediation Journal, 5:119-130.

Xu, J.Y., Y. Song, B. Min, L. Steinberg, and B.E. Logan. 2003. Microbial degradation of perchlorate: principles and applications. Environmental Engineering Science, 20:405-422.

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APPENDICES

IN SITU BIOREMEDIATION OF PERCHLORATE USING HORIZONTAL FLOW TREATMENT WELLS

ESTCP PROJECT ER-0224

APPENDIX A:

Analytical Methods

The attached methods are the *Shaw Environmental and Infrastructure Analytical and Treatability Laboratory* Standard Operating Procedures (SOP) for Analysis of:

(1) Perchlorate by EPA Method 314.0;
(2) Anions by EPA Method 300.0;
(3) Volatile Fatty Acids (no applicable EPA Method);
(4) Volatile Organic Compounds by EPA Method 8260.

The SOPs provide the specific laboratory methods and equipment used to perform each specified EPA analytical method.

Shaw E&I Analytical and Treatability Laboratory

Standard Operating Procedures

Volume I

Conventional Chemistry (Wet Chemistry and Ion Chromatography Methods)

January 2009

SHAW METHOD	**SHAW IC-003**
EPA METHOD #: 314.0 Rev1.0	**Approved (1999)**
TITLE:	**Perchlorate (Ion chromatography)**
ANALYTE:	**Perchlorate**
INSTRUMENTATION:	**IC**
VERSION.	**2006**
NUMBER	**2**

PERCHLORATE (SHAW IC-003; EPA 314.0)

1. SCOPE AND APPLICATION

1.1 This method covers the determination of perchlorate in reagent water, surface water, ground water, finished drinking water, soils and sludges using ion chromatography.

1.2 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained, and must be capable of yielding a baseline with no more than 5 nano-siemen (nS) noise/drift per minute of monitored response over the background conductivity.

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4 When this method is used to analyze unfamiliar samples for perchlorate, anion identification should be supported by the use of a laboratory fortified matrix sample. The fortification procedure is described in Section 9.4.1.

2.0 SUMMARY OF METHOD

2.1 A 1.0 mL volume of sample is introduced into an ion chromatograph (IC). Perchlorate is separated and measured, using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector.

NOTE: This large sample loop (1.0 mL) can be made using approximately 219 cm (86 inches) of 0.03 inch i.d. PEEK tubing.

3.0 DEFINITIONS

3.1 ANALYSIS BATCH -- A sequence of samples, which are analyzed within a 30 hour period and include no more than 20 field samples. An Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20. The required QC samples include:

Instrument Performance Check Standard (IPC)
Laboratory Reagent Blank (LRB)
Initial Calibration Check Standard (ICCS)
Laboratory Fortified Blank (LFB)
Continuing Calibration Check Standard (CCCS), when the batch contains more than 10 field samples
End Calibration Check Standard (ECCS)
Laboratory Fortified Matrix (MS)
Either a Field Duplicate, a Laboratory Duplicate or a duplicate of the MS
(if pretreated samples are included in batch) Pretreated LRB
(if pretreated samples are included in batch) Pretreated LFB
(if pretreated samples are included in batch) Pretreated LFM, for each pretreated matrix.

NOTE: Every field sample analysis, including both diluted and pretreated field samples, but excluding any MS/MSD or duplicate field sample analysis which qualify as QC samples, must be applied to the maximum of 20 total field samples permitted in an analysis batch.

3.1.1 A field sample(s), included in the analysis batch, can be reanalyzed following the ECCS provided the 30 hr time limit for the analysis batch has not expired. The laboratory can reanalyze that sample(s) but must initially conduct a second ICCS before the reanalysis and an ECCS after the final reanalysis. The ECCS must be completed within the 30 hr window.

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution(s) or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 INITIAL CALIBRATION STANDARDS --A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions (Section 10.2).

3.4 INITIAL CALIBRATION CHECK STANDARD (ICCS) --A CAL solution, which is analyzed initially, prior to any field sample analyses, which verifies the previously established calibration curve. The concentration for the initial calibration check standard MUST be at or

below the MRL (Section 3.17) level.

3.5 CONTINUING CALIBRATION CHECK STANDARDS (CCCS) -- A CAL solution which is analyzed after every tenth field sample analyses, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous ten field samples analyzed. The concentration for the continuing calibration check standards should be either at a middle calibration level or at the highest calibration level (Section 10.3.2).

3.6 END CALIBRATION CHECK STANDARD (ECCS) -- A CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curve and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check. The end calibration check standard should be either the middle or high level continuing calibration check standard (Section 10.3.2).

3.7 FIELD DUPLICATES (FD) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.8 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- solution containing a specific concentration of perchlorate used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.9 LABORATORY DUPLICATE (LD) --Two sample aliquots (LD1 and LD2), taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated specifically with the laboratory procedures by removing variation contributed from sample collection, preservation and storage procedures.

3.10 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water, or other blank matrix, to which a known quantity of perchlorate is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX (MS/MSD) – An aliquot of an environmental field sample to which a known quantity of

perchlorate is added in the laboratory. The MS/MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical result. The background concentrations of perchlorate, in the sample matrix, must be initially determined in a separate aliquot and the measured value in the MS/MSD corrected for this background concentration.

3.12 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with other samples. The LRB is used to determine if perchlorate or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.13 LINEAR CALIBRATION RANGE (LCR) – The concentration range over which the instrument response is linear.

3.14 MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.15 MATRIX CONDUCTIVITY THRESHOLD (MCT) – The highest permitted conductance of an unknown sample matrix, measured prior to conducting the analysis, which is used to determine when sample matrix dilution or pretreatment is required. The conductance of a sample matrix is proportional to the common anions present in the matrix (which contributes to the level of total dissolved solids [TDS]) which can greatly affect the integrity of this analysis. The value for this threshold is dependant on the conditions, hardware, and state of the hardware employed. Consequently, this threshold is not method defined and must be determined by the individual analytical laboratory during the Initial Demonstration of Capability (IDC) and confirmed in each analysis batch using the Instrument Performance Check (IPC) Solution. Matrix conductivity is measured in microsiemens/cm (uS/cm) or microMhos/cm (uMhos/cm) which are considered equivalent terms.

3.16 METHOD DETECTION LIMIT (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.[7, 8]

3.17 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a target analyte in a sample

following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.18 PEAK AREA TO HEIGHT RATIO (A/H) – The ratio of the peak area divided by the peak height which is used as a tool to monitor analytical performance. This ratio is used to establish and monitor the MCT and represents an objective means of assessing analytical performance when analyzing high conductivity matrices. A gradual distortion of the baseline is typically observed in the retention time window for perchlorate as the matrix conductivity increases (consistent with elevated levels of common anions) which will more significantly influence peak height relative to the influence on peak area. As the distortion of the baseline increases, this ratio increases, and the integrity of the measured perchlorate will be compromised.

3.19 PROFICIENCY TESTING (PT) or PERFORMANCE EVALUATION (PE) SAMPLE

- A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Often, results of these analyses are used as part of a laboratory certification program to objectively determine the capabilities of a laboratory to achieve high quality results.

3.20 LABORATORY CONTROL SAMPLE (LCS) – A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.21 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing perchlorate which is either prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.22 TOTAL DISSOLVED SOLIDS (TDS) -- Both organic and inorganic constituent which are dissolved in a sample matrix and are not removed by particulate filtration.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise.

4.2 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.2.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst MUST verify that these changes do not induce any negative affects on method performance by repeating and passing all the QC criteria as described in Section 9.

4.2.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that **sample dilution will alter your Minimum Reporting Limit (MRL)** by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution.

4.2.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. With any proposed pretreatment, the analyst must verify that the target analyte is not affected by monitoring recovery after pretreatment (additional pretreated MS requirement see Section 11.1.4.6) and that no background contaminants are introduced by the pretreatment (additional pretreated LRB requirement see Sections 9.3.1 and 11.1.4).

4.2.3.1 Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from

certain cartridges which can foul the guard and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) or use calibration chromatograms generated when the column was initially installed, to insure proper separation and similar response ratios between the target analytes are observed.

4.2.3.2 If LRB background problems are encountered in the retention time window for perchlorate when these pretreatment cartridges have been employed, increase the initial reagent water rinse of the cartridge to approximately five times the volume specified by the manufacturer.

4.3 Sample matrices with high concentrations of common anions such as chloride, sulfate and carbonate can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. This is evidenced by observing a protracted tailing following the initial elution of the more weakly retained anions (chloride, carbonate, and sulfate) which extends into the perchlorate retention time window. These common anion levels can be indirectly assessed by monitoring the conductivity of the matrix. Consequently, all sample matrices must be monitored for conductivity (Section 11.1.2) prior to analysis. When the laboratory determined Matrix Conductivity Threshold (MCT, see Section 9.2.8) is exceeded, procedures incorporating sample dilution and/or pretreatment must be performed as specified in Sections 11.1.3 and 11.1.4, respectively.

4.4 All reagent solutions (eluents, external water for ASRS suppressor, etc...) used by the instrument must be filtered through no larger than a 0.45 um nominal pore size membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. Sample filtration must also be employed on every sample prior to analysis. This applies not only to field samples but also to the laboratory reagent blank (LRB) and laboratory fortified blank (LFB). The LRB and LFB samples function as controls and must be filtered to confirm no bias is attributable to the filtration.[5] Filter the samples through a membrane or frit with no larger than a 0.45 um nominal pore size. Syringe mounted, cartridge type, filters work well.

4.5 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of perchlorate in a second, subsequent analysis. It is the responsibility of the user to confirm

that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are specifically listed below in Section 5.3 for hazardous materials.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable. Additional references on laboratory safety are available.[9-12]

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Potassium hydroxide (KOH), used in the preparation of the eluent is considered caustic.

6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph (IC) –a Dionex ICS 2000 system analytical system complete with a KOH eluent EG40 generator, a ion chromatographic pumps, injection valves, both guard and analytical separator columns, suppressor, conductivity detector, and computer based data acquisition system.

6.1.1 Anion guard column -- Dionex AG16 2 mm, or equivalent. This column functions as a protector of the separator column. If omitted from the system, the retention times will be shorter.

6.1.2 Anion separator column -- Dionex AS16, 2mm.

6.1.3 Anion suppressor device -- A Dionex Self Regenerating Suppressor (2 mm, ULTRAII) to give no more than a. combined baseline drift/noise of no more than 5 nS per minute over the background conductivity. Proper suppressor performance is essential to analytical data reproducibility and sensitivity of the conductivity detector.

6.1.3.1 The ASRS is set to perform electrolytic suppression at a current setting of 150 mA using the external water mode. External water was delivered to the suppressor directly from a pressurized source at a flow rate of ~ 5 mL/min

6.1.3.2 If pretreated samples (Section 11.1.4), or sample matrices which contain appreciable concentrations of transition metal cations (e.g., Fe or Al) are frequently analyzed, cationic components may bind to the suppressor membrane and over time effect suppressor performance. If the instrument begins to have problems with reduced peak response or asymmetrical perchlorate peaks, the suppressor membranes should be cleaned. As a quick and easy cleaning step, the manufacturer's ASRS "Quickstart" procedure for installing a new ASRS should be followed. If this procedure does not correct the problem, follow the manufacturer's recommended cleaning procedure for removing metal contaminants.

6.1.4 Detector -- Conductivity cell (Dionex heated DS6, or equivalent) capable of providing data as required in Section 9.2.

6.1.5 Autosampler Dionex AS50 Autosampler, 10ml autosampler vial rack

6.2 Data Acquisition System -- The Dionex Chromeleon Data Chromatography Software is used to generate all the data

6.3 Conductivity Meter – Used to monitor sample matrix conductance which is directly related to the common anion levels in a matrix and used to determine if sample pretreatment is required. At a minimum, this meter should be capable of measuring matrix conductance over a range of 1 - 10,000 uS/cm.

6.4 Micro beakers -- Plastic, disposable - used during sample preparation.

6.5 Syringes -- Plastic, disposable- used during sample preparation.

6.6 Pipets --Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL. Micropipettes 20, 100, 1000 ul capacities.

6.7 Bottles -- High density polyethylene (HDPE) or glass, amber or clear, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions. Stability studies presented by the Interagency Perchlorate Steering Committee for Analytical Methods [6] and confirmed at the EPA, indicate perchlorate is neither photoreactive nor prone to adsorption to the walls of either HDPE plastic or glass bottles.

6.8 Particulate filters -- 0.45 micron syringe filters, specifically designed for IC applications (Gelman IC Acrodisc, PN 4485, or equivalent). These cartridges are used to remove particulates from the sample matrix while loading the sample manually or if the autosampler employed does not filter the sample during loading.

6.9 Matrix pretreatment cartridges in the barium form -- (Dionex OnGuard-Ba cartridges, PN 046072, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of sulfate.

6.10 Matrix pretreatment cartridges in the silver form – (Dionex OnGuard-Ag cartridges PN 039637, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of chloride.

6.11 Matrix pretreatment cartridges in the hydrogen form -- Dionex OnGuard-H cartridges (PN 039596) or equivalent. These cartridges are conditioned according to the manufacturer's directions and are used to reduce cations in the sample matrix. This protects the analytical column by removing silver which has leached from the Ag cartridge and may indirectly minimize the effect of carbonate by removing the cationic counter ion.

7.0 REAGENTS AND STANDARDS

7.1 Reagent water -- Deionized water 18.2 Mohm or better, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.2 Eluent solution -- 50 mM potassium hydroxide (KOH,) is automatically generated using Dionex eluent generator EG40.

7.3 Perchlorate stock standard solution, 1000 mg/L (1 mg/mL) – A certified stock standard solution is purchased (as a certified solution) or if unavailable it can be prepared from ACS reagent grade, sodium salt as listed below. (NOTE: Sodium perchlorate represents a molar weight fraction of 81.2 % perchlorate anion). A secondary stock (1,000 mg/L) is purchased for use in preparing the Laboratory Control Sample.

7.3.1 Perchlorate (ClO_4^-) 1000 mg/L --Dissolve 0.1231 g sodium perchlorate ($NaClO_4$, CASRN [7601-89-0] in reagent water and dilute to 100 mL in a volumetric flask.

7.3.2 Working standard solution (1,000 ug/L) are prepared from the Standard stock solution and the laboratory control stock by a 1:1000 dilution (0.1 ml into 100 ml) in ultrapure water.

NOTE: Stability of standards -- Perchlorate stock standards, stored at room temperature, appear to be very stable and may be stable for an extended period of time. However, specified expiration dates should be marked on each prepared stock standard as part of any laboratory's quality control program. In this regard, it is recommended that stock standards for perchlorate be held for no more than 12 months and an expiration date should be clearly specified on the label.

7.4 Mixed Common Anion Stock Solution - containing the anions chloride, sulfate and carbonate each at 25 mg/mL anion concentration. This solution is used to prepare simulated common anion samples in the determination of the MCT (Section 9.2.8).

7.4.1 Dissolve the following salts in reagent water to a final volume of 25.0 mL: 1.0 g sodium chloride (NaCl, CASRN [7647-14-5]) = 0.61 g Cl^-
0.93g sodium sulfate (Na_2SO_4, CASRN [7757-82-6]) = 0.63 g $SO_4^=$
1.1 g sodium carbonate (Na_2CO_3, CASRN [497-19-8]) = 0.62 g $CO_3^=$

7.5 Conductivity Meter Calibration Solution (1410uS/cm) is purchased as a certified standard

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples may be collected in certified cleaned plastic or glass bottles. The volume collected should be sufficient to insure a representative sample (~100 ml), allow for replicate analysis and laboratory fortified matrix analysis, if required, and minimize waste disposal.

8.2 Samples need to be shipped iced or stored cold in a refrigerator but every effort should be taken to protect the samples from temperature extremes. A thermally insulated sampling kit, designed to fit sampling bottles securely during shipment, should be used to protect the samples from these temperature extremes.

8.3 Soils should be collected in clean sample jars or bags and be kept cool and shipped on ice to laboratory.

8.4 Sample preservation and holding times for the anions are as follows:

Analyte	Preservation	Holding Time
Perchlorate	None required But filtration recommended	28 days

NOTE: Perchlorate has been shown to be stable for more than 28 days[6] but extended holding time studies (beyond 35 days) were not conducted by EPA. Internal stability studies have shown that

IF bacteria present that can degrade perchlorate, perchlorate **WILL DEGRADE** rapidly especially at room temperature unless sample is filtered through a 0.22 or 0.445 um filter to remove bacteria

9.0 QUALITY CONTROL

9.1 The laboratory is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory capability, and subsequent analysis in each analysis batch (Section 3.1) of an Instrument Performance Check Standard (IPC), Laboratory Reagent Blank (LRB), Initial Calibration Check Standard (ICCS), Laboratory Fortified Blank (LFB), Continuing and End Calibration Check Standards (CCCS/ECCS), Laboratory Fortified Sample Matrix (LFM) and either a Field, Laboratory or MS/MSD duplicate sample analysis. This section details the specific requirements for each of these QC parameters.

9.2 INITIAL DEMONSTRATION OF CAPABILITY

9.2.1 The Initial Demonstration of Capability (IDC) -- This is used to characterize instrument and laboratory performance prior to performing analyses by this method.

9.2.2 Initial demonstration of low system background -- See Section 9.3.1.

9.2.3 Initial Demonstration of Accuracy (IDA) -- Prepare and analyze 7 replicate LFBs fortified at 25.0 ug/L. Calculate the mean measured concentration (C_0) of the replicate values. To pass the IDA, the value derived for C_0 must be within ± 10% of the true value or between 22.5 ug/L and 27.5 ug/L.

9.2.4 Initial Demonstration of Precision (IDP) -- Using the data generated for Section 9.2.3, calculate the percent relative standard deviation (%RSD) of the replicate analysis, as indicated below. To pass the IDP, the %RSD must be less than 10%.

9.2.5 Laboratory Control Sample (LCS) – After calibration curves have initially been established or have been re-established, or as required to meet data quality needs, verify both the calibration and acceptable instrument performance with the preparation and analyses of an external/second source LCS. If the determined concentrations are not within ± 10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the IDC or continuing with on-going analyses.

9.2.6 Method Detection Limit (MDL) – An MDL must be established using reagent water (blank) fortified at a at or near the lowest concentration in the calibration curve. Follow Shaw's procedure outlined in its QAPP for MDL determination.

9.2.6.1 MDLs are verified on a yearly basis,

9.2.7 Minimum Reporting Level (MRL) – The MRL is set at 1.0 ug/L (2X) the lowest calibration standard.

9.2.8 Matrix Conductivity Threshold (MCT) – The MCT is an individual laboratory defined value which must be determined by preparing a series of sequentially increasing, common anion fortified, reagent water samples each contain a constant perchlorate concentration. Initially, a reagent water prepared LFB, containing no common anions, must be analyzed which contains perchlorate at a concentration of 25 ug/L perchlorate. Next, the series of sequentially increasing anionic solutions are prepared, each containing perchlorate at a concentration of 25 ug/L, which also containing the individual common anions of chloride, sulfate and carbonate, all included at uniform increasing concentrations of 200, 300, 400, 500, 600, 800, and 1000 mg/L for each anion.

9.2.8.1 Prepare the mixed common anion stock solution (see Section 7.4) containing chloride, sulfate and carbonate, each at 25 mg/mL.

9.2.8.2 Prepare a perchlorate secondary stock dilution standard at 1.00 mg/L from the 1000 mg/L perchlorate stock standard (Section 7.3) by diluting 0.50 mL of the stock solution to a final volume of 500 mL.

9.2.8.3 Prepare the LFB at a perchlorate concentration of 25 ug/L by diluting 0.625 mL of the perchlorate secondary stock dilution standard (Section 9.2.8.2) to a final volume of 25.0 mL.

9.2.8.4 Next, prepare the series of common anion fortified reagent water samples by adding 0.20 mL, 0.30 mL, 0.40 mL, 0.50 mL, 0.60 mL, 0.80 mL, and 1.00 mL of the mixed common anion stock solution (Section 7.4) into separate 25 mL volumetric flasks. Next, add 0.625 mL of the perchlorate secondary stock dilution standard (Section 9.2.8.2) to each 25 mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 25.0 ug/L.

9.2.8.5 Measure and record the conductance of each of these prepared solutions on a calibrated conductivity meter (This meter must be calibrated as described in Section 10.4 prior to measuring conductance). To use as a relative reference conductance, the 400 mg/L mixed anion sample, which contains chloride at 400 mg/L, sulfate at 400 mg/L and carbonate at 400 mg/L, should display a conductance of between 3200 uS/cm and 3700 uS/cm.

9.2.8.6 Analyze each solution, recording the peak area to height (A/H) ratio and the quantified concentration of perchlorate. In the Dionex data acquisition and instrument control software, the peak area to height ratio is a definable parameter which can be specified for printout on the analysis report.

9.2.8.7 Both the A/H ratio and quantified perchlorate concentration for the LFB and the 200 mg/L mixed common anion solution should be reproducibly consistent but as the common anion levels increase, the A/H ratio will also begin to increase as the peak height is distorted and reduced. As the peak is distorted, the area will also eventually begin to be distorted and the quantitated concentration will be reduced, but this is typically secondary, with the ratio of peak area to height initially predicting this pending quantitation problem.

9.2.8.8 Calculate the A/H ratio percent difference ($PD_{A/H}$) between the average A/H ratio for the LFB (A/H_{LFB}) and the average A/H ratios for each mixed common anion solutions (A/H_{MA}) using the following equation.

$$PD_{A/H} = \frac{*(A/H_{LFB} - A/H_{MA})*}{A/H_{LFB}} \text{ X } 100$$

9.2.8.9 The MCT is set at the conductance level of the highest mixed anion solution which yielded a $PD_{A/H}$ value below the 20 % threshold.

9.2.8.10 Finally, confirm the perchlorate MRL in a mixed common anion solution which reflects a conductance near (within +/- 10%) that specified as the MCT. This solution must contain perchlorate, at the laboratory determined MRL (lowest calibration point), as well as the common anions chloride,

sulfate and carbonate, prepared consistent with the instruction for the mixed anion solutions in this section and at a concentration estimated to generate a conductance near the MCT. The conductance of this solution must be measured at within ±10% of the MCT and following the analysis, the recovered perchlorate must be between 70 - 130% of the MRL concentration. If the MRL recovery fails these criteria, the MCT should be lowered by 10% and this MRL verification must be repeated.

9.2.8.11 Prior to conducting any field sample analysis, the conductivity of that matrix must be determined. When the conductance of a field sample is above the MCT, sample dilution or pretreatment, as described in respective Sections 11.1.3 and 11.1.4 must be performed.

9.3 ASSESSING LABORATORY PERFORMANCE - The following items must be included in every analysis batch (Section 3.1).

9.3.1 Laboratory Reagent Blank (LRB) – An LRB must be prepared and treated exactly as a typical field sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with field samples. Data produced are used to assess instrument performance of a blank sample and evaluate contamination from the laboratory environment. Values that exceed ½ the MRL indicate a laboratory or reagent contamination is present. The source of the contamination must be determined prior to conducting any sample analysis. Any sample included in an automated analysis batch which has an invalid LRB, indicated by a quantitated perchlorate that exceeds ½ the MRL, must be reanalyzed in a subsequent analysis batch after the contamination problem is resolved.

9.3.1.1 When sample matrices have been pretreated to reduce the risk of high common anion interference (Section 11.1.4), a second LRB must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects from the pretreatment process are present. If an analysis batch only contains pretreated samples, then only a pretreated LRB is required.

9.3.2 Instrument Performance Check (IPC) -- The MCT, which was determined as part of the IDC in Section 9.2.8, must be verified through the analysis of an IPC. The IPC is three tiered and is used to verify the state of the IC system, over time, to quantitate perchlorate in highly ionic matrices. This must be conducted with each analysis

batch since over time, column performance can change.

9.3.2.1 Prepare a mixed common anion solution which reflects a conductance near (within +/- 10%) that specified as the MCT. This solution must be prepared consistent with the instruction in Section 9.2.8, and containing the common anions chloride, sulfate and carbonate as well as perchlorate at a concentration of 25 ug/L.

9.3.2.2 Confirm the conductance of the IPC and analyze it as the initial sample in the analysis batch. If, after several weeks of storage, the measured conductance of this solution has shifted by more than 10% from the original measured value, prepare a fresh IPC solution. Following the analysis, calculate the $PD_{A/H}$ (Section 9.2.8.8), by comparing the peak area to height ratio of this IPC mixed anion standard (A/H_{MA}) for this analysis batch to the value that was derived for the LFB (A/H_{LFB}) either in the original IDC or in the previous analysis batch. As the first tier criteria, the value for $PD_{A/H}$ must be less than 25% before proceeding with the analysis batch.

9.3.2.3 At the second tier criteria, the measured recovery for perchlorate in this IPC must fall between 80% and 120 % (20.0 ug/L to 30.0 ug/L for a 25 ug/L fortification).

9.3.2.4 As a third tier and final criteria for the IPC, the laboratory must closely monitor the perchlorate retention time for this analysis. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if sudden shifts of more than 5% are observed in the perchlorate retention time; some type of instrument problem may be present. Potential problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The observed retention time for perchlorate should closely replicate the times established when the column was originally installed. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column requires cleaning (according to manufacturer's instructions) or replacement.

9.3.2.5 If any of the conditions defined in Section 9.3.2.2 through

9.3.2.4 are not met, the MCT must be repeated and revised to a more appropriate lower matrix conductivity threshold or the source of the problem must be determined and the IPC reanalyzed.

9.3.3 Laboratory Fortified Blank (LFB) – Prepare a secondary dilution stock using the same stock solution used to prepare the calibration standards. This separate, secondary dilution stock is used as a concentrate to fortify the LFB and the MS/MSDs (Section 9.4.1). An external source stock or LCS, which is used to verify the accuracy of the calibration curve when it was initially prepared (Section 10.2.5), should not be used to prepare this secondary dilution stock. Laboratories are required to analyze a LFB (filtered as if it were a field sample) with each analysis batch immediately following the ICCS. The LFB must be prepared with the same solution used to prepare the LFM and should be prepared at concentrations no greater than ten times the highest concentration observed in any field sample and should be varied to reflect the range of concentrations observed in field samples. By analyzing the LFB initially, a control check is performed on the concentrated solution used to prepare the MS. If any deviations in the perchlorate concentration are present, it will be reflected in the LFB and not exclusively attributed to a matrix upon analysis of the MS. Calculate accuracy as percent recovery (Section 9.4.1.3). The recovery for perchlorate must fall in the range of 85 - 115% prior to analyzing samples. If the LFB recovery for an analysis batch does not meet these recovery criteria the data are considered invalid, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3.1 When sample matrices have been pretreated to reduce the risk of high common anion interference (Section 11.1.4), a second LFB must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects or recovery bias induced by the pretreatment are present. If an analysis batch only contains pretreated samples, then only a pretreated LFB is required.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY -The following must be included in every analysis batch (Section 3.1).

9.4.1 Laboratory Fortified Sample Matrix (MS) – The laboratory must add a known amount of each target analyte to a minimum of 1 every 20 collected field samples or at least one with every analysis batch, whichever is greater. Samples which exceed the MCT must either be diluted or pretreated to reduce the common anion levels (Section

11.1.3). Samples which are pretreated have additional MS requirements described in Section 11.1.4.6, and must be fortified before pretreatment. For MS to be valid, the target analyte concentrations must be greater than the native level and should adhere to the requirement outlined below. The solutions used to fortify the MS are prepared from the same stocks used to prepare the calibration standards.

9.4.1.1 The fortified concentration must be equal to or greater than the native sample concentration. Fortified samples that exceed the calibration range must be diluted to be within the linear range. In the event that the fortified level is less than the observed native level of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration to fortified concentration ratio is greater than one.

9.4.1.2 Calculate the percent recovery for each target analyte, corrected for concentrations measured in the unfortified sample.

9.4.1.3 Recoveries may exhibit a matrix dependence. If the recovery for perchlorate falls outside 80 - 120%, and the laboratory's performance for all other QC performance criteria is acceptable, the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. Repeated failure to meet suggested recovery criteria indicates potential problems with the procedure and should be investigated.

9.4.2 FIELD, LABORATORY DUPLICATES OR DUPLICATE LFM – The laboratory must analyze either a field duplicate, a laboratory duplicate, or a duplicate MS for a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and ensure the quality of the data.

9.4.2.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_c) and duplicate quantitated concentration (D_c) using the following formula.

$$RPD = \frac{*(I_c - D_c)*}{([I_c + D_c]/2)} \times 100$$

9.4.2.2 Duplicate analysis may exhibit a matrix dependence. If the RPD for the duplicate measurements of perchlorate falls outside ± 15% and if all other QC performance criteria are met, laboratory precision is out of control for the sample and perhaps the analytical batch. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses), it indicates a problem with the instrument or individual technique that must be corrected.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required prior to the IDC and before any samples are analyzed, and is required intermittently throughout sample analysis to meet required QC performance criteria outlined in this method and summarized in Table 3. Initial calibration verification is performed using a LCS as well as with each analysis batch using an initial, continuing (when more than 10 field samples are analyzed), and end calibration check standards. The procedures for establishing the initial calibration curve are described in Section 10.1. The procedures to verify the calibration with each analysis batch is described in Section 10.3.

10.2 INITIAL CALIBRATION CURVE

10.2.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

10.2.2 Prepare the calibration standards by carefully adding measured volumes of the stock standard diluting to volume with reagent water as described below:

Final Perchlorate conc	Amount of (1,000 ug/L) standard	Amount of reagent water
0.5 ug/L	2.5 ul	4.9975 ml
1.0 ug/L	5.0ul	4.995 ml
5.0 ug/L	25.0 ul	4.975 ml
10.0 ug/L	50.0 ul	4.950 ml
20.0 ug/L	100.0 ul	4.900 ml
50.0 ug/L	250.0 ul	4.750 ml
100.0 ug/L	500.0 ul	4.500 ml
200.0 ug/L	1000.0 ul	4.000 ml

10.2.3 Inject 1.0 mL of each calibration standard. Tabulate peak area responses against the perchlorate concentration. The results are used to prepare a calibration curve. This is done automatically by the Dionex software. Acceptable calibration is confirmed after reviewing the curve for linearity (r^2>0.995) and passing the criteria for the initial calibration check standard ±10% of true value.

10.2.3.1 Using peak areas, it is the analyst's responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks, since poorly drawn baselines will significantly influence peak areas.

10.2.4 After establishing or reestablishing calibration curves, the accuracy of this calibration must be verified through the analysis of a LCS or externally prepared second source. The LCS should be prepared at a concentration near the middle of the calibration curve. The determined concentrations must fall within ± 10% of the stated values.

10.2.5 Determine the Linear Calibration Range (LCR) -- The LCR is determined by running analysis of samples above the calibration curve (300ug/L, 400 ug/L etc.). The results of this analysis are plotted as an extension to the calibration curve to determine the full linear range. The final calibration point of the curve (200.0 ug/L) must be within 80% of the actually reflection point of the linear range. The linear calibration range must extend to at least 250 ug/L perchlorate.

10.3 CONTINUING CALIBRATION VERIFICATION -- Initial calibrations may be stable for extended periods of time. Once the calibration curve has been established it MUST be verified for each analysis batch, prior to conducting any field sample analysis using an Initial Calibration Check Standard. Continuing Calibration Check Standards and End Calibration Check Standards are also required as described in the sections below.

10.3.1 INITIAL CALIBRATION CHECK STANDARD (ICCS) – For each analysis batch the calibration must initially be verified prior to analyzing any samples. The lowest level standard used to prepare the linear calibration curve must be used. In cases where the analyst has chosen to set the MRL (1.0 ug/L) above the lowest standard, a standard at a concentration equal to the MRL is acceptable. Percent recovery for the ICCS must be in the range or 75 - 125% or as established by precision and accuracy evaluation before continuing the analysis batch and conducting any sample analyses.

10.3.2 CONTINUING CALIBRATION CHECK/END CALIBRATION CHECK STANDARDS (CCCS/ECCS) -- Continuing calibration check standards MUST be analyzed after every tenth field sample analysis and at the end of the analysis batch as an end calibration check standard. If more than 10 field samples are included in an analysis batch, the analyst must alternate between the middle and high continuing calibration check standard levels.

10.3.2.1 The percent recovery for perchlorate in the CCCS/ECCS must be between 85 - 115% or as established by precision and accuracy evaluation.

10.3.2.2 If during the analysis batch, the measured concentration for perchlorate in the CCCS or ECCS differs by more than the calibration verification criteria shown above, or if the perchlorate peak retention time shifts outside the retention time window, all samples analyzed after the last acceptable check standard are considered invalid and must be reanalyzed. The source of the problem must be identified and resolved before reanalyzing the samples or continuing analyses.

10.3.2.3 In the case where the end calibration fails to meet performance criteria, but the initial and middle calibration checks are acceptable, the samples bracketed by the acceptable calibrations may be reported. However, all field samples between the middle and end calibration checks MUST be reanalyzed.

10.4 CONDUCTIVITY METER CALIBRATION -- Prior to conducting the MCT and coinciding with each analysis batch, conductivity meter calibration must be verified or established using a standard KCl solution (Section 7.5).

10.4.1 Thoroughly rinse the conductivity electrode with reagent water. Place the electrode in the reagent water, turn on the meter and confirm the conductance of this blank is < 1 uS/cm.

10.4.2 Pour approximately 15 mL of the standard KCl solution (Section 7.5) into a plastic disposable micro beaker (Section 6.7) and place the electrode into the solution. The reference conductance for this solution is 1410 uS/cm at 25 $^{\circ}$C.[16] The conductivity meter must yield a conductance between 1380 uS/cm and 1440 uS/cm to be in calibration.

10.4.3 If the conductivity meter fails calibration, recalibrate the unit per Shaw's SOP SHAW CON-005.

11. ANALYTICAL PROCEDURE

11.1 SAMPLE PREPARATION

11.1.1 Samples are to be refrigerated as a standard practice for sample control, ensure the samples have come to room temperature prior to conducting sample analysis.

11.1.1.1 Aqueous samples need to be filtered either during field collection or they should be filtered immediately upon arrival at the lab to preclude any biological degradation of perchlorate.

11.1.1.2 Soil samples need to be extracted with laboratory DI water prior to analysis. A sample aliquot of 5 to 10 grams can be extracted in a volume of water to give a 5 fold dilution (5 g/25ml) in a sterile centrifuge tube. The slurry is placed on a rotary shaker for ~ 1 hr. The aqueous phase is collected after centrifugation and the sample is filtered through a 0.45 um nylon filter prior to analysis. A subsample of the soil is analyzed for moisture content in order to adjust final perchlorate concentration to a dry weight basis.

11.1.2 MATRIX CONDUCTANCE VERIFICATION - Prior to conducting the analysis of a field sample matrix, the conductance of that matrix must be measured unless there is historical data available for site samples. Matrix conductivity is directly related to the common anion levels which, at high concentrations, can influence the integrity of the perchlorate analysis.

11.1.2.1 Measure the conductivity of the sample using ~15 ml of sample with a calibrated conductivity meter.

11.1.2.2 If the conductance is less than the MCT, continue to Section 11.1.5.

11.1.2.3 If the conductance is greater than the MCT, the matrix requires dilution or pretreatment prior to analysis. The dilution procedure is found in Section 11.1.3. Pretreatment is described in Section 11.1.4.

11.1.2.4 Discard this aliquot of sample and be certain to thoroughly rinse the electrode with reagent water between each matrix conductivity measurement.

11.1.3 MATRIX DILUTION

11.1.3.1 A sample can be analyzed diluted with reagent water to a conductance below the MCT. The exact magnitude of this dilution will adversely increase the MRL by an equivalent proportion.

11.1.3.2 Knowing the matrix conductance exceeds the MCT, estimate the proportion required for the dilution by dividing the measured matrix conductance by the MCT. Round up to the next whole number and dilute the sample by a proportion equivalent to this value. For example, if the established MCT is 6100 uS/cm and a sample reflecting a conductance of 8000 uS/cm was measured, dilute the sample with reagent water by a factor of 2.

11.1.3.3 Measure the conductance of the diluted sample to confirm it is now below the MCT. Analyze the sample as specified in Section 11.1.5 with the understanding that the MRL has now been elevated by a proportion equivalent to the dilution. Adjust for dilution factor in reporting results.

11.1.4 PRETREATMENT FOR MATRICES WHICH EXCEED THE MCT

If sample dilution did not yield the required results, sample pretreatment should be employed. When the MCT is exceeded, it is most often due to a high levels of common anions (chloride, sulfate, and carbonate) in a particular matrix. To effectively reduce a significant amount of these anions which contribute to the high conductivity reading, a series of pretreatment cartridges must be employed. For this pretreatment, three cartridges are attached in series in the following order: Ba, Ag, and H.

11.1.4.1 Individually and thoroughly rinse each pretreatment cartridge with reagent water in order to insure all residual background contaminants are removed from the cartridge. Perform this rinse per manufacturer's instructions.

11.1.4.2 Prior to pretreating any field samples, prepare and pretreat a LRB and an LFB. This pretreatment is conducted by placing the cartridges in the following prescribed series (–>Ba–>Ag–>H). A 0.45 um filter is placed between the Ag and H cartridges to collect any silver residue. The

pretreated LRB and LFB are used to verify that no background interference or bias is contributed by the pretreatment. If a response is observed in the pretreated LRB, triple or quadruple the volume of reagent water rinse is used to wash the filters prior to use. Repeat analysis of the blank to ensure that it measures no more than ½ the MRL. If this additional rinsing procedure is required, it must be consistently applied to all the cartridges prior to conducting any matrix pretreatment.

11.1.4.3 Filter 3 mL of sample through the series of rinsed, stacked cartridges as an initial sample rinse (Ba, Ag, 0.45 um filter, and H) at a flow rate of 1.0 mL/ min or less (approximately one drop every 3 to 4 seconds). This flow rate is critical to the pretreatment and must be carefully followed. Discard this fraction and begin collecting the pretreated sample aliquot of collected sample.

11.1.4.4 When sufficient volume has been collected, the conductance of the pretreated sample aliquot should be reanalyzed as long as there is sufficient sample quantity to determine if the sample is below the MCT. If the conductance is still above the MCT double pretreatment cartridges may need to be applied.

11.1.4.5 Place this aliquot of pretreated sample into an autosampler vial as described in Section 11.1.3.

11.1.4.6 In order to ensure data quality, samples which fail the MCT and have been selected for pretreatment, must also be used to prepare an MS. This MS must be fortified with perchlorate at concentrations close to, but greater than, the level determined in the native sample prior to the pretreatment. Initially, the pretreated sample is analyzed and perchlorate level is determined. Then, a second aliquot of sample must be fortified with perchlorate, pretreated to reduce the high common anion levels, and analyzed to assess perchlorate recovery from that matrix. This additional QC is required to rule out matrix effects and to confirm that the laboratory performed the pretreatment step appropriately. **If the perchlorate recovery falls outside the acceptance range of 80 - 120%, that particular sample should be reported as suspect/matrix.**

11.1.4.7 The pretreatments prescribed above are effective at reducing

the chloride and sulfate content of a sample matrix but will not reduce matrix concentrations of other anions such as nitrate or phosphate.

11.1.5 Samples not requiring pretreatment. Using a Luer lock, plastic 10 mL syringe, withdraw approximately 10 mL of sample and attach a 0.45 µm particulate filter, directly to the syringe. Filter the sample into an autosampler vial

11.2 SAMPLE ANALYSIS

11.2.1 Table 1 summarizes the operating conditions for the ion chromatograph.

11.2.2 Establish a valid initial calibration and verify this calibration by conducting a LCS as described in Section 10.2. Following the LCS analyze the IPC solution, followed by the LRB. Then confirm the IC system calibration by analyzing an ICCS (Section 10.3.1) and, if required, recalibrate as described in Section 10.2. Lastly, analyze the LFB.

11.2.3 Inject 1.0 mL of each filtered sample using the AS50 autosampler. The same size loop for standards and samples. The data report generated by the Chromelean software includes the resulting peak size in area and height units, ug/L concentration based on calibration curve, and the retention time for each analyte.

11.2.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of retention time may be used as a suggested window size but the retention time window should not extend beyond ± 5% of the retention time for perchlorate. The experience of the analyst should weigh heavily in the interpretation of these chromatograms.

11.2.5 If the response of a sample analyte exceeds the calibration range, the sample must be diluted with an appropriate amount of reagent water and reanalyzed.

11.2.6 Should more complete resolution be needed between perchlorate and a coeluting, shoulder peak, the eluent may be diluted. This will spread out the peaks, causing later elution of perchlorate. Analysts are advised to carefully evaluate any of these eluent dilutions since when these eluent changes are incorporated, other coelutions may be encountered which were not initially evident. This should only be

done under supervision of the laboratory director.

11.2.7 Analysis sequences must be carefully constructed to meet required QC specifications and frequency.

11.2.8 Additional batches may be added sequentially on to the end of these types of schedules as long as all QC samples, which define an individual batch (IPC, LRB, ICCS, LFB, MS/MSD, etc.) are individually reanalyzed with each successive serial batch and the QC criteria for these analyses are continually met (from the IPC through ECCS).

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identify perchlorate in the sample chromatogram by comparing the retention time of a suspect peak within the retention time window to the actual retention time of a known analyte peak in a calibration standard. If the perchlorate retention time has slightly shifted (generally towards shorter times) since the initial calibration, but is still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibration check standards to confirm the presence or absence of perchlorate anion.

12.1.1 If a low concentration of perchlorate is suspected in an unknown sample, but the retention time has drifted to the edge of the retention time window, a low level perchlorate MS, prepared at nearly the same concentration as the suspect peak, should be prepared from this sample matrix to confirm the matrix induced retention time shift. If the fortified sample reveals a split or shouldering peak response, the low concentration in the unfortified sample is likely an interferant and should not be reported as perchlorate.

12.2 Compute sample concentration using the initial calibration curve generated in Section 10.2. This is automatically done by the Dionex software. Dilution factors can be integrated into the sample peak table to account for any dilution adjustments.

12.3 Report ONLY those values that fall between the MRL and the highest calibration standards. Report results in µg/L.

13. METHODS PERFORMANCE

See Shaw's QAPP for precision and accuracy evaluation.

REFERENCES

"Determination of Perchlorate by Ion Chromatography." State of California, Department of Health Services, Sanitation and Radiation Laboratories Branch, Rev. No. 0 (June 3, 1997).

"Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography." Application Note 121, Dionex Corporation, Sunnyvale, CA (1998).

"Perchlorate by Ion Chromatography, Modified EPA 300.0 Using IonPac AS11." Standard Operating Procedure, Montgomery Watson Laboratories (March 17, 1998).
Jackson, P.E.; Laikhtman, M.; and Rohrer, J.S. "Determination of Trace Level Perchlorate in Drinking Water and Ground Water by Ion Chromatography," Journal of Chromatography A, 850 (1999), 131-135.

Okamoto, H.S.; Rishi, D.K.; Steeber, W.R.; Baumann, F.J.; and Perera, S.K. "Using Ion Chromatography to Detect Perchlorate," Journal AWWA, Vol. 91 (October 1999), 73-84.
Inter-Agency Perchlorate Steering Committee, Analytical Subcommittee Report (1998). Report on the interlaboratory validation of IC methods for perchlorate.

Glaser, J.A.; Foerst, D.L.; McKee, G.D..; Quave, S.A. and Budde, W.L. "Trace Analyses for Wastewater," Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

Code of Federal Regulations 40, Pt. 136, Appendix B (July 1, 1998).

"OSHA Safety and Health Standards, General Industry," (29CFR1910). Occupational Safety and health Administration, OSHA 2206, (Revised, Jan. 1976).
ASTM Annual Book of Standards, Part II, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986. 11.

"Carcinogens-Working with Carcinogens," Publication No. 77-206, Department of Health, Education, and Welfare, Public Health Service, Center for Disease control, National Institute of Occupational Safety and health, Atlanta, Georgia, August 1977.

"Safety In Academic Chemistry laboratories," 3rd Edition, American Chemical Society Publication, Committee on Chemical Safety, Washington, D.C., 1979.

U.S. EPA Method 300.1. EPA Document number: EPA/600/R-98/118. NTIS number PB98-169196 INZ.

"Anion Self-Regenerating Suppressor (ASRS) Quickstart Procedure", Document Number 031368-01, Dionex Corporation, Sunnyvale, CA, March,1988.

"Installation Instructions and Troubleshooting Guide for the Anion Self-Regenerating Suppressor-Ultra", Document Number 031367, Rev. 03, Section 5.1, Dionex Corporation, Sunnyvale, CA, December, 1988.

CRC Handbook of Chemistry and Physics. Standard Solutions for Calibrating Conductivity Cells, p. D-166, 70th Ed., 1989-1990, CRC Press, Boca Raton, Florida.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION

Standard Conditions and Equipment[(a)]:

Ion Chromatograph:	Dionex DX2000
Sample Loop:	1000 µL
Eluent generator:	60 mM KOH
Eluent Flow:	0.35 mL/min
Columns :	Dionex AG16, 2 mm / AS16, 2 mm
Typical System Backpressure:	1500 psi
Suppressor:	ASRS ULTRAII (P/N 53946), external water mode, 150 mA current
Detectors:	Suppressed Conductivity Detector, heated Dionex D6S Background Conductivity: 2 - 3 µS
Anion trap	Continuously regenerated CR-TC
Temperature	35 C column heater
Determined $MCT_{(b)}$:	1820 uS/cm

Recommended method total analysis time: 12-15 minutes

TABLE 2. INITIAL DEMONSTRATION OF CAPABILITY QC REQUIREMENTS.

Requirement	Specification and Frequency	Acceptance Criteria
Initial Demonstration of Low System Background	Analyze a method blank (LRB) and determine that all target analytes are below ½ of the proposed MRL prior to performing the IDC.	The LRB concentration must be #½ of the MRL.
Initial Demonstration of Accuracy (IDA)	Analyze 7 replicate LFBs fortified with perchlorate at 25 ug/L. Calculate the mean recovered concentration (C0) See Equation in Section 9.2.3.	The recovery must be ±10% of true value.
Initial Demonstration of Precision (IDP)	Calculate percent relative standard deviation (%RSD)of IDA replicates. See Equation in Section 9.2.	The %RSD must be ±10%
Quality Control Sample (LCS)	Initially, upon reestablishing calibration and with each sample batch analyze a LCS from an external/second source.	The LCS must be ± 10% of the true value.
Method Detection Limit (MDL) Determination	Select a fortifying level at or near the MRL. Analyze 107 replicate LFBs over multiple days and calculate MDL using Shaw's mdl procedure	
Minimum Reporting Level (MRL)	An MRL should be established for perchlorate during the IDC.	The low CAL standard can be lower than the MRL, but the MRL MUST be no lower than the low CAL standard
Matrix Conductivity Threshold (MCT) MRL verification	Prepare a series of LFB samples, each containing a suggested perchlorate concentration of 25 ug/L, at sequentially increasing fortified levels of common anions. Measure sample conductance and analyze each, calculate average A/H ratios and PDA/H (using equation in Section 9.2.8.8). Calculate MCT as outlined in SOP. Verify the MRL in a solution prepared at the MCT.	The MCT is set at the highest measured conductance observed in the last fortified MCT sample to yield a PDA/H value below 20%. Prepared within ±10% of the MCT. Perchlorate recovery must be 70-130% of the MRL.

TABLE 3. QUALITY CONTROL REQUIREMENTS FOR ANALYTICAL BATCH RUN

Requirement	Specification and Frequency	Acceptance Criteria
Sample Holding Time / Preservation / Storage	Perchlorate 28 days No Preservation technique required. Filtered sample preferred. Ship on Ice	Holding time must not be exceeded.
Initial Calibration	Generate calibration curve using eight standards	MRL MUST be no lower than the lowest calibration standard
Instrument Performance Check (IPC)	Designed to verify Matrix Conductivity Threshold (MCT). Prepare mixed common anion solution at the MCT. Confirm the sample's conductance and analyze at the beginning of each analysis batch.	Prepared within ±10% of the MCT. IPC solution conductance verified to within ± 10% of original measured value (when originally prepared) $PD_{A/H}$, (when compared to the A/H_{LFB}) must be < 25%. Perchlorate quantitated between 80 -120% of fortified level. <5% shift in perchlorate retention time.
Initial Calibration Check (ICCS)	With each analysis batch, initially verify calibration at the MRL by analyzing an initial low-level continuing calibration check standard (ICCS).	Recovery must be 75-125% of the true value.
Continuing Calibration (CCCS) and End Calibration Checks (ECCS)	Analyze separate mid and high level CCCS/ECCS after every 10 samples and after the last sample in an analysis batch.	Recoveries must fall between 85 - 115%
Laboratory Reagent Blank (LRB)	Include LRB with every analysis batch (up to 20 samples) Analyze prior to analyzing field samples	Perchlorate must be < ½ MRL
PRETREATED Laboratory Reagent Blank (LRB)	REQUIRED in any analysis batch which includes samples which have exceeded the MCT and have been pretreated in any way to reduce the anion levels.	Perchlorate must be < ½ MRL

TABLE 3. QUALITY CONTROL REQUIREMENTS FOR ANALYTICAL BATCH

(CONTINUED).

Requirement	Specification and Frequency	Acceptance Criteria
Laboratory Fortified Blank (LFB)	Laboratory must analyze LFB in each analysis batch following the ICCS. Calculate %REC prior to analyzing samples. The concentration selected for the LFB in subsequent analysis batches should be varied	Recovery for LFB MUST be 85 - 115% prior to analyzing samples. Sample results from batches that fail LFB are invalid.
PRETREATED Laboratory Fortified Blank (LFB)	REQUIRED in any analysis batch which includes samples which have exceeded the MCT and have been pretreated in any way to reduce the common anion levels. Fortification must be made prior to pretreatment	Recovery for pretreated LFB MUST be 85 - 115% prior to analyzing samples. Sample results from batches that fail a pretreated LFB are invalid.
Laboratory Fortified Sample Matrix (MS) SPECIAL LFM for matrices requiring pretreatment	Must add known amount of perchlorate to a minimum of 5% of field samples or at least one within each analysis batch. MS must be fortified above the native level and at no greater than 10 x the highest field sample concentration. Calculate target analyte recovery using formula. When a sample exceeds the MCT and pretreatment is employed to reduce the common anion levels, an additional MS must be prepared from this matrix and subsequently pretreated exactly as the unfortified matrix.	Recovery must be 80 - 120% If fortified sample fails the recovery criteria, label both as suspect/matrix. Same criteria, recoveries must be 80 -120%.
Field or Laboratory Duplicates or MSD Duplicate	Analyze either a field, laboratory or MS/MSD duplicate for a minimum of 5% of field samples or at least one within each analysis batch. Calculate the relative percent difference (RPD).	RPD must be ± 15%.

SHAW METHOD	**SHAW IC-001**
EPA METHOD #: 300.0 Rev2.1	**Approved by Office of water (1993)**
TITLE:	**Inorganic Anions (Ion chromatography)**
ANALYTE:	**Inorganic Anions**
INSTRUMENTATION:	**IC**
VERSION.	**2006**
NUMBER	**2**

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

ANIONS (SHAW IC-001; EPA 300.0)

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions:

Bromide	Nitrite as N
Chloride	Ortho-Phosphate-P
Fluoride	Sulfate
Nitrate as N	
Chlorite	
Chlorate	

1.2 The matrices applicable to each method are shown below:

1.2.1 Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after water extraction), leachates (when no acetic acid is used).

1.2.2 Drinking water and reagent waters

1.3 The single laboratory Method Detection Limit for the above analytes is listed in Shaw's QAPP. The MDL for a specific matrix may differ from depending upon the nature of the sample.

1.4 The method is recommended for drinking and wastewaters. The ranges tested for each anion are as follows:

Analyte	mg/L
Bromide	0.1 - 20.0
Chloride	0.1 - 20.0
Fluoride	0.1 – 20.0
Nitrate-N	0.1 - 20.0
Nitrite-N	0.1 - 20.0
Otho-Phosphate-P	0.1 - 20.0
Sulfate	0.1 - 20.0
Chlorate	0.1- 20.0

1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.6 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.6.

1.7 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Section 9.0.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample, 25 uL, is introduced into a Dionex 120 ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

22 An extraction procedure must be performed to use this method for solids (See Section 11.7).

2.3 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Section 9.0, QC.

3.0 DEFINITIONS

3.1 **Calibration Blank (CB) --** A volume of reagent water used to prepare the Calibration standards.

3.2 **Calibration Standard (CAL) --** A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Field Duplicates (FD) --** Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same

throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 **Instrument Performance Check Solution (IPC)** -- A solution known concentration of anions at a mid level range used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 **Laboratory Fortified Sample Matrix (MS/MSD)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

3.7 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.9 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10 **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 **Performance Evaluation Sample (PE)** -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12 **Laboratory Control Sample (LCS) --** A solution of method analytes of known concentrations that is used as a secondary check standard. The LCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 **Stock Standard Solution (SSS) --** A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.0 INTERFERENCES

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to l00 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no ClO2 remains.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sulfuric acid (Section 7.4)

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance -- Analytical, capable of accurately weighing to the nearest 0.000lg.

6.2 Ion chromatograph – Dionex DX 120 -Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1 Anion guard column: A protector of the separator column: the Dionex 4mm AG18 guard column (p/n 060551) is utilized.

6.2.2 Anion separator column: Dionex 4mm AS18 (p/n 060549) column will be used for all analytes.

6.2.3 Anion suppressor device: Dionex Ultra II ASRS 4mm suppressor (300mA current)

6.2.4 Detector -- Conductivity cell: Dionex Model DS4-1.

6.3 The Dionex Peak Net Data Chromatography Software version 6.4 is used to generate all data.

6.4 Dionex AS 40 autosampler with racks for 5-ml tubes.

6.5 Dionex AS40 autosampler vials purchased directly from Dionex with filter caps for autosampler tubes.

7.0 REAGENTS AND STANDARDS

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution: Potassium Hydroxide 32.8 mM. (2.8 ml of 45% KOH - high purity- to 1 L with deionized water).

7.4 Stock solutions, l000 mg/L (1 mg/mL): Stock standard solutions are purchased as certified solutions from Absolute Standards

7.5 Standard Stock solution. A 100mg/L mixed standard solution containing 8 anions (Fl, Cl, SO_4, Br, NO_3, NO_2, ClO_3, o-PO_4) is made by diluting 10 mls (using a 10 ml volumetric pipettes) of each of the stocks (1000 mg/L) to a final volume of 100 ml in a volumetric flask.

7.5.5 Standards and Check Standards are made from the Standard Stock solution (100 mg/L) fresh for each batch run. Dilutions are made directly into the 5-ml autosampler vial to give the appropriate concentration. A calibrated 5-ml Pipetman is used to deliver the water and Hamilton syringes are used to measure the Standard Stock solution according to the following table.

Amount of Standard Stock (100mg/L)	Amount of DI Water (ml)	Final Anion Concentration
5.0 ul	4.995	0.1 mg/L
10.0 ul	4.990	0.2 mg/L
25.0 ul	4.975	0.5 mg/L
50.0 ul	4.950	1.0 mg/L
100.0 ul	4.900	2.0mg/L
250.0 ul	4.750	5.0mg/L
500.0 ul	4.500	10.0mg/L
1000.0 ul	4.000	20.0 mg/L

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	immediately
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
0-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Laboratory Control Sample (LCS) – With each sample batch, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a LCS. If the determined concentrations are not within ±10% of the stated

values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of the estimated instrument detection limit

MDLs should be determined at least once a year or when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required lab determined control limits that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits. Internal performance data using a minimum of 20 analyses is determined on a yearly basis.

9.3.4 Instrument Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (MS/MSD) -- The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the MS/MSD aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.1 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range as determined by internal performance data.

9.4.3 If the recovery of any analyte falls outside the designated MS/MSD recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.4 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2.

9.4.7 When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques using MS fortification, must be used to confirm peak identity.

9.4.8 On an annual basis, control charts for LFBs, MS/MSD recoveries and RPDs are calculated.

10.0 CALIBRATION AND STANDARDIZATION

10. 1 For each analyte of interest, prepare calibration standards at a eight concentration levels (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 20.0 mg/L)and a blank by adding accurately measured volumes of one or more stock standards (Section 7.5) directly into 5 ml autosampler vials.

10.3 Using injections of 25 ul (determined by injection loop volume) of each calibration standard, tabulate area responses against the concentration. The results are used to prepare a calibration curve for each analyte. This is done automatically with the data software

10.4 The calibration curve must be verified on each working day, or whenever

the anion eluent is changed, and after every 10 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.

11.0 SAMPLE ANALYSIS PROCEDURE

11.1 The operating conditions are as follows.

IC-	DX-120
Dionex Column:	AS 18 (4mm)
Dionex Guard:	AG18 (4mm)
Sample loop:	25 ul
Eluent:	32.8 MM KOH;
Flow rate	0.70 ml/ min,
Suppressor:-	300mA current
Temperature:	room temp
Detection:	Suppressed conductivity, ASRS Ultra II , recycle mode.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 10.0.

11.3 Load and inject a fixed amount of well mixed sample using AS40 autosampler. The injection loop Is flushed thoroughly, using each new sample. A 25 ul sample loop is used for standards and samples. Record the resulting peak size in area or peak height units.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Phosphate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an

amount of reagent water equal to 5-10 times the weight of dry solid material taken as a sample. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 µ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of fortified samples.

11.8 It has been reported that lower detection limits for bromate (≈7 µg/L) can be obtained using a borate based eluent. The use of this eluent or other eluents that improve method performance may be considered as a minor modification of the method and as such still are acceptable.

11.9 Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3 Report results in mg/L.

12.4 Report NO_2 as N
NO_3 as N
ortho-PO_4 as P

13.0 PRECISION AND ACCURACY

13.1 See Current QAPP for summary of Precision and Accuracy measurements

REFERENCES

"Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, No. 4, pg 192.

Standard Methods for the Examination of Water and Wastewater, 20th Edition of Standard Methods (1998).

Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1988.

Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater", J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).

Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. of Chromatog., 602, (1992), 65-74.

SHAW METHOD	**SHAW IC-002**
EPA METHOD #:	**NONE**
TITLE:	**VFA (Ion Chromatography)**
ANALYTE:	**VFAs**
INSTRUMENTATION:	**IC**
VERSION.	**2006**
NUMBER	**2**

VOLATILE FATTY ACIDS (SHAW IC-002)

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of Volatile Fatty Acids in reagent water, surface water, ground water, and finished drinking water including Lactate, Acetate, Propionate, Formate, Citrate, Butyric acid, Pyruvic acid, and Valeric Acid.

1.2 The single laboratory Method Detection Limits for the above analytes are listed in Shaw's QAPP.

1.2.1 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained and must be capable of yielding a baseline with no more than 5 nS noise/drift per minute of monitored response over the background conductivity.

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4 When this method is used to analyze unfamiliar samples for any of the above VFAs identification should be supported by the use of a fortified sample matrix covering the VFAs of interest.

1.5 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described below.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample, 25-100ul is introduced into an ion chromatograph (Dionex 600). The VFAs of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

3.0 DEFINITIONS

3.1 **Calibration Blank (CB)** -- A volume of reagent water used to prepare the Calibration standards.

3.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Field Duplicates (FD)** -- Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 **Instrument Performance Check Solution (IPC)** -- A solution known concentration of anions at a mid level range used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 **Laboratory Fortified Sample Matrix (MS/MSD)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

3.7 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.9 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10 **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 **Performance Evaluation Sample (PE)** -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12 **Laboratory Control Sample (LCS)** -- A solution of method analytes of known concentrations that is used as a secondary check standard. The LCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.0 INTERFERENCES

4.1 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target VFA; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target VFA; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.1.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst must verify that these changes do not negatively affect performance by repeating and passing all the QC criteria.

4.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that sample dilution will alter your Minimum Reporting Limit (MRL) by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be

given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent as outlined.

4.1.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. It has been shown that high conductivity (salts can interfere with analysis). Dionex Ba and Ag columns can eliminate this interference. Prior to using any pretreatment, the analyst should be aware that all instrument calibration standards must be pretreated in exactly the same manner as the pretreated unknown field samples.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

4.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.4 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of analytes of interest in a second, subsequent analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and a conductivity detector.

Equipment used:

Dionex 600 Ion Chromatograph
Eluent Gradient Mixer
GP50 gradient pump
Gradient Mixer (GM-3)
Anion Trap Column (ATC-3)
Dionex AS11HC column (4mm x 250mm)
Dionex 4mm AG11HC Guard column (4mm x 50 mm)
Suppressed conductivity, Recycle Mode; Dionex ASRS 4mm ultra suppressor
DS3 Conductivity Detector set at 35^{o}C
AS50 Autosampler, 2ml autosampler vial rack

5.2 The Dionex Peaknet Data Chromatography Software was used to generate all the data.

5.3 Analytical balance, ±0.1 mg sensitivity. Used to accurately weigh target analytes for stock standard preparation.

5.4 Top loading balance, ±10 mg sensitivity. Used to accurately weigh reagents to prepare eluents.

5.5 Weigh boats, plastic, disposable - for weighing eluent reagents.

5.6 Syringes, plastic, disposable, 10 mL - used during sample preparation.

5.7 Pipets, Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.

5.8 Bottles, high density polyethylene (HDPE), opaque or glass, amber, 30 mL, 125mL, 250 mL. For sampling and storage of calibration solutions.

5.9 Micro beakers, plastic, disposable - used during sample preparation.

6.0 REAGENTS AND STANDARDS

6.1 Reagent water: Distilled or deionized water, free of the VFAs of interest. Water should contain particles no larger than 0.20 microns.

6.2 Eluent solution : Sodium Hydroxide – low concentration 5mM, high concentration 100 mM.

6.2.1 Reagent water must be purged for 10 minutes with helium prior to the addition of concentrated (50:50 certified grade NaOH) to prepare two eluent concentrations. This is to remove dissolved gases which may form micro bubbles in the IC compromising system performance and adversely affecting the integrity of the data.

6.3 Volatile Stock standard stock solutions, 1,000mg/l or 10,000 mg/L (1 mg/mL): Stock standard solutions are purchased as certified solutions from Ultra Scientific, ChemService or Alltech. Dilute standard stocks to 100 mg/L (100 ug/ml). These should be prepared quarterly, and kept at 4^{o}C for storage.

6.3.1 Working Standard Stock Solutions –

VFA Mix 1: (100ug/ml) of Lactate, acetate, propionate, formate, pyruvic acid, and valeric acid. Use 10 ml of 1,000 ug/ml stock solutions or 1.0 ml of 10,000 ug/ml stock solutions, mix and dilute to 100 ml final volume in volumetric flask.

VFA Mix 2: (100ug/ml) of butyric acid. Use 1.0 ml of 10,000 ug/ml stock solutions and dilute to 100 ml final volume in volumetric flask.

VFA Mix 3: (100ug/ml) of acetate, propionate, formate, and citrate. Use 10 ml of 1,000 ug/ml stock solutions or 1.0 ml of 10,000 ug/ml stock solutions, mix and dilute to 100 ml final volume in volumetric flask.

6.3.2 Standards and Check Standards are made from the Standard Stock solution (100 mg/L) fresh for each batch run. One ml sample dilutions are made directly into the 2-ml autosampler vial to give the appropriate concentration. A calibrated 1-ml Pipetman is used to deliver the water and Hamilton syringes are used to measure the Standard Stock solution according to the following table.

Amount of Standard Stock (100mg/L)	Amount of DI Water (ul)	Final VFA mix Concentration
2.0 ul	998.0	0.2 mg/L
5.0 ul	995.0	0.5 mg/L
10.0 ul	990.0	1.0 mg/L
20.0 ul	980.0	2.0 mg/L
50.0 ul	950.0	5.0 mg/L
100.0 ul	900.0	10.0mg/L
200.0 ul	800.0	20.0mg/L
500.0 ul	500.0	50.0mg/L
1000.0 ul	0.00	100.0 mg/L

7.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

7.1 Samples should be collected in 40-ml clean VOA vials without any preservative.

7.2 Sample holding times for VFAs analysis is 14 days. Samples should be kept cool and should be shipped on ice Cool to 4^{o}C

8.0 QUALITY CONTROL

8.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory performance, and subsequent analysis in each analysis batch of a Laboratory Reagent Blank, Laboratory Fortified Blank, calibration check standards, Laboratory Fortified Sample Matrices (MS) and either Field, Laboratory or LFM duplicate sample analyses. This section details the specific requirements for each of these QC parameters. The laboratory is required to maintain performance records that define the quality of the data that are generated.

8.2 INITIAL DEMONSTRATION OF PERFORMANCE

8.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of accuracy through the analysis of the LCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

8.2.2 Laboratory Quality Control Sample (LCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a LCS. If the determined concentrations are not within ± 20% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

8.2.3 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit. MDLs should be determined once a year, when a new operator begins work or whenever there is a significant change in the background, or instrument response.

8.3 ASSESSING LABORATORY PERFORMANCE

8.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each analysis batch). Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

8.3.2 Laboratory Fortified Blank - (LFB) -- The LFB (check standard) should be prepared at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the MS/MSD. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required concentration dependant control limits, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

8.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

8.4.1 Laboratory Fortified Sample Matrix (MS/MSD) -- The laboratory must add a known amount of analyte to a minimum of 5% of the field samples within an analysis batch. The MS/MSD sample must be prepared from a sample matrix which has been analyzed prior to fortification. The analyte concentration must be high enough to be detected above the original sample. It is recommended that the solutions used to fortify the MS be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

8.4.1.1 If the fortified concentration is less than the observed background concentration of the unfortified matrix, the

recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration is so high.

8.4.1.2 The MS should be prepared at concentrations no greater than five times the highest concentration observed in any field sample.

8.4.1.3 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample.

8.4.1.5 If the recovery of any analyte falls outside the designated MS recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to be matrix induced and the results for that sample and the MS are reported with a "matrix induced bias" qualifier.

8.4.2 FIELD OR LABORATORY DUPLICATES -- The laboratory must analyze either a field or a MSD for a minimum of 10% of the collected field samples or at least one with every analysis batch, whichever is greater. Calculate the percent difference (RPD) between duplicate analysis.

9.0 CALIBRATION AND STANDARDIZATION

9. 1 Standard calibration is performed from either 1.0 mg/L up to 100 mg/L or 1.0 mg/L up to 50 mg/ as some analytes are only linear up to 50 mg/L (acetate, propionate, valeric acid and butyric acid). For each analyte of interest, prepare calibration standards at a seven concentration levels (1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0 mg/L) and a blank by adding accurately measured volumes of one or more stock standards (Section 6.3) directly into 2 ml autosampler vials. Up to three separate curves are created using the three different VFA mixes as specified in Section 6.3 depending on the analytes of interest. Butyric acid is calibrated separately because its elution time is very close to formate, therefore a separate calibration curve is utilized for quantitation of this analyte.

9.2 Using an injection volume of 25 ul of each calibration standard, tabulate area responses against the concentration. The results are used to prepare a calibration curve for each analyte. The results are used to prepare calibration curves using a linear least squares fit for each analyte. This is done automatically with the data software. For analytes that are not linear up to 100 mg/L, discard the 100 mg/L calibration point.

9.3 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 10 samples. If the response or retention time for any analyte varies from the expected values by more than ±20%, the test must be repeated, using fresh calibration standards. If the

results are still more than ±20%, a new calibration curve must be prepared for that analyte.

9.4 For some projects, a low detection limit (200 ug/L) is required. In this case a LOW Calibration Curve is created using 7 standards (0.2. 0.5, 1.0, 2.0, 5.0, 5.0, 10.0, 20.0 mg/L) and a larger injection volume – 100.0 ul.

10. PROCEDURE

10.1 The operating conditions for the ion chromatograph for VFA analysis is listed below

Run Conditions:

Condition One: (Analytes: Lactate, Acetate, Propionate, Formate, Butyric, Pyruvic and Valeric acid)

Eluent Flow rate:	1.8 ml/min
Suppressor current:	220ma
Eluent:	Low concentration 5mM NaOH High concentration 100mM NaOH
Run conditions:	
Initial Column Cleaning:	60mM NaOH from-13.0 min to -10.0 min
Column equilibration:	0.25mM NaOH from -10.0 min to 0 min
Sample injection	0.0 min; 25 uL
Sample Elution	0.25 mM NaOH from 0.0 to 15 min 0.75 mM from 15 min to 30 min 2.5 mM from 30 to 35 min 60 mM from 35 to 37 min; End Run
Sample Tray temp:	15^{o}C

Condition Two: (Analytes: Acetate, Proprionate, Formate, Citrate)

Eluent Flow rate:	1.8 ml/min
Suppressor current	268mA
Eluent:	Low concentration 5mM NaOH High concentration 100mM NaOH
Run conditions:	

Initial Column Cleaning:	60mM NaOH from-13.0 min to -10.0 min
Column equilibration:	0.30 mM NaOH from -10.0 min to 0 min
Sample injection	0.0 min; 25uL
Sample Elution	0.30 mM NaOH from 0.0 to 15 min 1.5 mM from 15 min to 20 min 5.0 mM from 20 to 35 min 60 mM from 35 to 37 min; End Run
Sample Tray temp:	15^{o}C

10.2 Check system calibration daily and, if required, recalibrate

10.3 Sample Preparation

10.3.1 For refrigerated or samples arriving to the laboratory cold, ensure the samples have come to room temperature prior to conducting sample analysis by allowing the samples to warm on the bench for at least 1 hour.

10.4 Using a Luer lock, plastic 10 mL syringe, withdraw the sample and attach a 0.45 um particulate filter (demonstrated to be free of ionic contaminants) directly to the syringe. Filter the sample into an autosampler vial.

10.5 Inject 25 uL of each sample using the Standard Calibration Curve or 100 uL if the LOW calibration curve is to be used. The peak area responses is tabulated against the concentration using the data software. During this procedure, retention times must be recorded. Use the same size for standards and samples.

10.6 If the response of a sample analyte exceeds the calibration range, the sample may be diluted with an appropriate amount of reagent water and reanalyzed.

10.7 If upon review of a chromatogram, it shows there to be one or more large peak response(s) of > 300 uS after 35 min, then these samples contain an interfering high salt concentration. For these samples, they must be pretreated with the Dionex ion exchange pretreatement columns Ba and Ag to remove chloride and sulfate from the samples. Follow the Dionex protocol to treat the samples and then reanalyze for VFAs. The presence of high salts interferes with the VFA analysis, because you can not suppress the background conductivity enough to detect the small conductivity response of the VFAs.

11. 0 DATA ANALYSIS AND CALCULATIONS

11.1 Prepare a calibration curve for each analyte by plotting instrument response, as peak area, against standard concentration. Compute sample

concentration by comparing sample response with the standard curve. If a sample has been diluted, multiply the response by the appropriate dilution factor.

11.2 Report ONLY those values that fall between the lowest and the highest calibration standards. Samples with target analyte responses exceeding the highest standard should be diluted and reanalyzed. Samples with target analytes identified but quantitated below the concentration established by the lowest calibration standard should be reported as below the minimum reporting limit (MRL).

11.3 Report results for in mg/L

12.0 METHODS PERFORMANCE

12.1 See QAPP for tabulation of precision and accuracy.

Shaw E&I Analytical and Treatability Laboratory

Standard Operating Procedures

Volume II

Organic Chemistry
(GC, GC/MS, HPLC Chromatography Methods and Organic Prep SOPs)

December 2008

SHAW METHOD **SHW-846 METHOD 8260A**	**SHAW ORG-008** **1996**
TITLE:	**Analysis of Volatile Organic Compounds**
ANALYTE:	**VOCs**
INSTRUMENTATION:	**GC/MS**
VERSION.	**2006**
NUMBER	**3**

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY MASS SPECTROMETRY((SHAW ORG-008; Method 8260A)

1.0 Scope and Application

Shaw Environmental Analytical Laboratory will abide by SW846 EPA Method 8260B Revision 2, Method 8000B, Method 5030B, and Method 5035 as published December 1996 on the web http://www.epa.gov/epaoswer/hazwaste/test/main.htm. with the following specifications/modifications as listed below.

1.1 Target Compounds.
The following VOC analytes will be analyzed by Shaw Environmental using this method.

Target Compound	CAS#	Target Compound	CAS #
Dichlorodifluoromethane	75-71-8	bromoform	75-25-2
chloromethane	74-87-3	isopropyl benzene (cumene)	98-82-8
vinyl chloride	75-01-4	bromobenzene	108-86-1
bromomethane	74-83-9	1,1,2,2-tetrachloroethane	79-34-5
chloroethane	75-00-3	1,2,3-trichloropropane	96-18-4
trichlorofluoromethane	75-69-4	n-propyl benzene	103-65-1
1,1-dichloroethylene	75-35-4	2-chlorotoluene	95-49-8
methylene chloride	75-09-2	4-chlorotoluene	106-43-4
trans-1,2-dichloroethylene	156-60-5	1,3,5-trimethylbenzene	108-67-8
1,1-dichloroethane	75-34-3	tert-butylbenzene	98-06-6
2,2-dichloropropane	594-20-7	1,2,4-trimethylbenzene	95-63-6
Cis 1,2- Dichloroethylene	156-59-2	sec-butylbenzene	135-98-8
bromochloromethane	74-97-5	1,3-dichlorobenzene	541-73-1
chloroform	67-66-3	4--isopropyltoluene	99-87-6
1,1,1-trichloroethane	71-55-6	1,4-dichlorobenzene	106-46-7
carbon tetrachloride	56-23-5	1,2-dichlorobenzene	95-50-1

Target Compound	CAS#	Target Compound	CAS #
1,1-dichloropropene	563-58-6	n-butylbenzene	104-51-8
1,2-dichloroethane	107-06-2	1,2,4-trichlorobenzene	120-82-1
trichloroethylene	79-01-6	hexachlorobutadiene	87-68-3
1,2-dichloropropane	78-87-5	naphthalene	91-20-3
dibromomethane	74-95-3	1,2,3-trichlorobenzene	87-61-6
bromodichloromethane	75-27-4	Methyl tertiary butyl ether	1634-04-4
cis-1,3-dichloropropene	10061-01-5	Acetone	67-64-1
toluene	108-88-3	carbon disulfide	75-15-0
trans-1,3-dichloropropene	10061-02-6	2-Butanone (MEK)	78-93-3
1,1,2-trichloroethane	79-00-5	Tetrahydrofuran (THF)	109-99-9
tetrachloroethylene	127-18-4	4-methyl-2-Pentanone (MIBK)	108-10-1
1,3-dichloropropane	142-28-9	2-hexanone	591-78-6
Dibromochloromethane	124-48-1	2-chloroethyl vinyl ether	110-75-8
1,2-Dibromoethane	106-93-4		
chlorobenzene	108-90-7		
1,1,1,2-tetrachloroethane	630-20-6		
ethylbenzene	100-41-4		
xylenes (m/p)	1330-20-7		
o-xylene	95-47-6		
styrene	100-42-5		

2.0 **Summary of Method**

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. Purge and trap (method 5030) is used to liberate the volatile compounds from the matrix by passing an inert gas through the aqueous sample or soil extract. The volatile compounds are then trapped on a bed of adsorbent media (Type "K" trap ,Vorcarb^{TM} 3000). This media is then quickly heated and backflushed with carrier gas to desorb and transfer the analytes to the GC capillary column. A standard split/splitless injection port is used to split the desorb flow which allows a higher desorb flow rate while maintaining a lower column flow of ~1.0 ml/min. The column is temperature-programmed to separate the analytes which are then detect with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2. Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion relative to an internal standard using a six - point calibration curve (from 5.0 ug/L to 100 ug/L) for all compounds except for the following compounds (MTBE, acetone, carbon disulfide, 2-butanone, tetrahydrofuran, MIBK, 2-hexanone and 2-chloroethyl vinyl ether) ketones which will be calibrated using a 5 - point calibration (10 ug/L to 100 ug/L).

3.0 Interferences

3.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and if necessary the purge gas filter.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. To prevent this problem rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, it may be necessary to run a blanks to check for cross-contamination.

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing.

4.0 Apparatus And Materials

4.1 Purge-and-Trap device for aqueous samples consists of an Archon autosampler and Tekmar Stratum concentrator for the System 1 unit. System 2 consists of a Tekmar 2016 autosampler with heating mantles and a Tekmar 3000 concentrator

4.2. The System 1 GC unit consists of a HP 5890 and the System 2 consists of a HP 6890.

4.3. The System 1 Mass Spectrometer consists of a HP 5971 and the System 2 unit a HP 5973, both equivalent capable of scanning form 35 to 300 amu every 2 sec or less. The MS is capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) the meets the criteria set forth in EPA 8260B.

4.4. Column Restek RT_x-502.2 (30meter, 0.25mm ID, 3-um film thickness) is used for System 1 and a Restek –VMS (30 meter, o.25 mm ID, 1.4-um film thickness) for System 2 is used.

5.0 Reagents

5.1 Reagent grade inorganic chemicals shall be used in all tests.

5.2 Organic-free Laboratory grade 1 water will be used.

5.3 HPLC grade methanol free of target analytes will be used.

5.4. Stock solutions for Calibration Standards and Calibration Checks are purchased from Restek at 2000 ug/L concentrations.

5.5 Secondary dilution standards are prepared from pure standard materials purchased from Restek. Dilution Standards at 25mg/L are prepared from the stock solutions (2000 mg/L) by adding 125ul of the stock to a final volume of 10 ml in methanol. Standards are stored in Teflon-lined crimped sealed serum vials at -20^{o}C. Two separate secondary stock solutions are made. One contains only the six VOC gas components (bromomethane, chloroethane, dichloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), and the other secondary mixture contains the remaining target VOC compounds.

5.6. Surrogate Standards/Internal Standards are purchased from Restek and are diluted in methanol to 25ppm of each in a single secondary dilution standard. Internal standards consist of fluorobenzene, chlorobenzene-d5, and 1,4-dichlorobenzene-d_4. Surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Each 10ml sample to be analyzed is spiked with 10ul of the IS/surrogate mix to achieve a final 25 ppb concentration of each compound for VOC analysis.

5.7. 4-Bromofluorobenzene (BFB) standard is purchased from Restek and diluted in methanol to 25ppm for use as the BFB tune evaluation.

5.8. Calibration Standards. A six point curve is used for calibration of the equipment. The following volumes from the secondary dilution standards are spiked into either 50 ml or 10ml of laboratory grade for VOC purge and trap analysis. For certain compounds ((MTBE, acetone, carbon disulfide, 2-butanone, tetrahydrofuran, MIBK, 2-hexanone and 2-chloroethyl vinyl ether) the 5ug/L standard is not used in the calibration curve, so for these compounds the calibration is based on a 5 point curve.

System 1:
The following volumes of the gas mix and VOC mega mix are combined into a 50 ml volumetric flask to achieve the final concentrations as shown. Forty ml VOA vials are then filled with the calibration standards and placed into the Archon autosampler for analysis.

Gas mixture 100mg/L	**VOC mega mix 100mg/L**	**Final VOC conc in 40ml VOA vial**
2.5 ul	2.5 ul	5 ug/L
5.0 ul	5.0 ul	10 ug/L
10 ul	10 ul	20 ug/L
25 ul	25 ul	50 ug/L
50 ul	50 ul	100 ug/L
100 ul	100 ul	200 ug/L

System 2:
The following volumes of the gas mix and VOC mega mix are combined into a 10 ml water purge to achieve the final concentrations as shown. A gas tight syringe 10 or 20ml is used to make the dilutions.

Gas mixture 25mg/L	**VOC mega mix 25mg/L**	**Final VOC conc in 10ml water sample**
2 ul	2 ul	5 ug/L
4ul	4ul	10 ug/L
8ul	8ul	20 ug/L
20ul	20ul	50 ug/L

30ul	30ul	75 ug/L
40ul	40ul	100 ug/L

5.9. Laboratory control (LC) samples. For the laboratory Control sample a separate mixture containing the following compounds (1,1-DCE, benzene, trichloroethene, toluene, and chlorobenzene is prepared from a second certified standard (8260 matrix spike mix) purchased from Restek. The secondary dilution is prepared as a 1:100 dilution of the 2,500 mg/L stock mix is made to give a final concentration of 25 mg/L. LCS analysis is done using 50 up of the secondary standard in a final 50 ml volumetric (for System 1 : 40 ml VOA vial is then filled from this dilution) or 10 up of the secondary standard in a final 10 ml aqueous volume (for System 2). The final observed concentration for both systems is 25 ug/L. LCS samples are run with each sample batch.

5.10. Matrix spiking . A second set of secondary dilutions (gas mixture and mega VOC mixture at 25 ppmv) are prepared from standards purchased from Supelco or from a different stock lot from Restek. These dilutions labeled as QC standards are used only for matrix spike samples.

6.0 Sample Collection, Preservation, and Handling

As per SW846 EPA Chapter One.

7.0 Procedure

7.1 Sample introduction will be via purge-and-trap for aqueous samples (Method 5030) and closed-system purge or methanol extraction for non aqueous samples as per Method 5035.

7.2 Chromatographic conditions System 1.

7.2.1 GC parameters. The instrument control parameters from the GC run method are as follows:

Zone Temperatures:
Inlet B 125 ^{o}C
Detector B 280^{o}C

Oven Program:
Initial Temperature 40^{o}C
Initial time 6.0 minutes
Ramp to 210^{o}C at 8^{o}C/min hold for 1 min
Run time 28.25 min
Constant flow pressure of 7.7 psi
Column Flow 1ml/min
Splitless injection

7.2.2 Purge-and Trap parameters are as follows:
Purge at 31^{o}C for 11 min. purge gas pressure at 40ml/min.
Dry purge for 1 min
Desorb at 240^{o}C for 2 min
Bake trap at 255^{o}C for 9.50 min
Valves at 110^{o}C
Transfer lines and heater lines at 125^{o}C

7.3 Chromatographic conditions System 2.

7.3.1 GC parameters. The instrument control parameters from the GC run method are as follows:
Zone Temperatures:
Inlet 200 ^{o}C
Detector B 280^{o}C

Oven Program:
Initial Temperature 40^{o}C
Initial time 6.0 minutes
Ramp to 220^{o}C at 8^{o}C/min hold for 3.5 min
Ramp to 240^{o}C at 24^{o}C/min for 0.5min
Run time 33.33 min
Constant flow pressure of 16.6 psi
Column Flow 1ml/min
Split injection 1:100

7.3.2 Purge-and Trap parameters are as follows:
Purge at 31^{o}C for 11 min. purge gas pressure at 40ml/min.
Dry purge for 1 min
Desorb at 220^{o}C for 2 min
Bake trap at 225^{o}C for 10.0 min
Valves at 150^{o}C
2016 valve 100^{o}C
Transfer lines and heater lines at 150^{o}C

7.4 Initial calibration.

7.4.1 BFB tune use 2ul of BFB standard for analysis. Use BFB mass intensity criteria as tuning acceptance as per Method 8260B.

7.4.2 Sample introduction. Draw 10 ml of laboratory grade water into a 10 or 20 ml gastight syringe equipped with an on/off valve. Add the appropriate volume of the secondary standard (see table above) directly to the 10ml of laboratory water through the valve using a Hamilton syringe. Then add 10.0 up of the internal standard/surrogate mix to the syringe. Close the valve and invert the syringe several times to mix the contents. Open the valve and load the purge and trap autosampler with the full 10 ml sample volume. Samples will be purged at room temperature under normal operating conditions.

7.3.3 Use the HP Cessation software to tabulate response factors and %Reds for each target analyte compounds. Response factors will be used for calibration unless the calibration requirements of Method 8260 are not met. To meet calibration requirements of Method 8260 the
%RSD for each target compound in the calibration curve must be $\leq$ 15%. If a compound falls outside of this limit then calibration may be done using linear regression analysis as long as the line is not forced through zero (0) . For linear calibration to be acceptable the r^2 value must be 0.995 or greater.

7.4 Calibration Verification

7.4.1. A BFB standard will be run and evaluated at the beginning of the run and every 12 hours thereafter.

7.4.2. Following the BFB evaluation, the initial calibration curve will be verified using a 20ppb standard at the beginning of the run and once every 12 hours thereafter.

7.4.3 A method blank will be analyzed following the calibration standard.

7.4.4 A laboratory control sample (LCS sample) will be run with every batch run.

7.4.5 SPCC/CCCC. All criteria for SPCC compounds and CCCC compounds must be met according to Method 8260B for the sample batch to proceed. The SPCC and CCCC compounds must have less than a 20% deviation in their relative response factor compared to the calibration curve. The internal standard retention time and area response must also meet the requirements as per Method 8260B for data set to be validated.

7.5 GC/MS analysis of samples

7.5.1 Samples will only be run if calibration verification has been met (Section 7.4). All samples are allowed to warm to room temperature before analysis.

7.5.2 A ten ml sample will be used for purging. In System 1 – 10 ml of sample is transferred from the Archon autosampler to the fritted sparge vessel on the Tekmar Stratum concentrator for sparging. In System 2 10 ml of sample is directly spared in the test tube using a needle sparer. If a sample needs to be diluted then an appropriate volume of the sample will be added to laboratory grade water either in a 40 ml VOA vial (40 ml final volume) or in a gas tight syringe to give a final volume of 10 ml for System 2. (i.e. 1ml sample and 9 ml dH_2O).

7.5.3 To each 10ml sample 10 ul of the internal standard/surrogate mixture (IS/Surr)is also added to give a final concentration of 25 ppb. For System 1 the IS/Surr mixture is added automatically into the 10 ml purge volume by the Archon autosampler. For System 2 the mixture is added manually to the gas tight syringe prior to loading the Tekmar 2016 autosampler. Dilutions may be made directly into a gastight syringe or in a volumetric flask.

7.5.4 Samples will be analyzed by purge and trap. Taking an aliquot from the sample destroys the validity of the remaining volume in the sample vial for future analysis.

7.5.5. If results indicate that the sample concentration is beyond linear concentration or is below the practical quantitation level in a diluted sample, then the sample must be rerun using an appropriate volume to be within the calibration curve for the target analytes. A new sample vial must be used for reevalution of the sample.

7.6 Qualitative analysis.

The qualitative identification of each compound is based on retention time and on comparison of the sample mass spectrum with characteristic ions in the standard calibration according to Method 8260B.

7.7 Quantitative analysis.

7.7.1 Once a compound is identified, quantitation will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one

nearest the retention time of that given analyte. Integration of identified compounds will be reviewed by the analyst before final processing of data for quality control.

7.7.2 Manual Integration. Manual of the peaks will be done by the analyst under the following conditions.

7.7.2.1 The target analyst is present in the chromatogram, but was not integrated by the software because its area counts were not picked up by the software. In this case the peak can be manually added.

7.7.2.2 The baseline is somewhat erratic (high or low) resulting in an incorrect integration by the software in determining the start and stop points of the peak. In this case the peak can be manually integrated to give the correct flat baseline of the peak. In no case however may a peak be trimmed to reduce its area counts for validation purposes.

7.7.2.3 There was a misidentification of a peak within the acceptable retention time shift. Occasional a two peaks having similar retention times and overlapping ions may be labeled incorrectly by the software. In this case, the analyst can correct the software error by manual integration.

8.0 Quality Control

8.1. Quality Control procedures as outlined in Method 8260B will be followed.

8.2. All procedures as outlined in Shaw Environmental's QAPP will be followed (see Attached).

8.3. Data validation.

8.3.1 Internal standard areas will be between +100% and -50% compared to the calibration check, surrogate recoveries shall met requirements. Any samples not meeting requirements will be noted in report and rerun as necessary to met requirements.

8.3.2. Spectra of all unknown compounds versus reference spectra from daily CCC will be verified. Library search against NIST library (05) will be performed if required to identify unknown spectra

8.3.3 In target review, all false positives will be deleted according to retention time shifts and/or spectral comparisons.

9.0 MDL evaluation

9.1 MDLs for aqueous matrix will be performed at a minimum of once a year using a 5.0 ug/L concentration for all target analytes except for MTBE, acetone, carbon disulfide, 2-butanone, tetrahydrofuran, MIBK, 2-hexanone and 2-chloroethyl vinyl ether which will be done at 10 ug/L. Injection will be done with a 10ml sample via purge-and-trap.

9.2 MDLs for soil matrix will be performed at a minimum of once a year using an effective soil concentration of 1000.0 ug/kg concentration for all target analytes. For soil matrix analysis, 5.0 g of a clean sand matrix containing a VOC spike of 1000.0 ug/kg of each target compound is extracted with 5.0 ml of methanol. A 0.1 ml methanol sample is used for injection into 10 ml of dI water in the purge and trap for a 1:100 dilution.

MDL calculation. Ten injections will be evaluated for mdl determination. All 10 replicates will be used to evaluate the MDL as described unless the result is discarded as an outlier as defined below. If one compound is determined to be an outlier in a run then the results of the entire run will be eliminated from the mdl determination.

The method for determining single sided outliers when both the population mean (μ) and the population standard deviation (σ) are unknown was described by Grubbs (F.E. Grubbs 1979) and is included in *Standard Methods*.

$T_n = (X_n - X_{ave})/s$ (high sided outliers)
$T_1 = (X_{ave} - X_1)/s$ (low sided outliers)

Where X_n (X_1) is the data point in question, X_{ave} is the sample mean, and s is the sample standard deviation. The value T_n or T_1 is then compared against a table of critical values. If T_n or T_1 is greater than the critical value for the appropriate number of replicates at the 1% significance level, the questionable data point is an outlier, and it may be rejected. The critical values for various numbers of replicates at the 1% significance level are given in the following table. When evaluating 10 replicate samples for the mdl determination the critical value is 2.41. Any test result that is greater than 2.41 will be discarded along with all of the results from that analytical run.

Table of Critical Values
(1% significance value)

# Observations	Critical Value
7	2.1
8	2.22
9	2.32
10	2.41
11	2.48
12	2.55
13	2.61
14	2.66

10.0 Precission and Accuracy (P/A)

10.1 An initial P/A study will be conducted when setting up any new equipment or when any significant procedural changes are made.

10.2 For Aqueous samples the P/A study will be conducted using a sample concentration of 25 ug/L and for a methanol extracted clean soil (sand) matrix the concentration will be 2,500ug/kg. A 10 ml purge volume will be used as with the normal analytical procedure. For the methanol extracted sample a 0.1ml methanol sample will be added to the 10 ml aqueous sample.

Calculate the average recovery (x) in and the standard deviation of the recovery (s) for each

analyte of interest using seven replicate sample results. Also calculate the %RSD (standard deviation / mean). For aqueous samples the average percent recovery must fall between 80 and 120% and the actual concentration and the %RSD must be less than 15%. For the soil matrix the average percent recovery must fall between 75 and 135% and the actual concentration and the %RSD must be less than 20%. If these criteria are met then the precision and accuracy is acceptable.

10.3 Continued precision and accuracy studies. Data from all Calibration Checks and MS/MSDs will be evaluated at least twice a year for precision and accuracy. Data will be evaluated for Accuracy (percent recovery of target analytes) in both check standards and from matrix spiked samples. Precision will be evaluated by calculating the RPDs between matrix spike and matrix spike duplicate samples. Results will be recorded in tables or charts. The results of these studies are used to develop the acceptable precision an accuracy criteria on a yearly basis.

APPENDIX B:

Standard Operating Procedure for Low Stress/Minimal Drawdown Ground-Water Sample Collection

STANDARD OPERATING PROCEDURE FOR LOW-STRESS (Low Flow) / MINIMAL DRAWDOWN GROUND-WATER SAMPLE COLLECTION

INTRODUCTION

The collection of "representative" water samples from wells is neither straightforward nor easily accomplished. Ground-water sample collection can be a source of variability through differences in sample personnel and their individual sampling procedures, the equipment used, and ambient temporal variability in subsurface and environmental conditions. Many site inspections and remedial investigations require the sampling at ground-water monitoring wells within a defined criterion of data confidence or data quality, which necessitates that the personnel collecting the samples are trained and aware of proper sample-collection procedures.

The purpose of this standard operating procedure (SOP) is to provide a method which minimize the amount of impact the purging process has on the ground water chemistry during sample collection and to minimize the volume of water that is being purged and disposed. This will take place by placing the pump intake within the screen interval and by keeping the drawdown at a minimal level (0.33 feet) (Puls and Barcelona, 1996) until the water quality parameters have stabilized and sample collection is complete. The flow rate at which the pump will be operating will be depended upon both hydraulic conductivity of the aquifer and the drawdown with the goal of minimizing the drawdown. The flow rate from the pump during purging and sampling will be at a rate that will not compromise the integrity of the analyte that is being sampled. This sampling procedure may or may not provide a discrete ground water sample at the location of the pump intake. The flow of ground-water to the pump intake will be dependent on the distribution of the hydraulic conductivity (K) of the aquifer within the screen interval. In order to minimize the drawdown in the monitoring well a low-flow rate must be utilized. Low-flow refers to the velocity with which water enters the pump intake from the surrounding formation in the

immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface, which can be affected by flow regulators or restrictions (Puls and Barcelona, 1996). This SOP was developed by the Superfund/RCRA Ground Water Forum and draws from an USEPA's Ground Water Issue Paper, Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedure, by Robert W. Puls and Michael J. Barcelona. Also, available USEPA Regional SOPs regarding Low-Stress(Low Flow)Purging and Sampling were used for this SOP.

SCOPE AND APPLICATION

This SOP should be used primarily at monitoring wells which have a screen or an open interval with a length of ten feet or less and can accept a sampling device which minimizes the disturbance to the aquifer or the water column in the well casing. The screen or open interval should have been optimally located to intercept an existing contaminant plume(s) or along flowpaths of potential contaminant releases. Knowledge of the contaminant distribution within the screen interval is highly recommended and is essential for the success of this sampling procedure. The ground-water samples which are collected using this procedure are acceptable for the analyses of ground-water contaminants which may be found at Superfund and RCRA contamination sites. The analytes may be volatile, semi-volatile organic compounds, pesticides, PCBs, metals and other inorganic compounds. The screened interval should be located within the contaminant plume(s) and the pump intake should be placed at or near the known source of the contamination within the screened interval. It is critical to place the pump intake in the exact location or depth for each sampling event. This argues for the use of dedicated, permanently installed sampling devices whenever possible. If this is not possible then the placement of the pump intake should be positioned with a calibrated sampling pump hose sounded with a weighted-tape or using a pre-measured hose. The pump intake should not be placed near the bottom of the screened interval to avoid disturbing any sediment that may have settled at the bottom of the well.

Water-quality indicator parameters and water levels must be measured during purging, prior to sample collection. Stabilization of the water quality parameters as well as

monitoring water levels are a prerequisite to sample collection. The water-quality indicator parameters which are recommended include the following: specific electrical conductance, dissolved oxygen, turbidity, oxidation-reduction potential, pH, and temperature. The latter two parameters are useful data, but are generally insensitive as purging parameters. Oxidation-reduction potential may not always be appropriate stabilization parameter, and will depend on site-specific conditions. However, readings should be recorded because of its value as a double check for oxidation conditions, and for fate and transport issues. Also, when samples are collected for metals, semi-volatile organic compounds, and pesticides every effort must be made to reduce turbidity to 10 NTUs or less (not just the stabilization of turbidity) prior to the collection of the water sample. In addition to the measurement of the above parameters, depth to water must be measured during purging (U.S. Environmental Protection Agency, 1995).

Proper well construction, development and maintenance are essential for any ground-water sampling procedure. Prior to conducting the field work, information on the construction of the well and well development should be obtained and that information factored into the site specific sampling procedure. The attached Sampling Checklist is an example of the type of information that is useful.

Stabilization of the water-quality indicator parameters is the criterion for sample collection. But if stabilization is not occurring and the procedure has been strictly followed, then sample collection can take place once three (minimum) to six (maximum) casing volumes have been removed (Schuller et al., 1981 and U.S. Environmental Protection Agency., 1986; Wilde et al., 1998; Gibs and Imbrigiotta., 1990). The specific information on what took place during purging must be recorded in the field notebook or in the ground-water sampling log.

This SOP is not to be used where non-aqueous phase liquids (immiscible fluids) are present in the monitoring well.

EQUIPMENT

- Depth-to-water measuring device - An electronic water-level indicator or steel tape and chalk, with marked intervals of

0.01 foot. Interface probe for determination of liquid products (NAPL) presence, if needed.

- Steel tape and weight – Used for measuring total depth of well. Lead weight should not be used.
- Sampling pump – Submersible or bladder pumps with adjustable rate controls are preferred. Pumps are to be constructed of inert materials, such as stainless steel and teflon®. Pump types that are acceptable include gear and helical driven, centrifugal (low-flow type) and air-activated piston. Adjustable rate, peristaltic pump can be used when the depth to water is 20 feet or less.
- Tubing – Teflon® or Teflon® lined polyethylene tubing is preferred when sampling for organic compounds. Polyethylene tubing can be used when sampling inorganics.
- Power Source – If a combustion type (gasoline or diesel-driven) generator is used, it must be placed downwind of the sampling area.
- Flow measurement supplies – flow meter, graduated cylinder and a stop watch.
- Multi-Parameter meter with flow-through-cell – This can be one instrument or more contained in a flow-through cell. The water-quality indicator parameters which must be monitored are pH, ORP/EH, dissolved oxygen (DO), turbidity, specific conductance, and temperature. Turbidity readings must be collected before the flow cell because of the potential for sediment buildup which can bias the turbidity measurements. Calibration fluids for all instruments should be NIST-traceable and there should be enough for daily calibration through-out the sampling event. The inlet of the flow cell must be located near the bottom of the flow cell and the outlet near the top. The size of the flow cell should be kept to a minimum and a closed cell is preferred. The flow cell must not contain any air or gas bubbles when monitoring for the water-quality indicator parameters.
- Decontamination Supplies – Including a reliable and documented source of distilled water and any solvents (if used). Pressure sprayers, buckets or decontamination tubes for pumps, brushes and non-phosphate soap will also be needed.
- Sample bottles, sample preservation supplies, sample tags or labels and chain of custody forms.
- Approved Field Sampling and Quality Assurance Project Plan.
- Well construction data, field and water quality data from the previous sampling event.
- Well keys and map of well locations.

- Field notebook, ground-water sampling logs and calculator. A suggested field data sheet (ground-water sampling record or ground-water sampling log) are provided in the attachment.
- Filtration equipment, if needed. An in-line disposable filter is recommended.
- Polyethylene sheeting which will be placed on ground around the well head.
- Personal protective equipment specified in the site Health and Safety Plan.
- Air monitoring equipment as specified in the Site Health and Safety Plan.
- Tool box -All needed tools for all site equipment used.
- A 55-gallon drum or container to contain the purged water.

Materials of construction of the sampling equipment (bladders, pumps, tubing, and other equipment that comes in contact with the sample) should be limited to stainless steel, Teflon®, glass and other inert material. This will reduce the chance of the sampling materials to alter the ground-water where concentrations of the site contaminants are expected to be near the detection limits. The sample tubing diameter thickness should be maximized and the tubing length should be minimized so that the loss of contaminants into and through the tubing walls may be reduced and the rate of stabilization of ground-water parameters is maximized. The tendency of organics to sorb into and out of material makes the appropriate selection of sample tubing material critical for trace analyses (Pohlmann and Alduino, 1992; Parker and Ranney, 1998).

PURGING AND SAMPLING PROCEDURES

The following describes the purging and sampling procedures for the Low-Stress (Low Flow)/ Minimal Drawdown method for the collection of ground-water samples. These procedures also describe steps for dedicated and non-dedicated systems.

Pre-Sampling Activities (Non-dedicated and dedicated system)

1. Sampling locations must begin at the monitoring well with the least contamination, generally up-gradient or furthest from the site or suspected source. Then proceed systematically to the monitoring wells with the most contaminated ground water.

2. Check and record the condition of the monitoring well for damage or evidence of tampering. Lay out polyethylene sheeting around the well to minimize the likelihood of contamination of sampling/purging equipment from the soil. Place monitoring, purging and sampling equipment on the sheeting.

3. Unlock well head. Record location, time, date and appropriate information in a field logbook or on the ground-water sampling log (See attached ground-water sampling record and ground-water sampling log as examples).

4. Remove inner casing cap.

5. Monitor the headspace of the monitoring well at the rim of the casing for volatile organic compounds (VOC) with a Photo-ionization detector (PID) or Flame ionization detector (FID), and record in the logbook. If the existing monitoring well has a history of positive readings of the headspace, then the sampling must be conducted in accordance with the Health and Safety Plan.

6. Measure the depth to water (water level must be measured to nearest 0.01 feet) relative to a reference measuring point on the well casing with an electronic water level indicator or steel tape and record in logbook or ground-water sampling log. If no reference point is found, measure relative to the top of the inner casing, then mark that reference point and note that location in the field logbook. Record information on depth to ground water in the field logbook or ground water sampling log. Measure the depth to water a second time to confirm initial measurement; measurement should agree within 0.01 feet or re-measure.

7. Check the available well information or field information for the total depth of the monitoring well. Use the information from the depth of water in step six and the total depth of the monitoring well to calculate the volume of the water in the monitoring well or the volume of one casing. Record information in field logbook or ground-water sampling log.

<u>Purging and Sampling Activities</u>

8A. Non-dedicated system – Place the pump and support equipment at the wellhead and slowly lower the pump and tubing down into the monitoring well until the location of the pump intake is set

at a pre-determined location within the screen interval. The placement of the pump intake should be positioned with a calibrated sampling pump hose, sounded with a weighted-tape, or using a pre-measured hose. Refer to the available monitoring well information to determine the depth and length of the screen interval. Measure the depth of the pump intake while lowering the pump into location. Record pump location in field logbook or groundwater sampling log.

8B. Dedicated system - Pump has already been installed, refer to the available monitoring well information and record the depth of the pump intake in the field logbook or ground-water sampling log.

9. Non-dedicated system and dedicated system - Measure the water level (water level must be measured to nearest 0.01 feet) and record information on the ground-water sampling log, leave water level indicator probe in the monitoring well.

10. Non-dedicated and dedicated system - Connect the discharge line from the pump to a flow-through cell. A "T" connection is needed prior to the flow cell to allow for the collection of water for the turbidity measurements. The discharge line from the flow-through cell must be directed to a container to contain the purge water during the purging and sampling of the monitoring well.

11. Non-dedicated and dedicated system - Start pumping the well at a low flow rate (0.2 to 0.5 liter per minute) and slowly increase the speed. Check water level. Maintain a steady flow rate while maintaining a drawdown of less than 0.33 feet (Puls and Barcelona, 1996). If drawdown is greater than 0.33 feet lower the flow rate. 0.33 feet is a goal to help guide with the flow rate adjustment. It should be noted that this goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience (Puls and Barcelona, 1996).

12. Non-dedicated and dedicated system - Measure the discharge rate of the pump with a graduated cylinder and a stop watch. Also, measure the water level and record both flow rate and water level on the groundwater sampling log. Continue purging, monitor and record water level and pump rate every three to five minutes during purging. Pumping rates should be kept at minimal flow to

ensure minimal drawdown in the monitoring well.

13. Non-dedicated and dedicated system - During the purging, a minimum of one tubing volume (including the volume of water in the pump and flow cell) must be purged prior to recording the water-quality indicator parameters. Then monitor and record the water-quality indicator parameters every three to five minutes. The water-quality indicator field parameters are turbidity, dissolved oxygen, specific electrical conductance, pH, redox-potential and temperature. Oxidation-reduction potential may not always be an appropriate stabilization parameter, and will depend on site-specific conditions. However, readings should be recorded because of its value as a double check for oxidizing conditions. Also, for the final dissolved oxygen measurement, if the readings are less than 1 milligram per liter, it should be collected and analyze with the spectrophotometric method (Wilde et al., 1998 Wilkin et al., 2001), colorimetric or Winkler titration (Wilkin et al., 2001). The stabilization criterion is based on three successive readings of the water quality field parameters; the following are the criteria which must be used:

Parameter	**Stabilization Criteria**	**Reference**
pH	± 0.1 pH units	Puls and Barcelona, 1996; Wilde et al.,
Specific electrical conductance (SEC)	± 3% FS/cm	Puls and Barcelona, 1996
oxidation-reduction potential (ORP)	± 10 millivolts	Puls and Barcelona 1996
turbidity	± 10 % NTUs (when turbidity is greater than 10 NTUs)	Puls and Barcelona, 1996 Wilde et al., 1998
dissolved oxygen	± 0.3 milligrams per liter	Wilde et al., 1998

Once the criteria have been successfully met indicating that the water quality indicator parameters have stabilized, then sample collection can take place.

14. If a stabilized drawdown in the well can't be maintained at 0.33 feet and the water level is approaching the top of the screened interval, reduce the flow rate or turn the pump off (for 15 minutes) and allow for recovery. It should be noted whether or not the pump has a check valve. A check valve is required if the pump is shut off. Under no circumstances should the well be

pumped dry. Begin pumping at a lower flow rate, if the water draws-down to the top of the screened interval again turn pump off and allow for recovery. If two tubing volumes (including the volume of water in the pump and flow cell) have been removed during purging then sampling can proceed next time the pump is turned on. This information should be noted in the field notebook or ground-water sampling log with a recommendation for a different purging and sampling procedure.

15. Non-dedicated and dedicated system - Maintain the same pumping rate or reduce slightly for sampling (0.2 to 0.5 liter per minute) in order to minimize disturbance of the water column. Samples should be collected directly from the discharge port of the pump tubing prior to passing through the flow-through cell. Disconnect the pump's tubing from the flow-through-cell so that the samples are collected from the pump's discharge tubing. For samples collected for dissolved gases or Volatile Organic Compounds (VOCs) analyses, the pump's tubing needs to be completely full of ground water to prevent the ground water from being aerated as the ground water flows through the tubing. The sequence of the samples is immaterial unless filtered (dissolved) samples are collected and they must be collected last (Puls and Barcelona, 1996). All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container. When filling the VOC samples a meniscus must be formed over the mouth of the vial to eliminate the formation of air bubbles and head space prior to capping. In the event that the ground water is turbid,(greater then 10 NTUs), a filtered metal (dissolved) sample also should be collected.

If filtered metal sample is to be collected, then an in-line filter is fitted at the end of the discharge tubing and the sample is collected after the filter. The in-line filter must be pre-rinsed following manufacturer's recommendations and if there are no recommendations for rinsing, a minimum of 0.5 to 1 liter of ground water from the monitoring well must pass through the filter prior to sampling.

16A. Non-dedicated system - Remove the pump from the monitoring well. Decontaminate the pump and dispose of the tubing if it is non-dedicated.

16B Dedicated system - Disconnect the tubing that extends from the plate at the wellhead (or cap) and discard after use.

17. Non-dedicated system - Before locking the monitoring well, measure and record the well depth (to 0.1 feet).
Measure the total depth a second time to confirm initial measurement; measurement should agree within 0.01 feet or re-measure.

18. Non-dedicated and dedicated system - Close and lock the well.

DECONTAMINATION PROCEDURES

Decontamination procedures for the water level meter and the water quality field parameter sensors.
The electronic water level indicator probe/steel tape and the water-quality field parameter sensors will be decontaminated by the following procedures:
1. The water level meter will be hand washed with phosphate free detergent and a scrubber, then thoroughly rinsed with distilled water.

2. Water quality field parameter sensors and flow-through cell will be rinsed with distilled water between sampling locations. No other decontamination procedures are necessary or recommended for these probes since they are sensitive. After the sampling event, the flow cell and sensors must be cleaned and maintained per the manufacturer's requirements.

Decontamination Procedure for the Sampling Pump

Upon completion of the ground water sample collection the sampling pump must be properly decontaminated between monitoring wells. The pump and discharge line including support cable and electrical wires which were in contact with the ground water in the well casing must be decontaminated by the following procedure:

1. The outside of the pump, tubing, support cable and electrical wires must be pressured sprayed with soapy water, tap water and distilled water. Spray outside of tubing and pump until water is flowing off of tubing after each rinse. Use bristle brush to help remove visible dirt and contaminants.
2.Place the sampling pump in a bucket or in a short PVC casing (4-in. diameter) with one end capped. The pump placed in this device must be completely submerged in the water. A small amount of phosphate free detergent must be added to the potable water

(tap water).
3. Remove the pump from the bucket or 4-in. casing and scrub the outside of the pump housing and cable.
4. Place pump and discharge line back in the 4-in. casing or bucket, start pump and re-circulate this soapy water for 2 minutes (wash).
5. Re-direct discharge line to a 55-gallon drum, continue to add 5 gallons of potable water (tap water)or until soapy water is no longer visible.
6. Turn pump off and place pump into a second bucket or 4-in. Casing which contains tap water, continue to add 5-gallons of tap water (rinse).
7. Turn pump off and place pump into a third bucket or 4-in. casing which contains distilled/deionized water, continue to add three to five gallons of distilled/deionized water (final rinse).
8. If a hydrophobic contaminant is present (such as separate phase, high levels of PCB's, etc.) An additional decon step, or steps, may be added. For example, an organic solvent, such as reagent-grade isopropanol alcool may be added as a first spraying/bucket prior to the soapy water rinse/bucket.

FIELD QUALITY CONTROL

Quality control (QC) samples must be collected to verify that sample collection and handling procedures were performed adequately and that they have not compromised the quality of the ground water samples. The appropriate EPA program guidance must be consulted in preparing the field QC sample requirements for the site-specific Quality Assurance Project Plan (QAPP).

There are five primary areas of concern for quality assurance (QA) in the collection of representative ground-water samples:

1. Obtaining a ground-water sample that is representative of the aquifer or zone of interest in the aquifer. Verification is based on the field log documenting that the field water-quality parameters stabilized during the purging of the well, prior to sample collection.
2. Ensuring that the purging and sampling devices are made of materials, and utilized in a manner, which will not interact with or alter the analyses.
3. Ensuring that results generated by these procedures are reproducible; therefore, the sampling scheme should incorporate co-located samples (duplicates).

4. Preventing cross-contamination. Sampling should proceed from least to most contaminated wells, if known. Field equipment blanks should be incorporated for all sampling and purging equipment, and decontamination of the equipment is therefore required.
5. Properly preserving, packaging, and shipping samples.

All field quality control samples must be prepared the same as regular investigation samples with regard to sample volume, containers, and preservation. The chain of custody procedures for the QC samples will be identical to the field ground water samples. The following are quality control samples which must be collected during the sampling event:

Sample Type	Frequency
● Field duplicates	1 per 20 samples
● Matrix spike	1 per 20 samples
● Matrix spike duplicate	1 per 20 samples
● Equipment blank	Per Regional requirements or policy
● Trip blank (VOCs)	1 per sample cooler
● Temperature blank	1 per sample cooler

HEALTH AND SAFETY CONSIDERATIONS

Depending on the site-specific contaminants, various protective programs must be implemented prior to sampling the first well. The site Health and Safety Plan should be reviewed with specific emphasis placed on the protection program planned for the sampling tasks. Standard safe operating practices should be followed, such as minimizing contact with potential contaminants in both the liquid and vapor phase through the use of appropriate personal protective equipment.

Depending on the type of contaminants expected or determined in previous sampling efforts, the following safe work practices will be employed:

Particulate or metals contaminants

1. Avoid skin contact with, and incidental ingestion of, purge water.
2. Use protective gloves and splash protection.

Volatile organic contaminants

1. Avoid breathing constituents venting from well.
2. Pre-survey the well head space with an appropriate device as specified in the Site Health and Safety Plan.
3. If monitoring results indicate elevated organic constituents, sampling activities may be conducted in level C protection. At a minimum, skin protection will be afforded by disposable protective clothing, such as Tyvek®.

General, common practices should include avoiding skin contact with water from preserved sample bottles, as this water will have pH less than 2 or greater than 10. Also, when filling pre-acidified VOA bottles, hydrochloric acid fumes may be released and should not be inhaled.

POST-SAMPLING ACTIVITIES

Several activities need to be completed and documented once ground-water sampling has been completed. These activities include, but are not limited to:

1. Ensure that all field equipment has been decontaminated and returned to proper storage location. Once the individual field equipment has been decontaminated, tag it with date of cleaning, site name, and name of individual responsible.
2. All sample paperwork should be processed, including copies provided to the Regional Laboratory, Sample Management Office, or other appropriate sample handling and tracking facility.
3. All field data should be complied for site records.
4. All analytical data when processed by the analytical laboratory, should be verified against field sheets to ensure all data has been returned to sampler.

REFERENCES

Gibs, J. and T.E. Imbrigiotta, 1990, Well-Purging Criteria for Sampling Purgeable Organic Compounds; Ground Water, Vol. 28, No. 1, pp 68-78.

Pohlmann, K.F. and A.J. Alduino, 1992, Ground-Water Issue Paper: Potential Sources of Error in Ground-Water Sampling at Hazardous Waste Sites, EPA/540/S-92/019.

Puls, R.W. and M.J. Barcelona, 1996, Low-Flow (Minimal

Drawdown) Ground-Water Sampling Procedure, EPA/540/S-95/504, 12 pp.

Schuller, R.M., J.P. Gibb and R.A Griffin, 1981, Recommended Sampling Procedures for Monitoring Wells; Ground Water Monitoring Review, Spring 1981, pp. 42-46.

Parker, L.V. and T.A. Ranney, 1998, Sampling Trace-Level Organic Solutes with Polymeric Tubing: Part 2, Dynamic Studies; Ground Water Monitoring and Remediation, Vol. 18, No. 1, pp. 148-155.

U.S. Environmental Protection Agency, 1986, RCRA Ground-Water Monitoring Technical Enforcement Guidance Document; OSWER-9950.1, U.S. Government Printing Office, Washington, D.C., 208 pp., appendices.

U.S. Environmental Protection Agency, 1995, Ground Water Sampling - A Workshop Summary, Texas, November 30-December 2, 1993, EPA/600/R-94/205, 146 pp.

U.S. Environmental Protection Agency Region 1, 1996, Low Stress (low flow) Purging and Sampling Produre For the collection of Ground water Samples From Monitoring Wells, SOP#: GW 0001, July 30, 1996.

U.S. Environmental Protection Agency Region 2, 1998, Ground Water Sampling Procedure Low Stress (Low Flow) Purging and Sampling, GW Sampling SOP Final, March 16, 1998.

Wilde, F.D., D.B. Radtke, J.Gibs and R.T. Iwatsubo, eds., 1998, National Field Manual for the Collection of Water-Quality Data; U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9, Handbooks for Water-Resources Investigations, variously paginated.

Wilkin, R.T., M.S. McNeil, C.J. Adair and J.T. Wilson, 2001, Field Measurement of Dissolved Oxygen: A Comparison of Methods, Ground Water Monitoring and Remediation, Vol. 21, No. 4, pp. 124-132.

SAMPLING CHECKLIST

Well Identification:_____

Map of Site Included: Y or N
Wells Clearly Identified w/ Roads: Y or N
Well Construction Diagram Attached: Y or N

Well Construction:

Diameter of Borehole:_____ Diameter of Casing:_____
Casing Material:_____ Screen Material:_____

Screen Length:_____ Total Depth:_____

Approximate Depth to Water:_____
Maximum Well Development Pumping Rate:_____
Date of Last Well Development:_____

Previous Sampling Information:

Was the Well Sampled Previously: Y or N
(If Sampled, Fill Out Table Below)

Table of Previous Sampling Information

Parameter	Previously Sampled	Number of Times Sampled	Maximum Concentration	Notes (include previous purge rates)

Ground-Water Sampling Log

Site Name: **Well #:** **Date:**

Well Depth(Ft-BTOC[1]): **Screen Interval**(Ft):

Well Dia.: **Casing Material:** **Sampling Device:**

Pump placement(Ft from TOC[2]):

Measuring Point: **Water level (static)**(Ft):

Water level (pumping)(Ft): **Pump rate**(Liter/min):

Sampling Personnel:

Other info: (such as sample numbers, weather conditions and field notes)

Water Quality Indicator Parameters

Time	Pumping rates (L/min)	Water level (ft)	DO (mg/l)	ORP (mv)	Turb. (NTU)	SEC[3] (FS/cm)	pH	Temp. (C^{o})	Volume pumped (L)

Type of Sample collected:

1-casing volume was:

Total volume purged prior to sample collection:

Stabilization Criteria		
DO	±	0.3 mg/l
Turb.	±	10%
SEC	±	3%
ORP	±	10 mv
pH	±	0.1 unit

[1]**BTOC-Below Top of Casing**
[2]**TOC-Top of Casing**
[3]**Specific electrical conductance**

APPENDIX C:

Quality Assurance Project Plan (QAPP)

Appendix C: Quality Assurance Project Plan (QAPP)

C.1 Purpose and Scope

This section presents the project-specific Quality Assurance Project Plan (QAPP) for the HFTW demonstration. This QAPP specifies the procedures the demonstration will follow to ensure that data of known quality are generated. These procedures are integral to the demonstration and complement the sampling procedures presented in Section 3.5 of the Final Report. Tables and figures accompanying this document are located immediately after the text.

Both laboratory analytical and field screening methods will be used to measure parameters indicative of the electron donor biostimulation demonstration's performance. The purpose of this QAPP is to outline steps to ensure that: (1) data generated during the course of the demonstration are of an acceptable and verifiable quality (*i.e.*, quality assurance); and (2) a sufficient number of control measurements are taken for proper data evaluation (*i.e.*, quality control).

C.2 Quality Assurance Responsibilities

Key QA personnel for the project and their responsibilities are outlined below.

Paul Hatzinger, Ph.D. is the Principal Investigator for the demonstration, and has overall project QA responsibility.

Mr. Jay Diebold, P.E., P.G. is the Project Coordinator for the demonstration. Mr. Diebold will insure that all field sampling is completed in accordance with the demonstration plan requirements to insure that reliable data can be derived from the samples.

Randi Rothmel, Ph.D. is the Manager of Shaw's Analytical and Treatability Laboratory, and will have laboratory QA responsibility for analytical data during the project. Dr. Rothmel will perform external audits of the independent laboratories conducting Fe and Mn analysis. Dr. Rothmel will report directly to Dr. Hatzinger.

C.3 Data Quality Parameters

This section describes all of the measurements that will be made to achieve the project's objectives.

The laboratory program for the biostimulation demonstration will include measuring the concentrations of perchlorate and selected volatile organic compounds (VOCs) (trichloroethene (TCE), cis 1,2-dichloroethylene (DCE), vinyl chloride (VC), and other CVOCs) in groundwater samples. Anions (bromide, nitrate, sulfate, and chloride), Volatile Fatty Acids (VFAs) (lactate, acetate, citrate, formate, propionate), selected metals (iron and manganese), and other performance-related parameters (DO, redox, pH) in groundwater monitoring well samples will also be measured. These measurements are outlined in Table 3.5. Shaw's Analytical and Treatability Laboratory (New Jersey-certified, non-CLP) will be used for routine off-site analysis of these parameters. For all groundwater analyses, standard U.S. EPA methods will be used, as outlined in: (1) *U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW846*, Third Edition, revised November 1986, Update II, September 1994, Update IIB, January 1995, and Update III, June 1997; (2) *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater* (EPA-600/4-85 054); (3) *U.S. EPA Methods for Analysis of Water and Wastes* (EPA-600/4-79-020, 1979); and (4) *Methods for Determination of Organic Compounds in Drinking Water* (EPA-600/4-88/039).

Additional groundwater parameters may be screened in the field using electronic meters. These parameters will be measured using methods approved or accepted by the U.S. EPA for reporting purposes. Groundwater field-measured parameters will include oxidation reduction potential (ORP), pH, specific conductivity, dissolved oxygen (DO) and temperature.

C.4 Calibration Procedures, Quality Control Checks, and Corrective Action

C4.1 Quality Control Objectives

The goal of the biostimulation demonstration is to accomplish the following: 1) Evaluate the efficacy of the biostimulation technology with respect to perchlorate and TCE degradation; 2) Develop the design criteria and protocol necessary for full-scale application of the technology; and 3) Evaluate the cost-effectiveness of the technology compared to existing perchlorate and TCE remediation technologies. As such, the project data quality objectives (Project DQOs) are as follows:

1. collect data of sufficient quantity and quality to determine destruction efficiencies and biodegradation rates of perchlorate and TCE as a function of electron donor addition;

2. collect data of sufficient quantity and quality to assess (a) site-specific biostimulation operating characteristics, (b) the extent of biostimulation operator attention required, and (c) the optimal range of biostimulation for treatment of groundwater at the demonstration site;

3. collect data suitable for use in designing a full-scale biostimulation system; and

4. collect data suitable for preparing a cost comparison analysis.

To meet the Project DQOs stated above, individual measurements must meet particular quantitative QA objectives for precision, accuracy, method detection limits, and completeness, as well as qualitative QA objectives for comparability and representativeness. This section describes the quality assurance objectives for the electron donor biostimulation demonstration in order to meet the specific Project DQOs stated above.

The specific data QA objectives are as follows:

- establish sample collection and preparation techniques that will yield results representative of the media and conditions analyzed;
- collect and analyze a sufficient number of field blanks to evaluate the potential for contamination from ambient conditions or sample collection techniques;
- collect and analyze a sufficient number of field duplicates to assess the homogeneity of samples received by the laboratory as well as the homogeneity of contaminants in the matrix; and
- analyze method blanks, laboratory duplicates, matrix spikes, matrix spike duplicates, and surrogate spikes as required by the specific analytical methodology to determine if QA goals established for precision and accuracy are met for off-site laboratory analyses.

The data generated during the demonstration will be used primarily for assessing the efficacy of the electron donor biostimulation technology for remediating perchlorate- and TCE-contaminated groundwater. In an effort to produce data that will be useful for this assessment, definitions of data usage, data types, data acquisition, and data quality level have been made for each medium. These defined data parameters are collectively defined as DQOs. Table C.1 presents the DQOs for this technology demonstration. Table C.1 correlates data use with the required degree of analytical sophistication. This approach is based on the generalized DQOs presented by the U.S. EPA (1987). Five levels of data quality are used, ranging from Level I (field screening) to Level V (CLP special analytical services). Due to the variation in the types of monitoring throughout the demonstration, data quality objective Levels I and III will be used. Several geochemical parameters, such as pH, temperature, and DO, will be determined in the field with immediate response required for process control (Level I). All off-site analytical laboratory measurements will be performed using Level III criteria for production of validated data.

Quality assurance objectives have been established to evaluate the criteria of precision, accuracy, and completeness. The evaluation of these criteria for validated (Level III) off-site laboratory analyses will be based upon sample duplicates, matrix spikes, matrix spike duplicates, and surrogates, as described in Section C.4.3. The criteria for precision, accuracy, and completeness for all validated data will follow the guidelines established in Section C.6.1. Evaluation of method detection limits (MDLs) will be in accordance with the procedures outlined in Appendix B to Part 136 "Definition and Procedures for the Determination of Method Detection Limit - Revision 1.1," 40 Code of Federal Regulations (CFR) 136, 1984.

C.4.2 Analytical Procedures and Calibration

Analytical Procedures. All laboratory analyses will be performed according to the established SW-846 and U.S. EPA Methods (see Table 3.5 and Appendix B for key methods) found in *Shaw Analytical and Treatability Laboratory's Standard Operating Procedures, Volume I - Conventional Chemistry (Revised 01/2003), Volume II - Organic Chemistry (Revised 01/2003), Volume III-QA/QC, Microbiology, Analyze Immediate Parameter, Sample Management/Preparation/Cleanup (Revised 01/2003).*

Calibration Procedures and Frequency. Calibration refers to the checking of physical measurements of both field and laboratory instruments against accepted standards. It also refers to determining the response function for an analytical instrument, which is the measured net signal as a function of the given analyte concentration. These determinations have a significant impact on data quality and will be performed regularly. In addition, preventative maintenance is important to the efficient collection of data. The calibration policies and procedures set forth will apply to all test and measuring equipment. For preventative maintenance purposes, critical spare parts will be obtained from the instrument manufacturer.

All field and laboratory instruments will be calibrated according to manufacturers' specifications. All laboratory instruments will be calibrated in accordance with established Standard Operating Procedures. Calibration will be performed prior to initial use and after periods of non-use. A record of calibration will be made in the field logbook each time a field instrument is calibrated. A separate logbook will be maintained by laboratory QA personnel similarly for laboratory instrumentation.

Process and Field Measurements. The portable instruments used to measure field parameters (*e.g.*, temperature, pH, etc.) will be calibrated in accordance with manufacturer's instructions. Flow measuring devices will not be calibrated if calibration requires the instruments to be sent back to the manufacturer. All other manufacturer-recommended checks of the flow instruments will be performed. The instruments will be calibrated at the start and completion of the demonstration. The pH, DO, and ORP probes will be calibrated prior to every site check during the demonstration.

Field Measurements: Groundwater. Groundwater will be assessed for dissolved oxygen and oxidation/reduction potential. Depth to groundwater measurements will be taken using a water interface probe.

Dissolved Oxygen, Temperature, pH, Conductivity and Oxidation/Reduction Potential

Groundwater samples will be collected using a low-flow Waterra inertial pump. Samples will be measured for dissolved oxygen, temperature, pH, conductivity and redox potential using a multi-probe water quality meter (Horiba Model U-22, YSI probe, or similar). In order to minimize aeration of the sample, a continuous flow-through cell will be used when possible to provide a sampling chamber for the meter. A sufficient volume of water from the well or groundwater sampling point will be purged before sample collection to ensure that a sample representative of the formation is obtained.

Depth to Groundwater

The depth to groundwater in site wells will be measured with a water interface probe (ORS Model #1068013 or equivalent). The probe lead is a 50- to 200-ft measuring tape with 0.01-ft increments. The probe gives a constant beep when it encounters the water table. The water-level measurement will be recorded in the field logbook and the probe decontaminated between measurements.

Groundwater Sampling

Prior to sampling, the well or sampling point identification will be checked and recorded along with the date and time in the field logbook. Groundwater samples will be collected using a Waterra pump and flow-through cell and collected in 40-mL VOA vials with a teflon septa-lined cap. Samples will be analyzed for the target compound TCE and the potential TCE breakdown products 1,2-DCE and VC.

Laboratory Measurements. The calibration procedures for all off-site analyses will follow the established SW-846 and U.S. EPA guidelines for the specific method (see Appendix B for method SOPs). Certified standards will be used for all calibrations and calibration check measurements. The frequency and acceptance criteria for all off-site analyses will follow the guidelines outlined below.

Initial Calibration. During initial calibration, a minimum of one blank and five calibration standards that bracket the validated testing range will be analyzed singularly on one day. The concentration of the calibration standards will be prepared in the matrix that results from all the preparation steps of the method, taking into account any steps that are part of the method. Concentrations in the matrix will correspond to those in the environmental matrix as if the method preparation steps had been performed.

In addition to the initial calibration standards, the analysis of a calibration check standard is required prior to analysis of any samples. If the method requires what could be an initial calibration each day an analysis is performed, then the calibration check standards will be analyzed once each week rather than each day.

If the results of the calibration check standard are not acceptable, immediate re-analysis of the calibration check standard will be performed. If the results of the re-analysis still exceed the limits of acceptability, the system will be considered to have failed calibration. Sample analysis will be halted and will not resume until successful completion of initial calibration. Corrective actions taken to restore initial calibration will be documented in the analyst's notebook.

Daily Calibration. Calibration standards will be analyzed each day analyses are performed to verify that instrument response has not changed from previous calibration. Each day before sample analysis, a mid-range concentration standard will be analyzed. The response must fall within the required percentage or two standard deviations of the mean response for the same concentration, as determined from prior initial/daily calibrations (see below). If the response fails this test, the daily standard will be re-analyzed. If the response from the second analysis fails this range, initial calibration will be performed before analyzing samples.

Each day after sample analyses are completed, a second standard will be analyzed. If the response is not within the required percentage or two standard deviations of the mean response from prior initial/daily calibrations, the daily standard will be re-analyzed. If the response from the second analysis fails this range, the system will be considered to have failed calibration. Initial calibration will then be performed and all samples re-analyzed since the last acceptable calibration will be re-analyzed.

For non-linear or non-zero-intercept calibration curves, daily calibration will consist of analysis of the low, middle, and high standards at the beginning of the day. When sample analyses are completed at the end of the day, the low and high standards will be analyzed. Instrument responses for each concentration determination must fall within two standard deviations of the mean response, as described previously, for the appropriate standard. For calibrations fitted by the quadratic equation, a minimum of four standards over the validated range are required, along with the highest level standard analyzed at the end of the day. For all other equations, one more standard than needed to meet the degrees of freedom for any lack-of-fit is required, as a minimum.

Calibration Check Standards. Calibration check standards will be analyzed during each initial calibration. The calibration check standard will contain all analytes of interest for the method in question at a concentration as required by the method. Results of the calibration check standards must fall within the limits of acceptability as described below:

Case 1 - A certified check standard is available from the U.S. EPA or some other source with both the true value and limits of acceptability specified by the supplier. The results must fall

within the limits specified by the supplier, or ± 20% for inorganics and ± 15% for organics, whichever is less.

Case 2 - A certified check standard is available from the U.S. EPA or some other source with a true value specified but without limits of acceptability. The results must fall within ± 20% for inorganics and within ± 15% for organics.

Case 3 - If no certified check standard is available, the laboratory shall prepare a check standard using a second source of reference material. This standard shall be prepared by a different analyst than the one who prepared the calibration standard. If weighing of the material is required, a different balance will be used, if possible. The results must fall within ± 20% for inorganics and within ± 15% for organics.

Case 4 - If there is only one source of reference material available, then the calibration and calibration check standards must be prepared from the same source. The standards shall be prepared by different analysts. If weighing is required, different balances will be used, if possible. The results must fall within ± 20% for inorganics and within ± 15% for organics.

For all cases listed above, after the seventh acceptable check standard, the limits of acceptability will be ± two standard deviations, as determined from the first seven points.

For multi-analyte methods, the calibration check standard will contain all analytes of interest (target analytes). For the check standard to be deemed acceptable, at least two-thirds of the analytes must meet the limits of acceptability as defined above. In addition, if a single target analyte falls outside the limits of acceptability for two consecutive times, then the calibration check standard will be deemed unacceptable. If a calibration check standard is not acceptable, the procedures detailed above will be followed.

C.4.3 Internal Quality Control Checks

Quality Control Samples. Internal QC data provides information for identifying and defining qualitative and quantitative limitations associated with measurement data. Analysis of the following types of QC samples will provide the primary basis for quantitative evaluation of analytical measurement data quality:

Field QC Samples.

- trip blanks to evaluate the presence of contamination from handling errors or cross-contamination during transport;
- field/ collection duplicates to assess the homogeneity of samples received by the laboratory as well as the homogeneity of contaminants in the matrix, respectively.

Laboratory QC Samples.

- method blanks, laboratory duplicates, matrix spikes, and matrix spike duplicates to determine if QA goals established for precision and accuracy are met by the analytical laboratory.

The number, type, and frequency of laboratory QC samples will be dictated by the validated SW-846 or U.S. EPA Methods used by the Shaw E&I laboratory and by the off-site laboratories. The SW-846 and U.S. EPA Methods shown in Table 3.4 and Appendix B specify the number and types of laboratory QC samples required during routine analysis. This information will be supplied with the data package provided by the laboratory.

In addition to the internal QC samples described above, the off-site laboratories will provide, at a minimum, additional internal QC checks as follows:

- use of standard analytical reference materials for traceability of independent stock solutions prepared for calibration stocks, control spike stocks, and reference stock solutions;
- verification of initial calibration curves with independent reference stock solutions according to Section C.4.2;
- verification of initial calibration curves with daily calibration standards according to Section C.4.2;
- verification of continued calibration control by analysis of calibration standards to document calibration drift;
- analysis of control spikes to document method performance and control with respect to recent performance.

An attempt will be made to analyze all samples within the calibrated range of the analytical method. Dilution of a sample extract with extracting solvent, or of the original sample matrix with distilled/de-ionized water, will be performed if the concentration of an analyte is greater than the calibrated range of the method.

Blank Samples.
Blanks are artificial samples designed to detect the introduction of contamination or other artifacts into the sampling, handling, and analytical process. Blanks are the primary QC check of measurements for trace-level concentrations.

Trip Blanks. Trip blanks will be prepared by the analytical laboratory with purified water for groundwater and soil samples. The water will be sent to the site in the same containers to be used for collection of the samples. Trip blanks will be submitted at a frequency of one trip blank per shipment of samples for SW8260B VOC analysis. For non-VOC analyses, no trip blanks will be submitted.

Method Blanks. Method blanks will be prepared by the off-site laboratories to evaluate the impact of the analytical process on detected concentrations of contaminants. Method blanks will be prepared for each batch of samples run for a given method of analysis. The method blanks will be processed through the entire preparation and analytical procedure in the same manner as field samples. The method blanks will provide data to assess potential systematic contamination of the measurement system.

Field Duplicate Samples. Duplicate samples will be analyzed to evaluate the accuracy of the analytical process. Duplicate samples will be analyzed as described below. Each duplicate will be run at a frequency of at least 5 percent of the total number of environmental samples. A comparison of the detected concentrations in the duplicate samples will be performed to evaluate precision. The evaluation will be conducted using Equation C.2 for Relative Percent Difference (RPD) as described in Section C.6.1.

Collection Duplicate. This duplicate is obtained by collecting a second discrete sample from the same sample location and submitting the collections as discrete samples to the laboratory. The purpose of the collection duplicate is to assess the homogeneity of the contaminants in the matrix.

Laboratory Control Samples. Laboratory control samples will be used by the laboratory to assess analytical performance under a given set of standard conditions. These samples will be specifically prepared to contain some or all of the analytes of interest at known concentrations. The samples will be prepared independently of the calibration standards. Types of laboratory control samples that may be used are laboratory duplicates, matrix spikes, matrix spike duplicates, and surrogate spikes. Analysis of laboratory control samples will be used to estimate the analytical bias and accuracy by comparing measured results obtained during analysis to theoretical concentrations. This comparison will be measured using Equation C.1 as presented in Section C.6.0. The matrix spike/matrix spike duplicate samples will be used to evaluate precision according to Equation C.2. The accepted range of RPD values for *matrix spike/matrix spike duplicate* samples for each laboratory analysis will be in accordance with the Methods presented in Appendix B. Stock solutions used to spike QC samples will be prepared independently of stocks used for calibration as required by appropriate EPA methods. Validation of spiked solutions will be performed on a regular basis before the solution is used.

C.4.4 Sample Documentation

The on-site Field Engineer will coordinate with the off-site laboratories for shipment and receipt of sample bottle, coolers, icepacks, chain-of-custody (COC) forms, and Custody Seals. Upon completion of sampling, the COC will be filled out and returned with the samples to the laboratory. An important consideration for the collection of environmental data is the ability to demonstrate that the analytical samples have been obtained from predetermined locations and that they have reached the laboratory without alteration. Evidence of collection, shipment, laboratory receipt, and laboratory custody until disposal must be documented to accomplish this. Docu-

mentation will be accomplished through a COC Record that records each sample and the names of the individuals responsible for sample collection, transport, and receipt. A sample is considered in custody if it is:

- in a person's actual possession;
- in view after being in physical possession;
- sealed so that no one can tamper with it after having been in physical custody; or
- in a secured area, restricted to authorized personnel.

Sample custody will be initiated by field personnel upon collection of samples. As discussed in Section 3, samples will be packaged to prevent breakage or leakage during transport, and will be shipped to the laboratory via commercial carrier, or transported via car or truck.

Sample Identification. A discrete sample identification number will be assigned to each sample. These discrete sample numbers will be placed on each bottle and will be recorded, along with other pertinent data in a field notebook dedicated to the project. For blind samples, the sample location will be recorded in the field notebook along with a note indicating that the sample was submitted to the laboratory as a blind sample. The sample identification number will designate the sample location ("MW-" for specific monitoring well, and "B" for blind samples) and date collected. For example, a sample collected from the MW-4 groundwater sample port collected November 22, 2003 would be identified as follows:

MW-B-11/22/03

Chain-of Custody Forms. The COC Record used by Shaw's laboratory is shown in Figure C.1. The independent laboratories will supply their own COCs with sample bottles that are shipped to the site. All samples collected for off-site analysis will be physically inspected by the Field Engineer prior to shipment.

Each individual who has the sample in their possession will sign the COC Record. Preparation of the COC Record will be as follows:

- The COC Record will be initiated in the field by the person collecting the sample, for every sample. Every sample shall be assigned a unique identification number that is entered on the COC Record.
- The record will be completed in the field to indicate project, sampling person, etc.
- If the person collecting the samples does not transport the samples to the laboratory or ship the samples directly, the first block for "Relinquished By _____, Received By _____" will be completed in the field.

- ♦ The person transporting the samples to the laboratory or delivering them for shipment will sign the record for as "Relinquished By _____".
- ♦ The original COC Record will be sealed in a watertight container, taped to the top (inside) of the shipping container, and the shipping container sealed prior to being given to the commercial carrier. A copy of the COC Record will be kept on-site.

If shipping by commercial carrier, the waybill will serve as an extension of the COC Record between the final field custodian and receipt by the off-site laboratory.

- Upon receipt by the off-site laboratory, the laboratory QC Coordinator, or designated representative, shall open the shipping container(s), compare the contents with the COC Record, and sign and date the record. Any discrepancies shall be noted on the COC Record.
- The COC Record is completed after sample disposal.
- COC Records will be maintained with the records for the project, and become part of the data package.

Laboratory Sample Receipt. Following sample receipt, the Laboratory Manager will:

- ♦ Examine all samples and determine if proper temperature has been maintained during transport. If samples have been damaged during transport, the remaining samples will be carefully examined to determine whether they were affected. Any samples affected shall be considered damaged. It will be noted on the COC Record that specific samples were damaged and that the samples were removed from the sampling program. Field personnel will be instructed to re-sample, if appropriate.
- ♦ Compare samples received against those listed on the COC Record.
- ♦ Verify that sample holding times have not been exceeded.
- ♦ Sign and date the COC Record, attaching the waybill if samples were shipped for off-site analysis.
- ♦ Denote the samples in the laboratory sample log-in book which will contain, at a minimum, the following information:

    - Project Identification Number
    - Sample numbers
    - Type of samples
    - Date and time received

Place the completed COC Record in the project file.

The date and time the samples are logged in by the Sample Custodian or designee should agree with the date and time recorded by the person relinquishing the samples. Any nonconformance

to the stated procedures that may affect the cost or data quality should be reported to the Principal Investigator.

Other Documentation. Following sample receipt at the laboratory, the Laboratory Manager or sample custodian will clearly document the processing steps that are applied to the sample. The analytical data from laboratory QC samples will be identified with each batch of related samples. The laboratory log book will include the time, date, and name of the person who logged each sample into the laboratory system. This documentation will be thorough enough to allow tracking of the sample analytical history without aid from the analyst. At a minimum, laboratory documentation procedures will provide the following:

- Recording in a clear, comprehensive manner using indelible ink;
- Corrections to data and logbooks made by drawing a single line through the error and initialing and dating the correction;
- Consistency before release of analytical results by assembling and cross-checking the information on the sample tags, custody records, bench sheets, personal and instrument logs, and other relevant data to verify that data pertaining to each sample are consistent throughout the record;
- Observations and results identified with the project number, date, and analyst and reviewer signatures on each line, page, or book as appropriate;
- Data recorded in bound books or sheaf of numbered pages, instrument tracings or hard copy, or computer hard copy; and,

Data tracking through document consolidation and project inventory of accountable documents: sample logbook, analysis data book, daily journal, instrument logbook, narrative and numerical final reports, etc.

C.4.5 Data Reduction, Validation, and Reporting

This section describes procedures for reducing, validating, and reporting data. All validated analytical data generated within the off-site laboratories will be extensively checked for accuracy and completeness by laboratory and project personnel. Records will be kept throughout the analytical process, during data generation, and during reporting so that adequate documentation to support all measurements is available. Recordkeeping, data reduction, validation, and reporting procedures are discussed in this section.

Data Reduction. Data reduction will follow the requirements contained in the SW-846 and U.S. EPA analytical methods cited previously. Reduction involves the reformatting of data to present the desired end-product, *i.e.*, the concentrations of the contaminants. Reformatting will involve the process of performing calculations on the raw data and presenting all values in appropriate

units. The information generated by the data reduction step will be used in the interpretation of the data qualifiers.

The responsibility for data acquisition and reduction of raw data resides with the analysts who perform the analysis. Raw data for the quantitative VOC analysis procedures used during this project will consist of peak areas for surrogates, standards, and target compounds. Analytical results will be reduced to concentration units appropriate for the medium being analyzed, i.e. micrograms per liter (μg/L) for aqueous samples.

Data Validation. Data validation involves a review of the QC data and the raw data in order to identify any qualitative, unreliable, or invalid measurements. As a result, it will be possible to determine which samples, if any, are related to out-of-control QC samples. Laboratory data will be screened for inclusion of and frequency of the necessary QC supporting information, such as detection limit verification, initial calibration, continuing calibration, duplicates, matrix spikes, surrogate spikes, and the method and preparation blanks. QC supporting information will be screened to determine whether any datum is outside established control limits. If out-of-control data are discovered, appropriate corrective action will be determined based upon QC criteria for precision, accuracy, and completeness. Any out-of-control data without appropriate corrective action will be cause to qualify the affected measurement data.

Levels of data validation for the demonstration are defined below:

- **Level I.** For Level I field screening data quality, a data "package" including the results from sample blanks, method blanks, and supporting calibration information, will be recorded in the field logbook and on log sheets maintained within a folder on-site. The extent of contamination and the achievement of detection limits can be determined from this information. The sample results and QC parameters will be routinely evaluated by site personnel, and 10% of the analytical raw data results will be reviewed by the Project Manager to verify sample identity, instrument calibration, quantification limits, numerical computation, accuracy of transcriptions, and calculations.

- **Level III.** For Level III validated data quality, a CLP-like data package will be provided. For the SW8260B VOC analyses, this includes CLP-like summary forms 1 through 10 and all raw data associated with the samples, without the chromatograms of calibration standards, matrix spikes, or matrix spike duplicates. The laboratory deliverable format for the New Jersey-certified laboratories will follow the guidelines in Appendix A "Laboratory Data Deliverables Formats - Section III (Reduced Laboratory Data Deliverables - USEPA/CLP Methods)" CITE 25 of the New Jersey Register (NJR), February 3, 2003. Sample results will be evaluated according to the current version of the U.S. EPA functional guidelines for organic and inorganic analyses for selected QA/QC parameters, and 10% of the analytical raw data results will be reviewed to verify sample identity, instrument calibration, detection limits, numerical computation, accuracy of transcriptions, and calculations.

At a minimum, the following data validation procedures will be followed.

Each data package will be reviewed and the data validated prior to submission. Checklists will be used to demonstrate that the data review was accomplished. The Laboratory Manager or designee will perform the data review and validation.

The data review will include, but not be limited to, the following subjects:

- Completeness of laboratory data;
- Evaluation of data with respect to reporting limits;
- Evaluation of data with respect to control limits;
- Review of holding time data;
- Review of sample handling;
- Correlation of laboratory data from related laboratory tests;
- Comparison of the quality of the data generated with DQOs as stated in this Work Plan (on a daily basis, during routine analyses, and during internal laboratory audits); and
- QC chart review, performed weekly, following receipt of control charts for analyses performed the previous week. Review shall consist of assessing trends, cycles, patterns, etc. This review shall also assess whether control corrective actions have been implemented.

The elements of data validation shall include, but not be limited to, the following items:

- Examination of COC records to assess whether custody was properly maintained;
- Comparison of data on instrument printouts with data recorded on worksheets or in notebooks;
- Comparison of calibration and analysis dates and assessment of whether the same calibration was used for all samples within a lot;
- Examination of chromatographic outputs for manual integrations, and documentation of the reasons for any manual integrations;
- Comparison of standard, sample preparation, and injection records with instrument output to assess whether each output is associated with the correct sample;
- Examination of calibration requirements, as specified in the methods;
- Use of a hand-held calculator to perform all calculations on selected samples to assess the correctness of results; and
- Examination of all papers and notebooks to ensure that all pages are signed and dated, that all changes are initialed, dated, have sufficient explanation for the change, and that all items are legible.

Required record-keeping following a laboratory audit shall document that all lots were reviewed in the audit report. The audit report shall also identify any deficiencies that were noted. A copy of the audit report shall be placed in the applicable installation audit folder.

Data Reporting. Data and information generated during the demonstration will be summarized in a Technology Application Analysis Report, to be submitted at the completion of the project. QA/QC analysis reports will be generated by laboratory personnel as a product of validation procedures described above. All off-site Level III analyses will be accompanied by QA/QC data packages as described in the previous section. The summary QA/QC reports will not be included in the Technology Application Analysis Report, but will be made available upon request. The ultimate data set produced for project use will consist of all values reported in appropriate units flagged with respective data qualifiers for entry into the project database as described below. Analytical results will be reduced to concentration units appropriate for the medium being analyzed:

"µg/L" or "mg/L", depending on analyte and method, for aqueous samples.

The laboratory will retain all samples and sample extracts for 6 weeks following data package submittal.

The results for each analyte in spiked QC samples will be determined using the same acceptable calibration curve that is used for environmental samples in the lot. Values above the practical quantitation limit (PQL) shall be reported as the found value. Raw values that fall below the method detection limit (MDL) will be reported as "less than" the PQL. Values above the method detection limit (MDL) and less than the PQL will be reported and flagged with a "J̃". Results for QC samples will not be corrected, except as described below. Because all spike levels must be within the calibrated range, no dilutions should be required. Data will be reported using the correct number of significant figures.

Each day of analysis, the analyst will quantify each analyte in the method blank and spiked QC samples. A new lot of samples will not be introduced into the analytical instrument until results for QC samples in the previous lot have been calculated, plotted on control charts as necessary, and the entire analytical method shown to be in control. If time is a constraint, the calculation of associated environmental sample results may be postponed until a later date. The analyst will maintain control charts by the instrument so that the results of QC samples can be hand-plotted, in order to have an early indication of problems.

Data from the method blank will be reported, usually as less than the MDL for each analyte. Any values above the MDL shall be reported as the found value. Corrections to the QC samples, necessitated by background levels in the method blank, will be performed using instrument response values and not the found values calculated from the linear calibration curve. Reported entries will be in terms of concentration. The importance attached to finding measurable concentrations in the method blank is dependent on analyte and method. Identification of measurable concentrations in the method blanks will be reported in writing to the Principal Investigator for possible corrective actions.

The following additional data reporting procedures will be followed.

All data will be reported, and numerical results will be reported in terms of concentration in the environmental sample. Resultant found concentrations will be adjusted for dilution, etc. before being reported, and both the raw data and correction factors (*e.g.*, percent moisture, and dilution factor) will be recorded in the data package submitted. Laboratory comments on the usability of the data will also be included.

In reporting results, rounding to the correct number of significant figures will occur only after all calculations and manipulations have been completed. As many figures as are warranted by each analytical technique will be used in pre-reporting calculations. Rounding will be accomplished using the following rules:

Rule 1 - In expressing an experimental quantity, retain no digits beyond the second uncertain one.

Rule 2 - In rounding numbers (*i.e.*, in dropping superfluous digits):

- Increase the last retained digit by one if the first uncertain digit is larger than 5;
- Retain the last digit unchanged if the first uncertain digit is less than 5;
- Retain the last digit unchanged if even, or increase it by one if odd, if the first uncertain digit is 5 and the second uncertain digit is 0;
- Increase the last retained digit by one if the first uncertain digit is 5 and the second uncertain digit is greater than 0.

The correct number of reported significant figures, by validation type, is 3 significant figures. The number of allowable significant figures is reduced when added uncertainties are included in the analysis, *i.e.*, the results for samples diluted into the validated range allow one less significant figure due to the uncertainty added by the dilution process.

C.4.6 Corrective Action Plan

If routine procedures (*e.g.*, equipment calibration), QC sample analysis, or performance and system audits indicate that sampling or analysis systems are unsatisfactory, a corrective action shall be implemented. During performance audits, if performance evaluation (PE) samples do not meet the QA criteria for accuracy and precision specified in Section C.6.0, analytical work will stop until the problems are identified and resolved. Before work resumes, another blind PE sample must be analyzed, and results must meet the acceptance criteria. Results of all PE samples will be included in the Application Analysis Report. If previously reported data are effected by the situation requiring correction or if the corrective action will impact the project budget or schedule, the action will directly involve the Principal Investigator. ESTCP will be informed of all major performance problems, and will be included in corrective action planning.

Corrective actions are of two kinds:

1. Immediate, to correct or repair non-conforming equipment and systems. The need for such an action will most frequently be identified by the analyst or technician as a result of calibration checks and QC sample analyses. Immediate corrective actions address problems peculiar to a single measurement or lot of samples. Immediate corrective action may include:

    - Re-run of analyses if sample holding times have not been exceeded;
    - Instrument re-calibration using freshly prepared standards;
    - Replacement of reagents or solvents that give unacceptable blank values;
    - Examination of data calculation errors; and
    - Replacement of reference standards that have been degraded.

If corrective action indicates that non-conformance is due to problems with laboratory equipment, procedures, and/or calibration, once the problem is resolved, the non-conforming samples will be re-analyzed if holding times have not been exceeded. If holding times have been exceeded, new samples will be collected if the completeness criteria specified in Section C.6.0 require that these samples be collected. If corrective action indicates that non-conformance of duplicate samples is due to sampling technique, once the problem is corrected, new samples will be collected if the completeness criteria specified in Section C.6.0 requires that these samples be collected.

2. Long-term, to eliminate causes of non-conformance. The need for such actions will probably be identified by audits. Long-term corrective actions may address procedural deficiencies or unsatisfactory trends or cycles in data that affect multiple lots of samples. Examples of long-term corrective action may include:

    - Staff training in technical skills or in implementing the QAPP;
    - Rescheduling of laboratory routine to ensure analysis within allowed holding times;
    - Identifying alternate vendors to supply reagents of sufficient purity; and
    - Revision of the QAPP.

For either immediate or long-term corrective action, steps comprising a closed-loop corrective action system will be implemented as follows:

- Define the problem;
- Assign responsibility for investigating the problem;
- Investigate and determine the cause of the problem;
- Determine a corrective action to eliminate the problem;
- Assign responsibility for implementing the corrective action; and
- Verify that the corrective action has eliminated the problem.

Unsatisfactory items or situations may be identified by anyone involved with the project, particularly the analysts, field engineers, technicians, or QA personnel. Depending on the nature of the problem, the corrective action employed may be formal or informal.

To enhance the timeliness of corrective action and thereby reduce the generation of unacceptable data, problems identified by assessment procedures will be resolved at the lowest possible management level. Problems that cannot be resolved at this level will be reported to the Project Manager. The Project Manager will determine the management level at which the problem can best be resolved, and will notify the appropriate manager. Monthly progress reports from the on-site Field Engineer will detail all problems and subsequent resolutions.

In all cases, the occurrence of the problem, the corrective action(s) employed, and verification that the problem has been eliminated will be documented. In addition, if the corrective action results in the preparation of a new standard or calibration solution(s), then a comparison of the new versus the old standard or solution will be performed, and the results supplied with a full QC report as verification that the problem has been eliminated. Corrective action reports that relate to a particular lot analysis will be included in the data package for that lot.

C.5 Calculation of Data Quality Indicators

C.5.1 Quantitative QA Objectives: Accuracy, Precision, Completeness, and Method-Detection Limit

Accuracy: Accuracy indicates the degree of bias in a measurement system, and is the degree of agreement of a measurement with an accepted reference value. Sample measurement uses laboratory equipment. The percent recovery of matrix spike/matrix spike duplicate samples measures the accuracy of the laboratory equipment, calculated according to the following equation:

$$\%R = (C_I - C_o)/ C_t * 100 \qquad \text{(Equation C.1)}$$

Where: %R = percent recovery
C_I = measured concentration; spiked sample aliquot
C_o = measured concentration, unspiked sample aliquot
C_t = actual concentration of spike added

Precision: Precision is the reproducibility of measurements under a given set of conditions. For large data sets, precision is expressed as the variability of a group of measurements compared to

their average value. Variability may be attributable to field practices or chemical analyses. Precision is expressed as relative percentage difference, determined using Equation C.2 below.

Precision is measured by calculating the Relative Percent Difference (RPD) of laboratory duplicates, matrix spike/matrix spike duplicate sample pairs, surrogate spikes, and field duplicate samples.

$$RPD = (C_1 - C_2) * 100 / ((C_1 + C_2)/2) \quad \text{(Equation C.2)}$$

Where: RPD = relative percent difference
C_1 = the larger of the two observed values
C_2 = the smaller of the two observed values

Completeness: Completeness is defined as the qualified and estimated results, and represents the results usable for data interpretation and decision making. Results qualified as rejected or unusable, or that were not reported because of sample loss, breakage, or analytical error, negatively influence completeness and are subtracted from the total number of results to calculate completeness. Percent completeness is determined by using the following equation:

$$\% \text{ Completeness} = (VDP / TDP) * 100 \quad \text{(Equation C.3)}$$

Where: VDP = number of valid data points
TDP = number of total samples obtained

Completeness will be calculated for each method and matrix during the demonstration. The completeness objective for all validated data is 95 percent.

Method-Detection Limits. Method detection limits (MDLs) and practical quantitation limits (PQLs) must be distinguished for proper understanding and data use. The MDL is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The PQL represents the concentration of an analyte that can be routinely measured in the sampled matrix with "reasonable" confidence in both identification and quantitation. PQLs are often based on analytical judgement and experience, and should be verifiable by having the lowest non-zero calibration standard or calibration check sample concentration at or near the PQL. Table C.2 presents the MDL range and PQLs for the analytical methods to be used during the demonstration. The limits shown in Table C.2 assume optimal conditions. MDLs may be higher, particularly in contaminant mixtures, due to dilution limits required for analysis. Concentrations detected below the PQL will be appropriately flagged. These flagged concentrations will be considered below the practical quantification limits of the analytical method used, but will not negatively impact completeness.

The evaluation of method detection limits (MDLs) will be in accordance with the procedures outlined in Appendix B to Part 136 "Definition and Procedures for the Determination of Method Detection Limit - Revision 1.1," 40 Code of Federal Regulations (CFR) 136, 1984. Method quantification limits and detection limits will be reported for each sample set of validated data. The calculated MDL shall be equal to or less than the Required Detection Level (RDL). If the calculated MDL is lower than the level the laboratory deems practical, the calculated MDL may be raised to a higher level. In no instance shall the reported MDL be below the calculated level. The method documentation shall include both the calculated MDL and the request for an increased reportable MDL. Raising the reportable MDL to a higher level will be contingent upon approval by Shaw's Principal Investigator and ESTCP.

C.5.2 Qualitative QA Objectives: Comparability and Representativeness

Comparability refers to the confidence with which one data set can be compared to another. Comparability is essential for the evaluation of technology performance compared to that of similar technologies. Comparable data will be generated by following standard SW-846 and U.S. EPA protocols for all laboratory analyses, and manufacturers' instructions for all on-site test kits and meters.

Representativeness is a measure of the degree to which data accurately and precisely represent the conditions of the parameter represented by the data. Collected samples must be representative of the matrix characteristics and contamination concentrations. Representativeness is affected by errors introduced through the sampling process, field contamination, preservation, handling, sample preparation, and analysis.

Representativeness will be ensured through the following practices:

- selecting the necessary number of samples, sample locations, and sampling procedures that will depict as accurately and precisely as possible the matrix and conditions measured;
- developing protocols for storage, preservation, and transport that preserve the representativeness of the collected samples;
- using documentation methods to ensure that protocols have been followed and that samples are properly identified to maintain integrity and traceability; and
- using standard, well-documented analytical procedures to ensure consistent, representative data.

While none of these practices can be quantified as a measure of representativeness, QC samples will be collected to indicate factors that may affect representativeness. The QC samples to be used for this purpose are as follows:

- field duplicates (field split samples and collection duplicates) to indicate variations caused by sampling techniques;

- trip blanks to indicate contamination of samples during transport; and
- field blanks to indicate contamination introduced through ambient conditions.

C.6 Quality Assurance Reports

To provide information to the client project manager and Shaw project manager on the performance of the QA program for this project, the QA officer will meet with the project manager and laboratory manager on a monthly basis to review quality control data summary, documentation, and other pertinent information.

A QA report on project performance will be presented to the laboratory manger. Facts will be presented in summary forms and charts, where applicable. The quality facts to be reported are:

- percentage duplication or replication of determinations
- results of intra-laboratory precision and accuracy
- results of performance and system audits
- data quality assessments

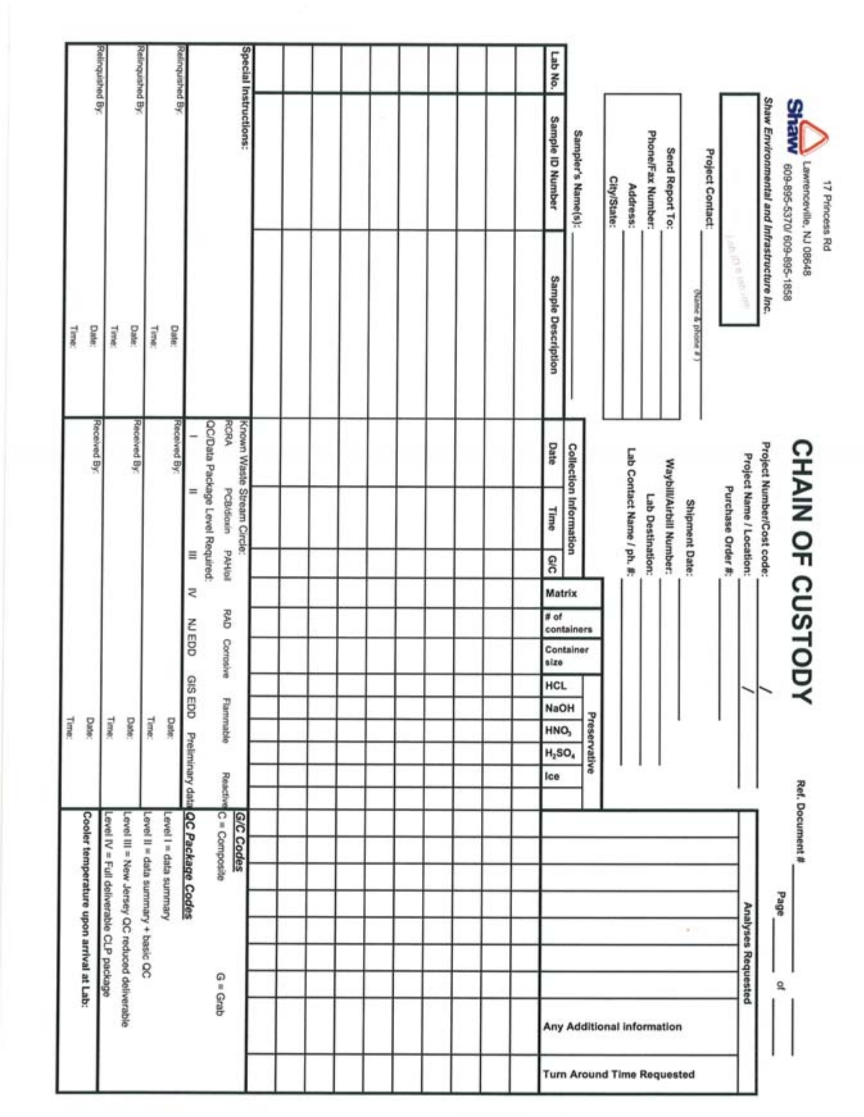
significant QA problems and recommended solutions.

In addition to the internal QA reports to Shaw management, the results of the QA/QC activities will also be reported to the GenCorp Aerojet site project manager for the project.

C.7 Data Storage and Archiving Procedures

All raw data, documentation, records, test plans, analyses, reports and correspondence generated as a result of this demonstration will be properly stored and archived in paper and electronic file formats as appropriate. Project data and analyses will be stored in an organized fashion to facilitate retrieval in an expedient fashion. Paper files will be maintained and stored so as to minimize deterioration during and after the project is complete. Electronic files associated with the project will be automatically backed-up on a monthly basis during the active phase of the project. Electronic files will be archived on CD-ROM upon completion of the project to ensure data integrity.

Figure C.1 Example of Shaw Chain of Custody Form.


Shaw
17 Princess Rd
Lawrenceville, NJ 08648
609-895-5370/ 609-895-1858
Shaw Environmental and Infrastructure Inc.

CHAIN OF CUSTODY

Ref. Document # ____ Page ____ of ____

Project Contact: ____ (Name & phone #)
Send Report To:
Phone/Fax Number:
Address:
City/State:
Sampler's Name(s):

Project Number/Cost code:
Project Name / Location:
Purchase Order #:
Shipment Date:
Waybill/Airbill Number:
Lab Destination:
Lab Contact Name / ph. #:

Lab No.	Sample ID Number	Sample Description	Collection Information: Date	Time	G/C	Matrix	# of containers	Container size	Preservative: HCL	NaOH	HNO_3	H_2SO_4	Ice	Analyses Requested	Any Additional information	Turn Around Time Requested

Special Instructions:

Known Waste Stream Circle:
RCRA PCB/dioxin PAH/oil RAD Corrosive Flammable Reactive
QC/Data Package Level Required:
I II III IV NJ EDD GIS EDD Preliminary data

G/C Codes
C = Composite G = Grab

QC Package Codes
Level I = data summary
Level II = data summary + basic QC
Level III = New Jersey QC reduced deliverable
Level IV = Full deliverable CLP package

Relinquished By:	Date: Time:	Received By:	Date: Time:
Relinquished By:	Date: Time:	Received By:	Date: Time:
Relinquished By:	Date: Time:	Received By:	Date: Time:

Cooler temperature upon arrival at Lab:

Table C.1. Data Quality Objectives (DQO).

Environmental Media	Data Usage	Data Types	Data Acquisition	Data Quality/ Analytical level	Levels of Concern
Groundwater	Site Characterization	Define contamination in the test plot	Collect groundwater samples from the test plot; perchlorate and VOC analysis	Laboratory analysis (Level III)	Limit of Detection
	Technology effectiveness	Determine effectiveness of technology for removal of the target compounds	Sample and analyze groundwater samples before and after field demonstration; perchlorate and VOC analysis	Laboratory analysis (Level III)	Limit of Detection

Table C.2. Range of Method Detection Limits and Quantification Limits for Analytical Methods Used During Demonstration. Refer to Appendix B for laboratory Methods and SOPs.

Sample Matrix	Analysis	Method	Reporting Method Detection Limits	Quantitation Limits
Groundwater	Perchlorate	314.0	0.19 □g/L	4.0 □g/L
	VOCs (TCE, DCE, VC, ethene, ethane)	8260B	0.32-0.83 □g/L	2-5 □g/L
	Metals (Fe, Mn)	200.7	0.05, 0.01 mg/L	0.05, 0.01 mg/L
	VFAs (lactate, acetate, citrate, formate, propionate)	300.0m	0.10-1.0 mg/L	1.0 mg/L
	Alcohols (ethanol, methanol)	8015B	0.31-0.53 mg/L	5.0 mg/L
	Anions (NO_3^-, NO_2^-, SO_4^-, Br^-,Cl^-,PO_4^-)	300.0	0.01-0.03 mg/L	0.2 mg/L

Notes:

VOC - Volatile Organic Compounds
TCE - Trichloroethylene
DCE - cis 1,2 Dichloroethene
VC - Vinyl Chloride
VFA - Volatile Fatty Acids
NO_3^- - Nitrate
NO_2^- - Nitrite
SO_4^- - Sulfate
Br^- - Bromide
Cl^- - Chloride
PO_4^- - Phosphate
TOC - Total Organic Carbon
COD - Carbon Oxygen Demand
$cBOD_5$ - Carbonaceous Biological Oxygen Demand
N/A - Not Applicable

Appendix D:

Site-Specific Health and Safety Plan (HASP)

Health and Safety Plan
for
GenCorp Aerojet
Area D
Central Disposal Area

Rancho Cordova, California

Shaw Environmental and Infrastructure

May 2003

HEALTH AND SAFETY PLAN
FOR
GENCORP AEROJET, AREA D
RANCHO CORDOVA, CALIFORNIA

Submitted by:
Shaw Environmental and Infrastructure
2835 North Grandview Blvd.
Pewaukee, WI 53072-0090

May 2003

SUBMITTED BY:

Jay Diebold, P.E.
Principal Engineer/Project Manager
Shaw Environmental and Infrastructure
Pewaukee, Wisconsin

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1.0 INTRODUCTION

The objective of this Health and Safety Plan (HASP) is to provide the minimum safety practices and procedures for Shaw Environmental and Infrastructure and subcontractor personnel engaged in proposed site activities that are to be conducted at the GenCorp Aerojet Facility in Rancho Cordova, California.

In order to accomplish the objective, this HASP uses the latest available information regarding known or suspected chemical contaminants and potential and foreseeable physical hazards associated with the proposed work at the site identified at Area D also known as Central Disposal Area. This HASP has been designed to be used in accordance with the Shaw Environmental and Infrastructure ("Shaw") Corporate Health and Safety Plan (SCHASP). The SCHASP provides detailed information pertaining to procedures to be performed on site as directed by the HASP. Both the HASP and the SCHASP must be present at the site to comply with the requirements stipulated in the Occupational Safety and Health Administration (OSHA) standard 29 CFR 1910.120.

This HASP has been written to support proposed tasks and techniques associated with the scope of work as presented in Section 3.6.7. Should the proposed work site conditions and/or suspected hazards change, or if new information becomes available, this document will be modified. All changes to the HASP will be made with the approval of the Shaw Health and Safety Manager (HSM) and the Project Manager (PM). The PM will notify all affected personnel of all changes.

The elements of this HASP are in compliance with the requirements established by OSHA 29 CFR 1910.120, "Hazardous Waste Operations and Emergency Response" (HAZWOPER) and sections of 29 CFR 1926, "Safety and Health Regulations for Construction."

1.1 KEY PROJECT PERSONNEL AND ORGANIZATION

This section defines responsibility for site safety and health for Shaw and subcontractor employees engaged in on site activities. Personnel assigned to these positions shall exercise the primary responsibility for all on site health and safety. These persons will be the primary point of contact for any questions regarding the safety and health procedures and the selected control measures.

- The Shaw Project Manager (PM) is responsible for the overall direction and implementation of health and safety for this project.

- The Shaw Field Technician (FT) is responsible for implementation of this HASP with the assistance of an appointed Site Safety Officer (SSO). The FT manages field activities, executes the work plan, and enforces safety procedures, as applicable to the work plan.

- The SSO supports site activities by advising the FT on all aspects of health and safety on site. These duties may include the following:

    - Coordinates all health and safety activities with the FT.
    - Selects, inspects, implements, and maintains personal protective equipment.
    - Establishes work zones and control points.
    - Directs and assists in the development of decontamination areas and procedures.
    - Verifies training and medical status of on site personnel in relation to site activities.
    - Implements hazard communication, respiratory protection, and other associated safety and health programs, as necessary.
    - Coordinates emergency services.
    - Provides site-specific training for all on site personnel.

- Compliance with these requirements is monitored by the Project Health and Safety Officer (PHSO) and is coordinated through the Health and Safety Manager.

1.3 SITE INFORMATION AND PERSONNEL ASSIGNMENTS

Site Name: GenCorp Aerojet Area D- Central Disposal Area **Address:** Rancho Cordova, California

Site Point of Contact: Scott Neville **Phone Number:** 916-355-5500

Purpose of Site Visit: The objective of this project is to demonstrate in situ bioremediation of perchlorate and TCE in a contaminated aquifer using electron donor addition to stimulate naturally-occurring bacteria capable of perchlorate and TCE reduction.

Proposed Dates of Work: July 2003 until completion

Project Team:

Shaw Personnel:	Discipline/Tasks Assigned:
Jay Diebold, PE	Project Manager (PM)
Matthew Giovanelli, PG	Field Geologist
Cliff Florczak	Health and Safety Manager (HSM)
Michael Cushman	Field Technician (FT)
Matthew Giovanelli, PG	Site Safety Officer (SSO)
Jay Diebold, PE	Project Health and Safety Officer (PHSO)

Non-Shaw Personnel	Affiliation/Discipline/Tasks Assigned
TBD	
TBD	

2.0 EMERGENCY ACTION PLAN

2.1 INTRODUCTION

This section has been developed as part of a planning effort to direct and guide field personnel in the event of an emergency. All site activities will be coordinated with the client contact, Scott Neville. In the event of an emergency which cannot be mitigated using onsite resources, personnel will evacuate to a safe place of refuge and the appropriate emergency response agencies will be notified. It has been determined that the majority of potential emergency situations would be better supported by outside emergency responders. Based on this determination, Shaw and subcontractor personnel will not provide emergency response support beyond the capabilities of onsite response. Workers who are ill or who have suffered a non-serious injury may be transported by site personnel to nearby medical facilities, provided that such transport does not aggravate or further endanger the welfare of the injured/ill person or other site personnel. The emergency response agencies listed in this plan are capable of providing the most effective response, and as such, will be designated as the primary responders. These agencies are located within a reasonable distance from the area of site operations, which ensures adequate emergency response time. Aerojet contact Scott Neville will be notified anytime outside response agencies are contacted. This Emergency Action Plan conforms to the requirements of 29 CFR 1910.38(a), as allowed in 29 CFR 1910.120(l)(1)(ii).

Shaw, through necessary services, will provide the following emergency action measures:

- Initial stage fire fighting support and prevention
- Initial spill control and containment measures and prevention
- Removal of personnel from emergency situations
- Initial medical support for injuries or illnesses requiring basic first-aid
- Site control and security measures as necessary

2.2 PRE-EMERGENCY PLANNING

Through the initial hazard/risk assessment effort, it is anticipated that emergencies resulting from chemical, physical, or fire hazards are unlikely given the nature of site activities.

Nonetheless, to minimize and eliminate the potential for any emergency situations, pre-emergency planning activities will include the following (which are the responsibility of the FT):

- Coordinating with local Emergency Response personnel to ensure that Shaw emergency action activities are compatible with existing emergency response procedures. Aerojet Fire Protection and Emergency Response Services will be notified of scheduled events and activities. This is most imperative in situations where their services may be required such as confined space entry.

- Establishing and maintaining information at the project staging area (support zone) for easy access in the event of an emergency. This information will include the following:

  - Chemical Inventory (of chemicals used onsite), with Material Safety Data Sheets.
  - Onsite personnel medical records (Medical Data Sheets).
  - A log book identifying personnel onsite each day.
  - Hospital route maps with directions (these should also be placed in each site vehicle).
  - Emergency Notification - phone numbers.

The Shaw FT will be responsible for the following tasks:

- Identifying a chain of command for emergency action.

- Educating site workers to the hazards and control measures associated with planned activities at the site, and providing early recognition and prevention, where possible.

- Periodically performing practice drills to ensure site workers are familiar with incidental response measures.

- Providing the necessary equipment to safely accomplish identified tasks.

2.3 EMERGENCY RECOGNITION AND PREVENTION

2.3.1 Recognition

Emergency situations that may be encountered during site activities will generally be recognized by visual observation. To adequately recognize chemical exposures, site personnel must have a clear knowledge of signs and symptoms of exposure associated with site contaminants. This information is provided in Table 6-1. Tasks to be performed at the site, potential hazards associated with those tasks and the

recommended control methods are discussed in detail in Sections 5.0 and 6.0. Additionally, early recognition of hazards will be supported by periodic site surveys to identify any situation predisposed to an emergency. The FT will be responsible for performing surveys of work areas prior to initiating site operations and periodically while operations are being conducted. Survey findings will be documented by the FT in the site logbook, however, all site personnel will be responsible for reporting hazardous situations. Where potential hazards exist, Shaw will initiate control measures to prevent adverse effects to human health and the environment.

The above actions will provide early recognition for potential emergency situations, and allow Shaw to initiate necessary control measures. However, if the FT determines that control measures are not sufficient to eliminate the hazard, Shaw will withdraw from the site and notify the appropriate response agencies listed in Table 2-1.

2.3.2 Prevention

Shaw and subcontractor personnel will minimize the potential for emergencies by following this HASP, the Shaw Corporate Health and Safety Plan, and applicable OSHA regulations. Periodic site surveys of work areas and correction of any identified deficiencies prior to the commencement of that day's activities by the FT will also assist in prevention of illness/injuries when hazards are recognized early and control measures initiated.

2.4 EVACUATION ROUTES, PROCEDURES, AND PLACES OF REFUGE

An evacuation will be initiated whenever recommended hazard controls are insufficient to protect the health, safety or welfare of site workers. Specific examples of conditions that may initiate an evacuation include, but are not limited to the following: severe weather conditions; fire or explosion; and evidence of personnel overexposure to potential site contaminants.

In the event of an emergency requiring evacuation, all personnel will immediately stop activities and report to the designated safe place of refuge unless doing so would pose additional risks. When evacuation to the primary place of refuge is not possible, personnel will proceed to a designated alternate location and remain until further notification from the Shaw FT. Safe places of refuge will be identified prior to the commencement of site activities by the FT and will be conveyed to personnel as part of the pre-activities briefing session. This information will be reiterated during daily safety meetings and indicated on the Safe Work Permits. Whenever possible, the safe place of refuge will also serve as the telephone communications point for that area. During an evacuation, personnel will remain at the refuge location until directed otherwise by the Shaw FT or the on-site Incident Commander of the Emergency Response Team. The FT will perform a head count at this location to account for and to confirm the

location of all site personnel. Emergency response personnel will be immediately notified of any unaccounted personnel. The FT will document the names of all personnel onsite (on a daily basis) in the Field Logbook. This information will be utilized to perform the head count in the event of an emergency.

Evacuation procedures will be discussed during the pre-activities training session, prior to the initiation of project tasks. Evacuation routes from the site and safe places of refuge are dependent upon the location at which work is being performed and the circumstances under which an evacuation is required. Additionally, site location and meteorological conditions (i.e., wind speed and direction) may dictate evacuation routes. As a result, assembly points will be selected and communicated to the workers relative to the site location where work is being performed. Evacuation should always take place in an upwind direction from the site and away from water bodies.

2.5 EMERGENCY ALERTING AND ACTION/RESPONSE PROCEDURES

Shaw personnel will likely be working in close proximity to each other during planned site activities. Site personnel will initiate emergency notification to all onsite personnel by voice commands, hand signals, vehicle horns, or line of site communication to alert site personnel of an emergency. The Fire Department will provide rescue services. The details for notification must be documented in the permit.

If an emergency warranting evacuation occurs, the following procedures are to be initiated:

- Initiate the evacuation via appropriate and/or available communication method (hand signals, voice commands, etc.).
- Report to the designated refuge point.
- Once all non-essential personnel are evacuated, appropriate response procedures will be enacted to control the situation.
- Describe to the FT (serving as the Incident Coordinator) pertinent incident details.

In the event that site personnel cannot mitigate the hazardous situation, the FT will enact emergency notification procedures to secure additional assistance in the following manner:

Contact pertinent emergency contacts listed in Table 2-1 and report the incident. Give the emergency operator the location of the emergency, the type of emergency, the number of injured, and a brief description of the incident. Stay on the phone and follow the instructions given by the operator. The operator will then notify and dispatch the proper emergency response agencies.

2.6 EMERGENCY CONTACTS

Prior to initiating field activities, all personnel will be thoroughly briefed on the emergency procedures to be followed in the event of an accident. Table 2-1 provides a list of emergency contacts and their associated telephone numbers. This table must be posted where it is readily available to all site personnel. Facility maps should also be posted showing potential evacuation routes and designated meeting areas.

TABLE 2-1
EMERGENCY REFERENCE
GENCORP AEROJET

AGENCY	TELEPHONE
EMERGENCY (fire, ambulance, rescue, police)	911
Hospital: Mercy Hospital of Folsom	(916) 983-7400
Hospital: Mercy San Juan Hospital	(916) 537-5000
Poison Control Center – Sacramento Area	(800) 876-4766
Chemtrec National Response Center	(800) 424-9300 (800) 424-8802
Site Point of Contact Scott Neville	(916) 355-5500
Shaw, Pewaukee Office	(262) 549-6898
Health and Safety Manager Cliff Florzcak	(630) 771-9205
Project Health and Safety Officer Jay Diebold, PE	(262) 549-6898
Project Manager Jay Diebold, PE	(262) 549-6898

2.7 EMERGENCY ROUTE TO HOSPITALS

The closest hospital to the Aerojet Facility is the Mercy Hospital in Folsom, California. The alternate hospital is the Mercy San Juan Hospital in Carmichael, California. Maps showing the proximity of the Aerojet Facility to both of the hospitals are included as Figure 2-1 and 2-1A. Directions to both Mercy Hospital of Folsom and Mercy San Juan Hospital are provided below:

Mercy Hospital of Folsom

1650 Creekside Drive
Folsom, California 95630
916-983-7400

Exit the facility, heading northwest on Aerojet Road toward Folsom Boulevard. Turn right on Folsom Boulevard and follow for approximately 2.2 miles. Then turn right onto Blue Ravine Road and proceed approximately 2 miles. Turn right onto Bidwell Street and follow for approximately 0.25 miles, then turn left onto Creekside Drive. Mercy Hospital of Folsom is located at 1650 Creekside Drive.

Mercy San Juan Hospital

6501 Coyle Avenue
Carmichael, California 95608
916-537-5000

Exit the facility, heading northwest on Aerojet Road towards Folsom Boulevard. Turn left on Folsom Boulevard and follow for 0.4 miles. Then turn right onto Hazel Avenue and proceed 2.6 miles. Turn left on Madison Avenue and follow for 4.5 miles, then turn right onto Dewey Drive. Proceed 0.3 miles on Dewey Drive and turn left onto Coyle Avenue. Mercy San Juan Hospital is located at 6501 Coyle Avenue.

Figure 2-1

Route To Mercy Hospital of Folsom

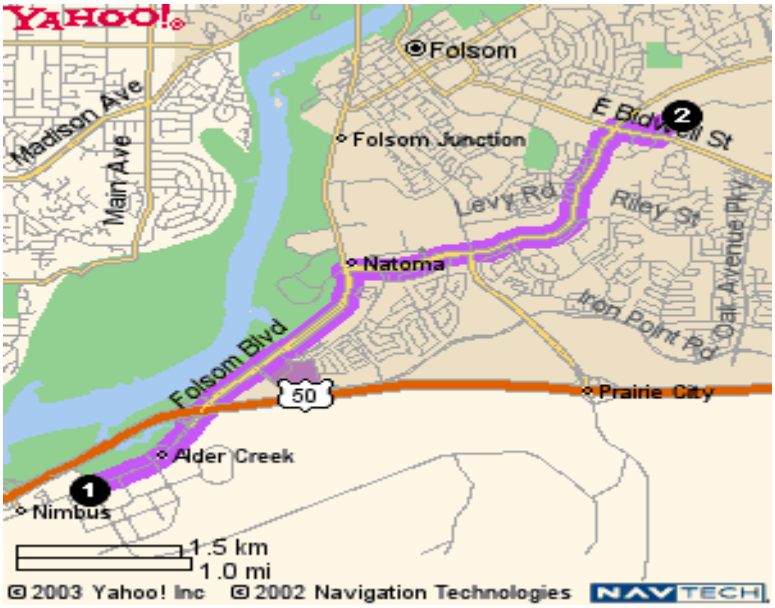
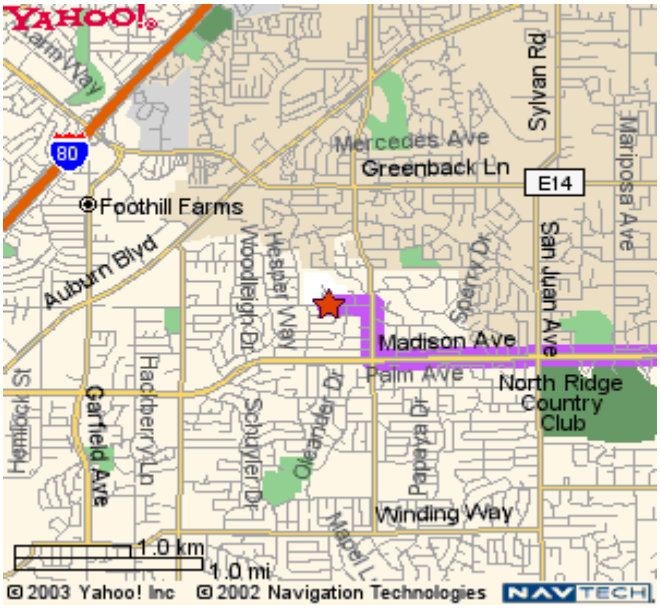


Figure 2-1A

Route To Mercy San Juan Hospital



2.8 DECONTAMINATION PROCEDURES / EMERGENCY MEDICAL TREATMENT

During any site evacuation, decontamination procedures will be performed only if doing so does not further jeopardize the welfare of site workers. Decontamination will not be performed if the incident warrants immediate evacuation. However, it is unlikely that an evacuation would occur which would require workers to evacuate the site without first performing the necessary decontamination procedures.

Shaw personnel will perform removal of personnel from emergency situations and may provide initial medical support for injury/illnesses requiring only first-aid level support. Medical attention above that level will require assistance and support from the designated emergency response agencies. Attachment I provides the form to be used when reporting an injury/illness.

2.9 INJURY AND ILLNESS REPORTING

Any pertinent information regarding allergies to medications or other special conditions will be provided to medical service personnel. This information is listed on Medical Data Sheets filed onsite. If an exposure to hazardous materials has occurred, provide hazard information from Table 6-1 to medical service personnel. As soon as possible, Aerojet contact Scott Neville must be informed of any incident or accident that requires medical attention.

2.10 PPE AND EMERGENCY EQUIPMENT

A first-aid kit, eye wash units (or bottles of disposable eyewash solution) and a fire extinguisher will be maintained onsite and shall be immediately available for use in the event of an emergency. This equipment will be located in the field office or site vehicle. Personnel identified within the field crew with bloodborne pathogen and first-aid training will be the only personnel permitted to offer first-aid assistance.

FIGURE 2-2

POTENTIAL EXPOSURE REPORT

Name: _____ Date of Exposure: _____

Social Security No.: _____ Age: _____ Sex: _____

Client Contact: _____ Phone No.: _____

Company Name: _____

I. Exposing Agent

Name of Product or Chemicals (if known): _____

_____

_____

Characteristics (if the name is not known)

Solid Liquid Gas Fume Mist Vapor

II. Dose Determinants

What was individual doing? _____

How long did individual work in area before signs/symptoms developed? _____

Was protective gear being used? If yes, what was the PPE? _____

Was there skin contact? _____

Was the exposing agent inhaled? _____

Were other persons exposed? If yes, did they experience symptoms? _____

III. Signs and Symptoms (circle appropriate symptoms)

Immediately With Exposure:

Burning of eyes, nose, or throat
Tearing
Headache
Cough
Shortness of Breath
Chest Tightness / Pressure
Nausea / Vomiting
Dizziness
Weakness

Delayed Symptoms:

Weakness
Nausea / Vomiting
Shortness of Breath
Cough
Loss of Appetite
Abdominal Pain
Headache
Numbness / Tingling

IV. Present Status of Symptoms (circle appropriate symptoms)

Burning of eyes, nose, or throat
Tearing
Headache
Cough
Shortness of Breath
Chest Tightness / Pressure
Cyanosis
Nausea / Vomiting
Dizziness
Weakness
Loss of Appetite
Abdominal Pain
Numbness / Tingling

Have symptoms: (please check off appropriate response and give duration of symptoms)

Improved: _____ Worsened: _____ Remained Unchanged: _____

V. Treatment of Symptoms (check off appropriate response)

None: _____ Self-Medicated: _____ Physician Treated: _____

3.0 SITE BACKGROUND

3.1 FACILITY HISTORY

The facility is located about 32 miles southeast of Sacramento in the northwest portion of Sonoma County. The Test Site is located within Aerojet General Corporation's (Aerojet) 8,500 acre California 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 Standard Industrial Classification (SIC) code for this facility has been replaced by the NAICS (North American Industry Classification System) code. This code for Aerojet is as follows: 336415 – Guided Missile and Space Vehicle Propulsion Unit and Propulsion Unit Parts Manufacturing.

4.0 SCOPE OF WORK

This section of the HASP addresses proposed site activities that are to be conducted at GenCorp Aerojet Area D- Central Disposal Area. The objective of the geoprobe and monitoring well installation is to investigate the magnitude of impacts of company-related activities at Area D and to assess the potential ecological and human health risks associated with the impacts. The scope of the field activities includes collecting both groundwater and soil samples. The activities to be conducted as part of the scope of work are as follows:

- Mobilization/demobilization
- Multi-media sampling, including:
  - Sub-Surface Water
  - Soil
- Decontamination of sampling equipment
- IDW management - This task includes the containerization, labeling, staging, monitoring, and final deposition of Investigation Derived Wastes (IDW).
- Surveying

Table 5-1, provides information related to each of these tasks that are to be performed as part of the scope of work. If other tasks, other than those identified, are to be performed at the site, this HASP will be modified.

4.1 MOBILIZATION/DEMOBILIZATION

This task includes, but not limited to, the following:

- The procurement and shipping of equipment, and materials for the field investigation.
- Review of planning documents (i.e., HASP, SCHASP, FSP Quality Assurance Plan, Applicable SOPs, etc.).
- Mobilizing all required subcontractors, equipment, and materials to the site
- Obtaining all necessary sampling permits.
- Attending an approximately 1-hour site-specific health and safety review meeting
- Delineating work zones required by the Health and Safety Plan (HASP)
- Secure, construct, or equip IDW storage facilities to support the field activities.
- Arranging an area to perform decontamination procedures
- Demobilizing all equipment and materials from the site; and
- Performing general site cleanup and removal of trash

4.2 DECONTAMINATION

The non-disposable equipment involved in field sampling activities will be decontaminated prior to and upon completion of sampling activities. Personnel will also perform decontamination procedures as required by the HASP before departing from the site.

Non-disposable sampling equipment decontamination will be performed using analyte-free water and phosphate-free soap (e.g., Alconox®) will be used for incidental cleaning of equipment. Field analytical equipment such as water-quality meters and probes will be rinsed with analyte-free water first and then with the sample liquid, before sampling water.

4.3 INVESTIGATION-DERIVED WASTE (IDW) MANAGEMENT

4.3.1 Decontamination Fluids

All liquid IDW accumulated during the field activities will be collected, containerized, and stored in Department-of-Transportation approved (specification 17-C/H) 55-gallon drums at the site. The drums will be labeled as soon as possible after they are filled and will be kept onsite, pending the results of surface

water and sediment analyses. Upon receipt of the analytical results, a determination will be made whether offsite disposal or treatment is required.

4.3.2 Personal Protective Equipment (PPE) and Miscellaneous Waste

The field team PPE will be disposed as required. These items, such as disposable latex gloves and paper towels, will be temporarily stored in plastic bags, with a daily transfer to dumpsters at the end of each workday.

5.0 TASKS/HAZARDS/ASSOCIATED CONTROL MEASURES SUMMARIZATION

Table 5-1 of this section serves as the primary portion of the site-specific HASP and identifies the tasks that are to be performed as part of the scope of work. This table will be modified and incorporated into this document as new or additional tasks are performed at the site. The anticipated hazards, recommended control measures, required Personal Protective Equipment (PPE), and decontamination measures for each site task are discussed in detail. This table and the associated control measures shall be changed, if the scope of work, contaminants of concern, or other conditions change.

Through using the table, site personnel can determine which hazards are associated with each task and at each site, and what associated control measures are necessary to minimize potential exposure or injuries related to those hazards. The table also assists field team members in determining which PPE and decontamination procedures to use.

As discussed earlier, a Shaw Corporate Health and Safty Plan (SCHASP) accompanies this table and HASP. The manual is designed to further explain supporting programs and elements for other site-specific aspects as required by 29 CFR 1910.120. The ECHASP should be referenced for additional information regarding decontamination activities, emergency response, hazard assessments, hazard communication program, medical surveillance, PPE, site control measures, standard work practices, and training requirements. Many of Shaw's SOPs are also provided in this Guidance Manual.

Safe Work Permits issued for sampling activities (See Section 10.10) will use elements defined in Table 5-1 as it's primary reference. The FT in completing the Safe Work Permit will add additional site-specific information. In situations where the Safe Work Permit is more conservative than the direction provided in Table 5-1 due to the incorporation of site-specific elements, the Safe Work Permit will be followed.

5.1 GENERAL SAFE WORK PRACTICES

In addition to the task-specific work practices identified on Table 5-1, the follow these safe work practices when conducting work involving known and unknown site hazards. These safe work practices establish a pattern of general precautions and measures for reducing risks associated with hazardous site operations.

- Refrain from eating, drinking, chewing gum or tobacco, taking medication, or smoking in contaminated or potentially contaminated areas or where the possibility for the transfer of contamination exists.
- Wash hands and face thoroughly upon leaving a contaminated or suspected contaminated area.
- Avoid contact with potentially contaminated substances.
- Be familiar with and adhere to all instructions in the site-specific HASP.
- Place cellular telephone or two way radios in a plastic bag to protect from water.
- Attend briefings on anticipated hazards, equipment requirements, Safe Work Permits, emergency procedures, and communication methods before going on site.
- Rehearse unfamiliar operations prior to implementation.
- Use the "buddy system". Establish hand signals or other means of emergency communication in case two-way radio failure.
- Maintain visual contact with each other and with other on-site team members by remaining in close proximity in order to assist each other in case of emergency.
- Establish appropriate decontamination procedures for leaving the site.
- Immediately report all injuries, illnesses, and unsafe conditions, practices, and equipment to the Site Safety Officer (SSO).
- Observe coworkers for signs of heat stress.

TABLE 5-1
TASKS/HAZARDS/CONTROL MEASURES FOR
GENCORP AEROJET, AREA D – RANCHO CORDOVA, CA

TASKS/OPERATION/ LOCATIONS	ANTICIPATED HAZARDS	RECOMMENDED CONTROL MEASURES	PERSONAL PROTECTIVE EQUIPMENT *(Items in italics are deemed optional as conditions or the FT or SSO require.)*	DECONTAMINATION PROCEDURES
Mobilization/ Demobilization	***Physical Hazards:*** 1) Lifting (strain/muscle pulls) 2) Pinches and compressions 3) Slip, trips, and falls 4) Ambient temperature extremes (heat stress) NATURAL HAZARDS: 5) Insect/animal bites and stings	1) Use machinery or multiple personnel for heavy lifts. Use proper lifting techniques. 2) Avoid moving parts. Use tools or equipment where necessary to avoid contacting pinch points. 3) Preview work locations for unstable/uneven terrain. 4) Wear appropriate clothing for weather conditions. Provide acceptable shelter and liquids for field crews. Additional information regarding heat stress concerns is provided in Envirogen Health and Safety Guidance Manual. 5) Avoid nesting areas, use commercially available insect repellents. Report potential hazards to the SSO. Follow guidance presented in the Health and Safety Guidance Manual.	Level D - (Minimum Requirements) - Standard field attire (Sleeved shirt; long pants) - Steel Toe Safety shoes - Safety glasses - Hardhat (when overhead hazards exists, or identified as a operation requirement) - Reflective vest for high traffic areas - Hearing protection for high noise areas, or as directed on an operation by operation scenario.	Not required
Multi-media sampling including ground water, and soil	***Chemical hazards:*** 1) Generally low concentrations of pH, ammonium perchlorate, and TCE See Table 6-1 for more information on the chemicals of concern. 2) Transfer of contamination into clean areas ***Physical hazards:*** 3) Lifting (strain/muscle pulls) 4) Slip, trips, and falls 5) Ambient temperature extremes (heat stress) 6) Water hazards/drowning 7) Pinches and compressions ***Natural hazards:*** 8) Insect/animal bites and stings 9) Inclement weather	1) Visually monitor sampling procedures, Avoid contact with potentially contaminated media. 2) Decontaminate all equipment and supplies between sampling locations and prior to leaving the site. 3) Use machinery or multiple personnel for heavy lifts. Use proper lifting techniques. 4) Preview work locations for unstable/uneven terrain. 5) Wear appropriate clothing for weather conditions. Provide acceptable shelter and liquids for field crews. Additional information regarding heat stress concerns is provided in the Envirogen Health and Safety Guidance Manual. 6.) Avoid nesting areas, use commercially available insect repellents. Report potential hazards to the SSO. Follow guidance presented in the Health and Safety Guidance Manual Report potential hazards to the SSO. 9) Suspend or terminate operations until directed otherwise by SSO	Level D protection will be utilized for the initiation of all sampling activities. Level D - (Minimum Requirements) - Standard field attire (Sleeved shirt; long pants) - Safety glasses - Surgical style gloves (double-layered if necessary) - Hat to protect from UV rays from the sun. - Hearing protection for high noise areas, or as directed on an operation by operation scenario. **Note:** The Safe Work Permit(s) for this task (see Attachment IV) will be issued at the beginning of each day to address the tasks planned for that day. As part of this task, additional PPE may be assigned to reflect site-specific conditions or special considerations or conditions associated with any identified task.	**Personnel Decontamination** will consist of a removal and disposal of non-reusable PPE (gloves, coveralls, etc., as applicable). The decon function will take place at an area adjacent to the site activities. This procedure will consist of: - Equipment drop - Outer coveralls, boot covers, and/or outer glove removal (as applicable) - Removal, segregation, and disposal of non-reusable PPE in bags/containers provided - Soap/water wash and rinse of reusable PPE (e.g., hardhat) if potentially contaminated - Wash hands and face, leave contamination reduction zone.
Decontamination of Sampling Equipment	***Chemical hazards:*** 1) Generally low concentrations of pH, ammonium perchlorate, and cadmium See Table 6-1 for more information on the chemicals of concern. 2) Decontamination fluids - Liquinox (detergent), acetone or isopropanol ***Physical hazards:*** 3) Lifting (strain/muscle pulls) 4) Slips, trips, and falls ***Natural hazards:*** 5) Ambient temperature extremes (heat stress)	1) and 2) Employ protective equipment to minimize contact with site contaminants and hazardous decontamination fluids. Obtain manufacturer's MSDS for any decontamination solvents used onsite. Use appropriate PPE as identified on MSDS. All chemicals used must be listed on the Chemical Inventory for the site, and site activities must be consistent with the Hazard Communication section of the Health and Safety Guidance Manual (Section 5). 3) Use multiple persons where necessary for lifting and handling sampling equipment for decontamination purposes. 4) Preview work locations for unstable/uneven terrain. 5) Wear appropriate clothing for weather conditions. Provide acceptable shelter and liquids for field crews. Additional information regarding cold/heat stress concerns is provided in the Shaw Health and Safety Guidance Manual.	For sampling equipment (trowels, MacroCore Samplers, bailers, etc.), the following PPE is required Level D Minimum requirements - - Standard field attire (Long sleeve shirt; long pants) - Steel-toe safety shoes - Nitrile outer gloves - Safety glasses In the event of overspray of chemical decontamination fluids employ PVC Rainsuits or PE or PVC coated Tyvek as necessary.	**Personnel Decontamination** will consist of a soap/water wash and rinse for reusable outer protective equipment (boots, gloves, PVC splash suits, as applicable). The decon function will take place at an area adjacent to the site activities. This procedure will consist of: - Equipment drop - Soap/water wash and rinse of outer boots and gloves, as applicable - Soap/water wash and rinse of the outer splash suit, as applicable - Disposable PPE will be removed and bagged. Sampling equipment will be decontaminated as per the requirements in the Sampling and Analysis Plan and/or Work Plan. MSDS for any decon solutions (Alconox, isopropanol, etc.) will be obtained and used to determine proper handling / disposal methods and protective measures (PPE, first-aid, etc.).

TABLE 5-1
TASKS/HAZARDS/CONTROL MEASURES FOR
GENCORP AEROJET, AREA D – RANCHO CORDOVA, CA

TASKS/OPERATION/ LOCATIONS	ANTICIPATED HAZARDS	RECOMMENDED CONTROL MEASURES	PERSONAL PROTECTIVE EQUIPMENT *(items in italics are deemed optional as conditions or the FT or SSO require.)*	DECONTAMINATION PROCEDURES
Geographical Survey	***Chemical hazards:*** Significant exposure to site contaminants is anticipated to be unlikely given the nature of this task. ***Physical hazards****:* 1) Slips, trips, and falls 2) Ambient temperature extremes (heat stress) ***Natural hazards:*** 3) Inclement weather 4) Insect/animal bites or stings, poisonous plants, etc.	1) Preview work locations and site lines for uneven and unstable terrain. Clear necessary vegetation, establish temporary means for traversing hazardous terrain (i.e., rope ladders, etc.) 2) Wear appropriate clothing for weather conditions. Provide acceptable shelter and liquids for field crews. Additional information regarding cold/heat stress is provided in the Health and Safety Guidance Manual. 3) Suspend or terminate operations until directed otherwise by SSO 4) Avoid nesting areas, use repellents. Report potential hazards to the SSO. Follow guidance presented in the Health and Safety Guidance Manual.	Surveying activities shall be performed in Level D protection Level D Protection consists of the following: - Standard field dress including sleeved shirt and long pants - Safety shoes (Steel toe/shank) - Safety glasses, hard hats (if working near machinery) - Snake chaps for heavily wooded area where encounters are likely. - Tyvek coveralls may be worn to provide additional protection against poisonous plants and insects, particularly ticks. Work gloves may be worn if desired. **Note:** The Safe Work Permit(s) for this task (see Attachment IV) will be issued at the beginning of each day to address the tasks planned for that day. As part of this task, additional PPE may be assigned to reflect site-specific conditions or special considerations or conditions associated with any identified task.	**Personnel Decontamination** - A structured decontamination is not required, as the likelihood of encountering contaminated media is considered remote. However, survey parties should inspect themselves and one another for the presence of ticks when exiting wooded areas, grassy fields, etc. This action will be employed to stop the transfer of these insects into vehicles, homes, and offices.

6.0 HAZARD ASSESSMENT

This section provides information regarding the chemical and physical hazards associated with GenCorp Aerojet Area D and the activities that are to be conducted as part of the scope of work. Table 6-1 provides various information related to the chemical hazards that may be present at the site. Specifically, toxicological information, exposure limits, symptoms of exposure, physical properties, and air monitoring and sampling data are also discussed in that table.

6.1 CHEMICAL HAZARDS

A wide range of chemicals of potential concern were identified, including ammonium perchlorate and trichloroethene.

Information on the toxicological, chemical, and physical properties of other potential contaminants of concern is addressed in Table 6-1 of this HASP. It is anticipated that the greatest potential for exposure to site contaminants is during activities in which contact with potential contaminated media exists (soil boring, monitoring well installations, sampling activities, etc.).

6.2 PHYSICAL HAZARDS

In addition to the chemical hazards discussed above, the following physical hazards may be present during the performance of site activities.

6.2.1 Slip, Trip and Fall Hazards

Various potential slip, trip, and fall hazards may be encountered during the performance of planned site activities. These hazards are associated with working out doors where uneven or wet terrain may be encountered, or near the edge of bodies of water, as well as on boat decks and docks. To minimize the potential for worker injury from these hazards, the following requirements must be observed:

- Maintain proper housekeeping in all work areas.

- Preview and inspect work areas to identify and eliminate slip, trip, or fall hazards. In outdoor locations, pay particular attention to sink holes or other depressions that may be encountered.

- Any work that is to be done on structures that are more than 6-feet above floor or ground level will require fall protection training and the use of 100% fall protection equipment.

- Cover, guard, barricade, and/or place warning posting over/at holes or openings that personnel may fall or step into.

- For traversing steep, slippery, or sloped terrain establish rope ladders to control ascent and descent to sampling areas or use alternative pathways.

6.2.2 Strains/Muscle Pulls

Worker injuries resulting from improper manual material handling activities are easily prevented through observation of proper lifting and carrying methods and utilization of material handling equipment where necessary and suitable. These types of injuries are not limited to merely the factor of the weight of the load. Other considerations include how many lifts will be involved (i.e., repetitive lifting of even small loads), the size, shape, and/or configuration of the load to be lifted, and whether or not the load will need to be lifted to another height or carried to another location. All workers involved with these types of activities are to be instructed by the SSO in the following manner:

- First estimate the weight and configuration of the load (i.e., is it bulky or hard to safely grasp/lift/control). If it appears to be too heavy or bulky to safely handle alone, either use a mechanical lifting device or obtain help from another employee to lift the load (Note: The use of mechanical lifting devices is always preferable over manual lifting).

- Bend at the knees (not at the waist) when attempting a lift.

- Ensure that a firm hold is obtained, and keep the load as close to the body as possible.

- Lift the load using your legs, and not the back.

- Avoid turning or twisting while holding a load.

- If the load is to be moved, preview the path of travel first to identify and eliminate any tripping hazards.

- Do not attempt to carry loads that obstruct the line of sight.

- When setting a load down, again use the leg muscles and do not bend at the waist.

- Break loads into smaller amounts for travel to remote locations.

- In all cases, where possible use mechanical equipment to transport equipment and resources to the desired location.

6.3 NATURAL HAZARDS

As most of the work to be conducted will occur in areas that are not improved or maintained, natural hazards and inclement weather may exist. This hazard is anticipated during the following activities:

Insect/animal bites and stings, poisonous plants, and inclement weather are natural hazards that may be present given the location of activities to be conducted. In general, avoidance of areas of known infestation or growth will be the preferred exposure control for insects/animals and poisonous plants. Specific discussion on principle hazards of concern follows:

6.3.1 Insect Bites and Stings

Insect bites and stings are difficult to control given the climate and environmental setting of GenCorp Aerojet Area D. However, in an effort to minimize this hazard the following control measures will be implemented where possible.

- Commercially available bug sprays and repellents will be used whenever possible – Pesticides analytical screening includes chlordane, endrin, lindane, methoxychlor, toxaphene and heptachlor. Commercially available repellants may be used providing they don't contain substances which appear on the analytical list for pesticide analysis. Products such as DEET should not be applied directly to the skin due to potential irritation. This product, when permitted for use, should be applied over clothing articles.

- Where possible, loose-fitting and light-colored clothing with long sleeves should be worn. This will also aid in insect control by providing a barrier between the field person and the insects and to provide easy recognition of crawling insects against the lighter background. Pant legs should be secured to the work-boots using duct tape to prevent access by ticks. Mosquito nets are also recommended for use when commercially available repellents are not permitted.

- Clothing/limited body checks for ticks and other crawling insects should be conducted upon exiting heavily vegetated areas. Workers should perform a more detailed check of themselves when showering in the evening. Ticks prefer moist areas of the body (arm-pits, genitals, etc.) and will migrate to those locations.

- The FT/SSO will preview all access routes and work areas in an effort to identify physical hazards including nesting areas in and around the work sites. These areas will be flagged and communicated to all site personnel.

- The FT/SSO must determine if site personnel (through completion of Medical Data Sheets), suffer allergic reactions to bee and other insect stings and bites. Field crewmembers that are allergic to bites should have their emergency kit containing antihistamine and a preloaded autoinjector of epinephrine readily available.

Any allergies (insect bites, bee stings, etc.) must be reported on the Medical Data Sheet and to the SSO.

Tick-Borne Disease

Tick-borne Lyme borreliosis disease may pose a potential health hazard in the northern coastal counties of California. Other tick-borne diseases that have been identified in California are ehrlichiosis and Rocky Mountain Spotted Fever. The longer a disease carrying tick remains attached to the body, the greater the potential for contracting these diseases. Wearing long sleeved shirts and long pants (tucked into boots). As well as performing frequent body checks will prevent long term attachment. Site first aid kits should be equipped with medical forceps and rubbing alcohol to assist in tick removal. For information regarding tick removal procedures, and symptoms of exposure consult the health and safety guidance manual**.**

Mosquito-Borne Illness

Mosquitoes in California may carry diseases including St. Louis encephalitis, Western Equine encephalitis, La Crosse encephalitis and West Nile virus.

Although mosquito-borne viral illnesses are rare in humans, a Kill Devil Hills, N.C., woman recently died after she came down with eastern equine encephalitis from an infected mosquito. The California Department of Health Services, along with a variety of agencies, routinely conducts testing in mosquitoes and birds to monitor for possible mosquito-borne viruses.

Mosquitoes become infected after biting infected birds. The symptoms for mosquito-borne illnesses may include headache, moderate to high fever, stiff neck and confusion. In serious cases coma, seizures or paralysis can result. Symptoms usually appear between 5 to 15 days after exposure to infected mosquitoes. Mosquito-borne illnesses may be mild or serious and can lead to death.

West Nile Virus

Encephalitis is an inflammation of the brain and can be caused by bacteria and viruses. West Nile encephalitis is caused by a virus transmitted to humans by mosquitoes. West Nile virus is commonly found in Africa, West Asia, and the Middle East. It is closely related to St. Louis encephalitis virus found in the United States. The West Nile-like virus that has been found in United States is genetically related to West Nile virus, but because of genetic differences it may be a new subtype of West Nile virus.

The mosquito becomes infected by feeding on birds infected with the West Nile virus. Infected mosquitoes then transmit the West Nile virus to humans and animals when biting (or taking a blood meal).

West Nile encephalitis is NOT transmitted from person-to-person. There is no evidence that a person can get the virus from handling live or dead infected birds. However, avoid barehanded contact when handling any dead animals, including dead birds. Ticks have not been implicated as vectors of West Nile-like virus.

Mild infections are common and include fever, headache, and body aches, often with skin rash and swollen lymph glands. More severe infection is marked by headache, high fever, neck stiffness, stupor, disorientation, coma, tremors, occasional convulsions, paralysis and, rarely, and death (especially in the elderly and very young). The incubation period of West Nile encephalitis is usually 3 to 12 days. There is no specific therapy or vaccine against West Nile encephalitis.

No cases had previously been reported in the U.S. prior to September 1999 (in New York). Since then, West Nile Virus has been detected in 44 states, including California. To date, over 4,000 cases have been reported in the United States, including 277 deaths.

Western Equine Encephalitis (WEE)

Western Equine Encephalitis is spread to horses and humans though the bite of an infected mosquito. The mosquito becomes infected after biting an infected bird. WEE can cause severe complications and even death. Infection can cause a range of illnesses, from no symptoms to fatal disease. People with mild illness often have only a headache and sometimes fever. People with more severe disease can have sudden high fever, headache, drowsiness, irritability, nausea, and vomiting, followed by confusion, weakness, and coma. Symptoms usually appear between 5 to 15 days after exposure to infected mosquitoes. Major complications, including brain damage, are reported in about 13% of infected persons. The disease is fatal to about 3% of persons who develop severe symptoms. There is no specific treatment for western equine encephalitis. Antibiotics are not effective against viruses, and no effective

anti-viral drugs have been discovered. Care of patients centers on treatment of symptoms and complications. Western equine encephalitis is a relatively rare disease in humans that can occur in isolated cases or in epidemics. Since 1964, 639 human cases have been confirmed in the United States. Fewer than 5 cases are reported each year. In the United States, cases in humans are usually first seen in June or July.

Precautions include:

- Limit outdoor activities during peak mosquito times – at dusk and dawn.
- Avoid standing water
- Wear long-sleeved shirts and long pants whenever you are outdoors.
- Apply insect repellent according to manufacturer instruction to exposed skin. An effective repellent will contain 20% to 30% DEET (N,N-diethyl-meta-toluamide). Avoid products containing more than 30% DEET.
- Spray clothing with repellents containing permethrin or DEET, as mosquitoes may bite through thin clothing.

6.3.3 Poisonous Plants

Various plants which can cause allergic reactions may be encountered during fieldwork. These include, poison ivy, poison oak, and poison sumac. Contact with these plants may occur when clearing vegetation for access to work areas, or as a result of movement through these plants. An irritating, allergic reaction can occur after direct contact with the plant or indirect contact through some piece of equipment or clothing article. Oils are transferred from the plant to exposed skin, clothing, or piece of equipment. The degree of the irritating, allergic reaction can vary significantly from one person to the next.

Protective measures to control and minimize the effects of this hazard may include, but not be limited to, the following:

- Identify plants for field personnel.
  - Poison Ivy - Characterized by climbing vines, three leaf configuration ovate to elliptical in shape, deep green leaves with a reddish tint, greenish flowers, and white berries.

- Poison Sumac - Characterized as a tall bush of the sumac family bearing compound leaves (7-13 entire leaflets), branched from a central axis, drooping, with axillary clusters of white fruit: However, these white fruits and berries may exist only during pubescent stages.

- Poison oak - Characterized as similar to poison ivy consisting of a shrub, stems erect, 0.3 to 2.0 meters tall, leaflets consist of broad thick lobes coarsely serrated configuration, denser at the base, less so than the top.

- Protective measures may include wearing disposable garments such as Tyvek when clearing brush. These may be carefully removed and disposed of along with any oils accumulated from the plants.

- Personal Hygiene - The oils obtained from the plants will only elicit an allergic response when the person's bare skin layer is contacted. This can be aggravated when skin pores are open (perspiring), or through breaks in the skin such as cuts, nicks, scratches, etc. This can also be accomplished when using excessively hot water for cleaning the skin, which also causes pores to open. Prior to break time, lunchtime, etc. personnel should wash with cool water and soap to remove as much of the oils as possible. In heavily vegetated areas of these plants, additional measures including barrier creams and blocks may be used to prevent the oils from accessing and penetrating the skin.

All of these plants present an airborne sensitization hazard when burned. This is not to occur as part of this scope of work and therefore will not be addressed.

6.3.4 Inclement Weather

Project tasks under this Scope of Work will be performed outdoors and near water. As a result, inclement weather may be encountered. In the event that adverse weather conditions arise (electrical storms, hurricanes, etc.), the FT and/or the SSO will be responsible for temporarily suspending or terminating activities until hazardous conditions no longer exist.

TABLE 6-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
GENCORP AEROJET

Substance	CAS No.	Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Ammonium Perchlorate	7790-98-9	OSHA Hazard Communication Standard [29 CFR 1910.1200]	**Recommended gloves:** Latexor PVC gloves, and safety glasses/goggles. Employees should wash hands and face before eating, drinking or using tobacco.	**Boiling Pt:** Not Applicable **Melting Pt:** Not available **Solubilityn:** Soluble **Flash Pt:** Not Applicable **LEL/LFL:** Not available **UEL/UFL:** Not available **Vapor Density:** Not Applicable **Vapor Pressure:** Not Applicable **Specific Gravity:** 1.98 **Incompatibilities:** **Appearance and Odor:** Solid Crystals, White, odorless	
Trichloroethylene (TCE)	79-01-6	Threshold Limit Value (TLV/TWA) 270 mg/m^3 Short-Term Exposure Limit (STEL) 1080 mg/m^3 Permissible Exposure Limit (PEL) 100 ppm	**Recommended gloves:** Solvent-resistant gloves, and safety glasses/goggles. Employees should wash hands and face before eating, drinking or using tobacco	**Boiling Pt:** 188 °F **Melting Pt:** -99°F **Solubility:** 0.1-1% **Specific Gravity:** 1.46 **Vapor Density:** 4.53 **Vapor Pressure:** 58 mm Hg **Flash Pt:** Not available **LEL:** 8.0% **UEL:** 10.5% **Incompatibles:** chemically active metals, strong bases, strong oxidizing agents, powdered metals **Appearance and Odor:** Clear, colorless liquid. Chloroform-like odor	**Routes of exposure:** inhalation and ingestion. Symptoms include Pulm edema, dysp, cough, chest tight, subs pain; head ; chills musc aches; nau, vomit, diarr; anos, emphy, prot, mild anemia; [carc] **Target Organs**: Resp sys, kidneys, prostate, blood [prostatic & lung cancer]
Groundwater with pH range of 4.3 to 4.8	Not Available	None established	Low pH groundwater may be encountered. **Recommended gloves:** Latexor PVC gloves, and safety glasses/goggles. Employees should wash hands and face before eating, drinking or using tobacco	**Boiling Pt:** Not available **Melting Pt:** Not available **Detonation Pt:** Not available **Solubility:** Insoluble **Specific Gravity:** Not available **TDP:** Not available **Vapor Density:** Negligible **Vapor Pressure:** Negligible **Flash Pt:** Not available **LEL:** Not available **UEL:** Not available **Incompatibles:** Not available **Appearance and odor:** Not available	Routes of exposure: Direct Contact The symptoms include; burning, redness, watering of eyes, irritation

7.0 TRAINING/MEDICAL SURVEILLANCE REQUIREMENTS

7.1 INTRODUCTORY/REFRESHER/SUPERVISORY TRAINING

This section is included to specify health and safety training and medical surveillance requirements for both Shaw and subcontractor personnel participating in site activities.

7.1.1 Requirements for Shaw Personnel

All Shaw personnel must complete 40 hours of introductory hazardous waste site training prior to performing work at the GenCorp Aerojet facility. Additionally, Shaw personnel who have had introductory training more than 12 months prior to site work must have completed 8 hours of refresher training in the past 12 months before being cleared for site work. In addition, 8-hour supervisory training in accordance with 29 CFR 1910.120 (e)(4) will be required for site supervisory personnel.

Documentation of Shaw introductory, supervisory, and refresher training as well as site-specific training will be maintained at the project site. Copies of certificates or other official documentation will be used to fulfill this requirement.

7.1.2 Requirements for Subcontractors

All Shaw subcontractor personnel must have completed introductory hazardous waste site training or equivalent work experience as defined in OSHA Standard 29 CFR 1910.120 (e). Additionally, personnel who have had the introductory training more than 12 months ago, are required to have 8 hours of refresher training meeting the requirements of 29 CFR 1910.120 (e)(8) prior to performing field work at the PNS facility if required. Shaw subcontractors must certify that each employee has had such training by sending Shaw a letter, on company letterhead, containing the information in the example letter provided as in Figure 8-1 and by providing copies of certificates for all subcontractor personnel participating in site activities.

FIGURE 7-1

OSHA TRAINING CERTIFICATION

The following statements must be typed on company letterhead and signed by an officer of the company and accompanied by copies of personnel training certificates:

LOGO
XYZ CORPORATION
555 E. 5th Street
Nowheresville, Kansas 55555

Month, day, year

Mr. Jay Diebold, P.E.
Envirogen, Inc.
Project Manager
2835 North Grandview Blvd.
Pewaukee, Wisconsin 53072-0090

Subject: HAZWOPER Training

Dear Mr. Diebold:

As an officer of XYZ Corporation, I hereby state that I am aware of the potential hazardous nature of the subject project. I also understand that it is our responsibility to comply with all applicable occupational safety and health regulations, including those stipulated in Title 29 of the Code of Federal Regulations (CFR), Parts 1900 through 1910 and Part 1926.

I also understand that Title 29 CFR 1910.120, entitled "Hazardous Waste Operations and Emergency Response," requires appropriate level of training for certain employees engaged in hazardous waste operations. In this regard, I hereby state that the following employees have had 40 hours of introductory hazardous waste site training or equivalent work experience as requested by 29 CFR 1910.120(e) and have had 8 hours of refresher training as applicable and as required by 29 CFR 1910.120(e)(8) and that site supervisory personnel have had training in accordance with 29 CFR 1910.120(e)(4).

LIST FULL NAMES OF EMPLOYEES AND THEIR SOCIAL SECURITY NUMBERS HERE.

Should you have any questions, please contact me at (555) 555-5555

Sincerely,

(Name and Title of Company Officer)

Enclosed: Training Certificates

7.2 SITE-SPECIFIC TRAINING

Shaw will provide site-specific training to all Shaw employees and subcontractor personnel who will perform work on this project. Site-specific training will also be provided to all personnel (U.S. Department of Defense, EPA, etc.) who may enter the site to perform functions that may or may not be directly related to site operations. Site-Specific training will include:

- Names of designated personnel and alternates responsible for site safety and health
- Safety, health, and other hazards present on site
- Use of personal protective equipment
- Safe use of engineering controls and equipment
- Signs and symptoms of overexposure
- Contents of the Health and Safety Plan
- Emergency response procedures (evacuation and assembly points)
- Incipient response procedures
- Review of the contents of relevant Material Safety Data Sheets
- Review of the use of Safe Work Permits

Site-specific documentation will be established through the use of Figure 8-2. All site personnel and visitors must sign this document upon receiving site-specific training.

7.3 MEDICAL SURVEILLANCE

7.3.1 Medical Surveillance Requirements for Shaw Personnel

All Shaw personnel participating in project field activities will have had a physical examination meeting the requirements of Shaw's medical surveillance program and will be medically qualified to perform hazardous waste site work using respiratory protection.

Documentation for medical clearances will be maintained in the Shaw Pewaukee office and made available, as necessary.

FIGURE 7-2

SITE-SPECIFIC TRAINING DOCUMENTATION

My signature below indicates that I am aware of the potential hazardous nature of performing remedial investigation activities at GenCorp Aerojet Area D and that I have received site-specific training which included the elements presented below:

- Names of designated personnel and alternates responsible for site safety and health
- Safety, health, and other hazards present on site
- Use of personal protective equipment
- Safe use of engineering controls and equipment
- Medical surveillance requirements
- Signs and symptoms of overexposure
- Contents of the Health and Safety Plan
- Emergency response procedures (evacuation and assembly points)
- Incipient response procedures
- Review of the contents of relevant Material Safety Data Sheets
- Review of the use of Safe Work Permits

I have been given the opportunity to ask questions and that all of my questions have been answered to my satisfaction, and that the dates of my training and medical surveillance indicated below are accurate.

Name (Printed and Signature)	Site-Specific Training (Date)	40-Hour Training (Date)	8-Hour Refresher Training (Date)	8-Hour Supervisory Training (Date)	Medical Exam (Date)

7.3.2 Medical Surveillance Requirements for Subcontractors

Subcontractors are required to obtain a certificate of their ability to perform hazardous waste site work and to wear respiratory protection. The "Subcontractor Medical Approval Form" provided in Figure 8-3 should be used to satisfy this requirement, providing it is properly completed and signed by a licensed physician.

Subcontractors who have a company medical surveillance program meeting the requirements of paragraph (f) of OSHA 29 CFR 1910.120 can substitute "Subcontractor Medical Approval Form" (See Figure 8-3) with a letter, on company letterhead, containing all of the information in the example letter presented in Figure 8-4 of this HASP.

7.3.3 Requirements for All Field Personnel

Each field team member (including subcontractors) and visitors entering the Exclusion Zone(s) shall be required to complete and submit a copy of Medical Data Sheet found in the Shaw Health and Safety Guidance Manual. This shall be provided to the SSO, prior to participating in site activities. The purpose of this document is to provide site personnel and emergency responders with additional information that may be necessary in order to administer medical attention.

7.4 SUBCONTRACTOR EXCEPTIONS

Subcontractors who will not enter the Exclusion Zone during intrusive operations, and whose activities involve no potential for exposure to site contaminants, will not be required to meet the requirements for training/medical surveillance other than those stated for site-specific training (See Section 8.2).

FIGURE 7-3

SUBCONTRACTOR MEDICAL APPROVAL FORM

For employees of _____
Company Name

Participant Name: _____ Date of Exam: _____

Part A

The above-named individual has:

1. Undergone a physical examination in accordance with OSHA Standard 29 CFR 1910.120, paragraph (f), and was found to be medically -

   ( ) qualified to perform work at the GenCorp Aerojet Area D work site
   ( ) not qualified to perform work at the GenCorp Aerojet Area D work site

   and,

2. Undergone a physical examination in accordance with OSHA 29 CFR 1910.134(b)(10) and was found to be medically -

   ( ) qualified to wear respiratory protection
   ( ) not qualified to wear respiratory protection

My evaluation has been based on the following information, as provided to me by the employer.

( ) A copy of OSHA Standard 29 CFR 1910.120 and appendices.
( ) A description of the employee's duties as they relate to the employee's exposures.
( ) A list of known/suspected contaminants and their concentrations (if known).
( ) A description of any personal protective equipment used or to be used.
( ) Information from previous medical examinations of the employee that is not readily available to the examining physician.

Part B

I, _____, have examined _____
Physician's Name (print) Participant's Name (print)

and have determined the following information:

FIGURE 7-3
SUBCONTRACTOR MEDICAL APPROVAL FORM
PAGE TWO

1. Results of the medical examination and tests (excluding finding or diagnoses unrelated to occupational exposure):

   _____
   _____
   _____

2. Any detected medical conditions which would place the employee at increased risk of material impairment of the employee's health:

   _____
   _____
   _____

3. Recommended limitations upon the employee's assigned work:

   _____
   _____
   _____

I have informed this participant of the results of this medical examination and any medical conditions which require further examination of treatment.

Based on the information provided to me, and in view of the activities and hazard potentials involved at the GenCorp Aerojet Area D work site, this participant

( ) may
( ) may not

perform his/her assigned task.

Physician's Signature _____

Address _____

Phone Number _____

NOTE: Copies of test results are maintained and available at:

_____
_

Address

FIGURE 7-4

MEDICAL SURVEILLANCE LETTER

The following statements must be typed on company letterhead and signed by an officer of the company:

LOGO
XYZ CORPORATION
555 E. 5th Street
Nowheresville, Kansas 55555

Month, day, year

Mr. Jay Diebold, P.E.
Project Manager
Envirogen, Inc.
2835 North Grandview Blvd.
Pewaukee, Wisconsin 53072-0090

Subject: Medical Surveillance for GenCorp Aerojet Area D

Dear Mr. Diebold:

As an officer of XYZ Corporation, I hereby state that the persons listed below participate in a medical surveillance program meeting the requirements contained in paragraph (f) of Title 29 of the Code of Federal Regulations (CFR), Part 1910.120, entitled "Hazardous Waste Operations and Emergency Response: Final Rule." I further state that the persons listed below have had physical examinations under this program within the past 12 months and that they have been cleared, by a licensed physician, to perform hazardous waste site work and to wear positive- and negative- pressure respiratory protection. I also state that, to my knowledge, no person listed below has any medical restriction that would preclude him/her from working at the GenCorp Aerojet Area D work site.

LIST FULL NAMES OF EMPLOYEES AND THEIR SOCIAL SECURITY NUMBERS HERE.

Should you have any questions, please contact me at (555) 555-5555.

Sincerely,

(Name and Title of Company Officer)

8.0 SITE CONTROL

This section outlines the means by which Shaw will delineate work zones and use these work zones in conjunction with decontamination procedures to prevent the spread of contaminants into previously unaffected areas of the site. It is anticipated that a three zone approach will be used during work at this site; exclusion zone, contamination reduction zone, and support zone.

8.1 EXCLUSION ZONE

The exclusion zone will be considered those areas of the site of known or suspected contamination. In many cases, however, significant amounts of contamination will not be encountered in the proposed work areas of this site until/unless contaminants are brought to the surface by site activities (i.e., test borings, groundwater sampling, etc.). Furthermore, once such activities have been completed and contamination has been removed, the potential for exposure is again diminished and the area can then be reclassified as part of the contamination reduction zone. Therefore, the exclusion zones for this project will be limited to those areas where active work is being performed and/or anywhere there is believed to be the potential for encountering any of the potential hazards defined in this HASP.

8.2 CONTAMINATION REDUCTION ZONE

The contamination reduction zone (CRZ) will be a buffer area between the exclusion zone and any area of the site where contamination is not suspected. The personnel and equipment decontamination area established for this project will take place in the CRZ. This area will serve as a focal point in supporting exclusion zone activities. In addition, this area will serve as the access and control points to the exclusion zone.

8.3 SUPPORT ZONE

The support zone for this project will include a staging area where site vehicles will be parked, equipment will be unloaded, and where food and drink containers will be maintained. In all cases, the support zones will be established at areas of the site where exposure to site contaminants would not be expected during normal working conditions or foreseeable emergencies.

8.4 SAFE WORK PERMITS

All work conducted in support of this project will be performed using Safe Work Permits to guide and direct field crews on a task by task basis. An example of the Safe Work Permit to be used is illustrated in Figure 9-1. Partially completed Permits for the work to be performed are included **in Attachment IV**. The daily meetings conducted at the site will further support these work permits. This effort will ensure all site-specific considerations and changing conditions are incorporated into the planning effort. All permits will require the signature of the FT and SSO. Use of these permits will provide the communication line for reviewing protective measures and hazards associated with each operation. This HASP will be used as the primary reference for selecting levels of protection and control measures. The work permit will take precedence over the HASP when more conservative measures are required based on specific site conditions.

8.5 SITE VISITORS

Site visitors for the purpose of this document are identified as representing the following groups of individuals:

- Personnel invited to observe or participate in operations by Shaw
- Regulatory personnel (DOD, OSHA, EPA, MDE, etc.)
- Aerojet personnel
- Other authorized visitors

It is not anticipated that this operation will result in a large number of site visitors. However, as some visitors can reasonably be expected, the following requirements will be enforced:

- All site visitors will be routed to the FT, who will sign them in to the field logbook. Information to be recorded in the logbook will include the individual's name (proper identification required), who they represent, and purpose for the visit.
- All site visitors will be required to produce the necessary information supporting clearance onto the site. This includes information attesting to applicable training and medical surveillance, as stipulated in Section 8 of this document. In addition, to enter the site's operational zones during planned activities, all visitors will be required to first go through site-specific training covering the topics stipulated in Section 8.2 of this document.

NOTE: All site visitors will be escorted at all times while at the site.

FIGURE 8-1

SAFE WORK PERMIT

Permit No. _____ Date: _____ Time: From _____ to _____

SECTION I: General Job Scope (To be filled in by person performing work)

I. Work limited to the following (description, area, equipment used): _____

II. Names: _____

III. Onsite Inspection conducted ☐ Yes ☐ No Initials of Inspector _____ _____
Envirogen

SECTION II: General Safety Requirements (To be filled in by permit issuer)

IV. Protective equipment required
Level D ☐ Level B ☐
Level C ☐ Level A ☐
Detailed on Reverse

Respiratory equipment required

Full face APR	☐ Escape Pack	☐
Half face APR	☐ SCBA	☐
SAR	☐ Bottle Trailer	☐
Skid Rig	☐ None	☐

Modifications/Exceptions: _____

V. Chemicals of Concern | Action Level(s) | Response Measures

VI. Additional Safety Equipment/Procedures

Hardhat	☐ Yes	☐ No	Hearing Protection (Plugs/Muffs)	☐ Yes	☐ No
Safety Glasses	☐ Yes	☐ No	Safety belt/harness	☐ Yes	☐ No
Chemical/splash goggles	☐ Yes	☐ No	Radio	☐ Yes	☐ No
Splash Shield	☐ Yes	☐ No	Barricades	☐ Yes	☐ No
Splash suits/coveralls	☐ Yes	☐ No	Gloves (Type)	☐ Yes	☐ No
Steel toe/shank Workboots	☐ Yes	☐ No	Work/rest regimen	☐ Yes	☐ No

Modifications/Exceptions: _____

VII. Procedure review with permit acceptors

	Yes	NA		Yes	NA
Safety shower/eyewash (Location & Use)	☐	☐	Emergency alarms	☐	☐
Procedure for safe job completion	☐	☐	Evacuation routes	☐	☐
Contractor tools/equipment inspected	☐	☐	Assembly points	☐	☐

VIII. Equipment Preparation

	Yes	No	NA
Utility Locating and Excavation Clearance completed	☐	☐	☐
Equipment and Foot Traffic Routes Cleared and Established	☐	☐	☐
Physical Hazards Barricaded and Isolated	☐	☐	☐
Emergency Equipment Staged	☐	☐	☐

IX. Additional Permits required (Hot work, confined space entry, excavation etc.). ☐ Yes ☐ No
If yes, fill out appropriate section(s) on safety work permit addendum

X. Special instructions, precautions: _____

Permit Issued by: _____ Permit Accepted by: _____
Job Completed by: _____ Date: _____

Following this, the site visitor will be permitted to enter the site and applicable operational areas. All visitors are required to observe the protective equipment and site restrictions in effect at the area of their visit. Any and all visitors not meeting the requirements as stipulated in this plan for site clearance will not be permitted to enter the site operational zones during planned activities. Any incidence of unauthorized site visitation will cause all onsite activities to be terminated until that visitor can be removed. Removal of unauthorized visitors will be accomplished with support from the GenCorp Aerojet Area D contact, if necessary.

8.6 SITE SECURITY

Site security will be accomplished using Shaw field personnel. Shaw will retain complete control over active operational areas. Exclusion Zone barriers, and any existing barriers at the site will be used to restrict the general public. The second line of security will take place at the work site referring interested parties to the FT or designee. The FT will serve as a focal point for all non-project interested parties, and serve as the final line of security and the primary enforcement contact.

8.7 SITE MAP

Once the areas of contamination, access routes, topography, and dispersion routes are determined, a site map will be generated and adjusted as site conditions change. When possible, these maps will be posted to illustrate up-to-date collection of contaminants and adjustment of zones and access points.

8.8 BUDDY SYSTEM

Personnel engaged in on-site activities will practice the "buddy system" to ensure the safety of all personnel involved in this operation.

8.9 MATERIAL SAFETY DATA SHEET (MSDS) REQUIREMENTS

Shaw and subcontractor personnel will provide MSDSs for all chemicals brought on site. The contents of these documents will be reviewed by the SSO with the user(s) of the chemical substances prior to any actual use or application of the substances on site. A chemical inventory of all chemicals used on site will be developed using the Health and Safety Guidance Manual. The MSDSs will then be maintained in a central location (i.e., temporary office) and will be available for anyone to review upon request.

8.10 COMMUNICATION

As personnel will be working in proximity to one another during field activities, a supported means of communication between field crews members will not be necessary. External communication will be accomplished by using the telephones at predetermined and approved locations. External communication will primarily be used for the purpose of resource and emergency resource communications. Prior to the commencement of activities, the FT will determine and arrange for telephone communications.

9.0 SPILL CONTAINMENT PROGRAM

9.1 SCOPE AND APPLICATION

It is not anticipated that bulk hazardous materials (over 55-gallons) will be handled at any given time, or that any cylinders or containers will be unearthed, as part of this scope of work. It is also not anticipated that such spillage of Investigative Derived Wastes (IDW) would constitute a danger to human health or the environment. However, as the job progresses, the potential may exist for accumulating (IDW) such as decontamination fluids, soil cuttings, and purge and well development waters, in a central staging area. Once these fluids and other materials have been characterized, they can be removed from this area and properly disposed.

9.2 POTENTIAL SPILL AREAS

Potential spill areas will be periodically monitored in an ongoing attempt to prevent and control further potential contamination of the environment. Currently, limited areas are vulnerable to this hazard including:

- Resource deployment
- Waste transfer
- Central staging

It is anticipated that all IDW generated as a result of this scope of work will be containerized, labeled, and staged to await further analyses. The results of these analyses will determine the method of disposal.

9.3 LEAK AND SPILL DETECTION

To establish an early detection of potential spills or leaks, a periodic walk-around by the personnel staging or disposing of drums or in the resource deployment area will be conducted during working hours to visually determine that storage vessels are not leaking. If a leak is detected, the contents will be transferred, using a hand pump, into a new vessel. The leak will be collected and contained using absorbents such as Oil-Dry, vermiculite, or sand, which are stored at the vulnerable areas in a conspicuously marked drum. This used material, too, will be containerized for disposal pending analysis. All inspections will be documented in the project logbook.

It is not anticipated that any cylinders or containers will be unearthed during site activities. Should a cylinder or container be uncovered, however, work will immediately be stopped and personnel will retreat to a safe area until directed by the FT or SSO.

9.4 PERSONNEL TRAINING AND SPILL PREVENTION

All personnel will be instructed in the procedures for incipient spill prevention, containment, and collection of hazardous materials in the site-specific training. The FT and the SSO will serve as the Spill Response Coordinators for this operation, should the need arise.

9.5 SPILL PREVENTION AND CONTAINMENT EQUIPMENT

The following represents the minimum equipment that may be maintained (depending on anticipated need) at the staging areas at all times for the purpose of supporting this Spill Prevention/Containment Program.

- Sand, clean fill, vermiculite, or other non combustible absorbent (Oil-dry)
- Drums (55-gallon U.S. DOT 17-E or 17-H)
- Shovels, rakes, and brooms

9.5.1 PPE for Spill Control

Minimal PPE for spill control will be employed as needed. These materials may include:

- Nitrile work and inner gloves
- Tyvek coveralls
- Hard Hat

- Steel toed shoes with neoprene boot covers

9.6 SPILL CONTROL PLAN

This section describes the procedures the Shaw field crewmembers will use upon the detection of a spill or leak.

1. Notify the SSO or FT immediately upon detection of a leak or spill. Activate emergency alerting procedures for that area to remove all non-essential personnel.

2. Use the personal protective equipment stored at the staging area. Take immediate actions to stop the leak or spill by plugging or patching the container or raising the leak to the highest point in the vessel. Spread the absorbent material in the area of the spill, covering it completely.

3. Transfer the material to a new vessel; collect and containerize the absorbent material. Label the new container appropriately. Await analyses for treatment and disposal options.

4. Re-containerize spills, including top cover impacted by the spill. Await test results for treatment or disposal options.

It is not anticipated that a spill will occur that the field crew cannot handle. Should this occur, notification of the appropriate Emergency Response agencies will be carried out by the FT or SSO in accordance with the procedures discussed in Section 2.0 of this HASP.

10.0 CONFINED-SPACE ENTRY

Personnel under the provisions of this HASP are not allowed, under any circumstances, to enter confined spaces. A confined space is defined as an area that has one or more of the following characteristics:

- Is large enough and so configured that an employee can bodily enter and perform assigned work.
- Has limited or restricted means for entry or exit (for example, tanks, manholes, sewers, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry).
- Is not designed for continuous employee occupancy.

Additionally, a Permit-Required Confined Space may also have one or more of the following characteristics:

- Contains or has a potential to contain a hazardous atmosphere.
- Has an internal configuration such that an entrant could be trapped or asphyxiated by inwardly caving walls or by a floor that slopes downward and tapers to a smaller cross-section.
- Contains any other recognized, serious, safety or health hazard.

For further information on confined space operations, consult the Health and Safety Guidance Manual or call the HSM. Any activity that may be considered a confined-space entry shall require modifications of this HASP and shall result in the immediate notification of the Project Health and Safety Officer. This determination shall be made by the FT and SSO.

11.0 MATERIALS AND DOCUMENTATION

The Shaw FT shall ensure the following materials/documents are taken to the project site and used when required.

- A complete copy of this HASP
- Health and Safety Guidance Manual
- Incident Reports
- Medical Data Sheets (multiple copies)
- Material Safety Data Sheets for all chemicals brought on site, including decon solutions, fuels, lime, sample preservatives, calibration gases, etc.
- A full-size OSHA Job Safety and Health Poster
- Training/Medical Surveillance Documentation Form (Blank) (multiple copies)
- Emergency Reference Information (Section 2.0, extra copy for posting)

11.1 MATERIALS TO BE POSTED OR MAINTAINED AT THE SITE

The following documentation is to be posted or maintained at the site for quick reference purposes. In situations where posting of these documents is not feasible (such as no office trailer), these documents should be filed in a transportable file container and immediately accessible. The file should remain in the FT's possession.

Chemical Inventory Listing (posted) - This list represents all chemicals brought on site, including decontamination solutions, sample preservatives, fuel, calibration gases, etc.. This list should be posted in a central area.

Material Safety Data Sheets (MSDSs) (maintained) - The MSDSs should also be in a central area accessible to all site personnel. These documents should match all the listings on the chemical inventory

list for all substances employed on site. It is acceptable to have these documents within a central folder and the chemical inventory as the table of contents.

The OSHA Job Safety & Health Protection Poster (posted) - This poster, as directed by 29 CFR 1903.2 (a)(1), should be conspicuously posted in places where notices to employees are normally posted. Each FT shall ensure that this poster is not defaced, altered, or covered by other material.

Site Clearance (maintained) - This is found within the training section of the HASP (See Figure 8-1). This list identifies all site personnel, dates of training (including site-specific training), and medical surveillance and indicates not only clearance but also status. If personnel do not meet these requirements, they do not enter the site while site personnel are engaged in activities.

Emergency Phone Numbers and Directions to the Hospital(s) (maintained) - This list of emergency numbers and hospital directions will be maintained at all phone communications points and in each site vehicle.

Medical Data Sheets/Cards (maintained) - Medical Data Sheets will be filled out by all onsite personnel and filed in a central location. The Medical Data Sheet will accompany any injury or illness requiring medical attention to the medical facility. A copy of this sheet or a wallet card will be given to all personnel to be carried on their person.

Investigative Derived Waste Inventory Log (maintained) – The FT and/or the SSO shall log collected containers of IDW. An updated inventory will be submitted to the Base POC at the termination of each shift.

12.0 GLOSSARY

ACGIH	American Conference of Governmental Industrial Hygienists
CFR	Code of Federal Regulations
CIH	Certified Industrial Hygienist
CNS	Central Nervous System
CO	Carbon Monoxide
CRZ	Contamination Reduction Zone
CSE	Confined Space Entry
CSP	Certified Safety Professional
CTO	Contract Task Order
DCA	Dichloroethane
DOD	Department of Defense
DOT	Department of Transportation
EPA	Environmental Protection Agency
eV	electron Volts
FID	Flame Ionization Detector
FT	Field Technician
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency Response
HSM	Health and Safety Manager
IDW	Investigative Derived Waste
LEL	Lower Explosive Limit
MDE	Maryland Department of Environment
MSDS	Material Safety Data Sheet
N/A	Not Available
NIOSH	National Institute Occupational Safety and Health
NO_2	Nitrogen Dioxide
O_2	Oxygen
OSHA	Occupational Safety and Health Administration (U.S. Department of Labor)
PE	Professional Engineer
PEL	Permissible Exposure Limit
PHSO	Project Health and Safety Officer
PID	Photo Ionization Detector
PM	Project Manager
PPE	Personal Protective Equipment
PVC	Poly Vinyl Chloride

SHAW	Shaw Environmental and Infrastructure
SCHASP	Shaw Corporate Health and Safety Plan
SOP	Standard Operating Procedure
SSO	Site Safety Officer
STEL	Short Term Exposure Limit
TBD	To Be Determined
TCE	Trichloroethylene
TPH	Total Petroleum Hydrocarbons
TWA	Time Weighted Average
UEL	Upper Explosive Limit
UST	Underground Storage Tank
UV	Ultraviolet

ATTACHMENT I

INJURY/ILLNESS PROCEDURE AND REPORT FORM

ATTACHMENT II

MEDICAL DATA SHEET

MEDICAL DATA SHEET

This Medical Data Sheet must be completed by all on-site personnel and kept in a central location during site operations. This sheet will accompany any personnel when medical assistance is needed or if transport to hospital facilities is required.

Project _____

Name _____ Home Telephone _____

Address _____

Age _____ Height _____ Weight _____

Name of Next Kin _____

Drug or other Allergies _____

Particular Sensitivities _____

Do You Wear Contacts? _____

Provide a Checklist of Previous Illnesses or Exposure to Hazardous Chemicals _____

_____

_____

What medications are you presently using? _____

_____

_____

Do you have any medical restrictions? _____

_____

_____

_____

Name, Address, and Phone Number of personal physician: _____

_____

_____ _____

Signature Date

ATTACHMENT III

SAFE WORK PERMITS

FIGURE 8-1

SAFE WORK PERMIT

Permit No. _____ Date: _____ Time: From _____ to _____

SECTION I: General Job Scope (To be filled in by person performing work)

I. Work limited to the following (description, area, equipment used): _____

II. Names: _____

III. Onsite Inspection conducted ☐ Yes ☐ No Initials of Inspector _____ _____
Envirogen

SECTION II: General Safety Requirements (To be filled in by permit issuer)

IV. Protective equipment required
Level D ☐ Level B ☐
Level C ☐ Level A ☐
Detailed on Reverse

Respiratory equipment required

Full face APR	☐ Escape Pack	☐
Half face APR	☐ SCBA	☐
SAR	☐ Bottle Trailer	☐
Skid Rig	☐ None	☐

Modifications/Exceptions: _____

V. Chemicals of Concern | Action Level(s) | Response Measures

VI. Additional Safety Equipment/Procedures

Hardhat	☐ Yes	☐ No	Hearing Protection (Plugs/Muffs)	☐ Yes	☐ No
Safety Glasses	☐ Yes	☐ No	Safety belt/harness	☐ Yes	☐ No
Chemical/splash goggles	☐ Yes	☐ No	Radio	☐ Yes	☐ No
Splash Shield	☐ Yes	☐ No	Barricades	☐ Yes	☐ No
Splash suits/coveralls	☐ Yes	☐ No	Gloves (Type)	☐ Yes	☐ No
Steel toe/shank Workboots	☐ Yes	☐ No	Work/rest regimen	☐ Yes	☐ No

Modifications/Exceptions: _____

VII. Procedure review with permit acceptors

	Yes	NA		Yes	NA
Safety shower/eyewash (Location & Use)	☐	☐	Emergency alarms	☐	☐
Procedure for safe job completion	☐	☐	Evacuation routes	☐	☐
Contractor tools/equipment inspected	☐	☐	Assembly points	☐	☐

VIII. Equipment Preparation

	Yes	No	NA
Utility Locating and Excavation Clearance completed	☐	☐	☐
Equipment and Foot Traffic Routes Cleared and Established	☐	☐	☐
Physical Hazards Barricaded and Isolated	☐	☐	☐
Emergency Equipment Staged	☐	☐	☐

IX. Additional Permits required (Hot work, confined space entry, excavation etc.). ☐ Yes ☐ No
If yes, fill out appropriate section(s) on safety work permit addendum

X. Special instructions, precautions: _____

Permit Issued by: _____ Permit Accepted by: _____
Job Completed by: _____ Date: _____

APPENDIX E:

Tracer Test and Modeling Results

Comparison of Field Tracer Data and Model Simulations

Flow Line Simulations

The following graphs provide a comparison with field tracer test data and AFIT model simulations. In field Tracer Test 1, 250 g of bromide was injected each day for 30 days into the u-HFTW, and both HFTWs were operated continuously at a net flow of ~ 6 GPM. The model simulation used the same net loading of bromide, but the simulated flow rate of the HFTWs was slightly higher (~ 7 GPM). The comparisons for this test and model simulation are provided in Figures E-1 to E-10.

In field Tracer Test 2, 250 g of bromide was injected each day for 15 days into the d-HFTW, and both HFTWs were operated continuously at a net flow of ~ 6 GPM. The model simulation used the same net loading of bromide over a 30 rather than a 15-day period and the simulated flow rate of the HFTWs was slightly higher (~ 7 GPM). The comparisons for this test and model simulation are provided in Figures E-11 to E-20.

Comparison of Field Tracer Data and Model Simulations from Tracer Test 1 (Tracer Added to u-HFTW)

Figure E-1. Bromide Concentrations in Wells 3519 and 4440 during Tracer Test 1.

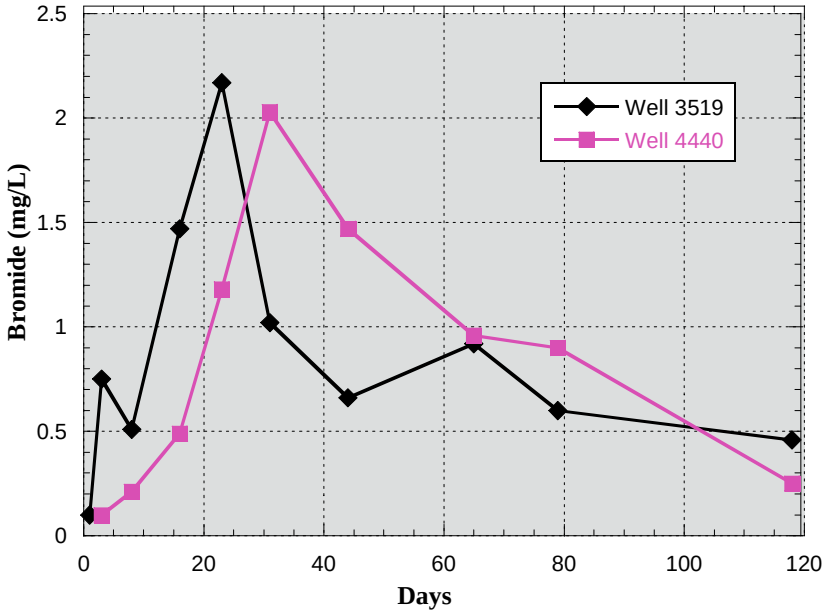


Figure E-2. Model Simulation of Bromide Concentrations in Wells 3519 and 4440. The two symbols for Well 4440 depict simulations at two different screen intervals as this pre-existing well was screened at two depths.

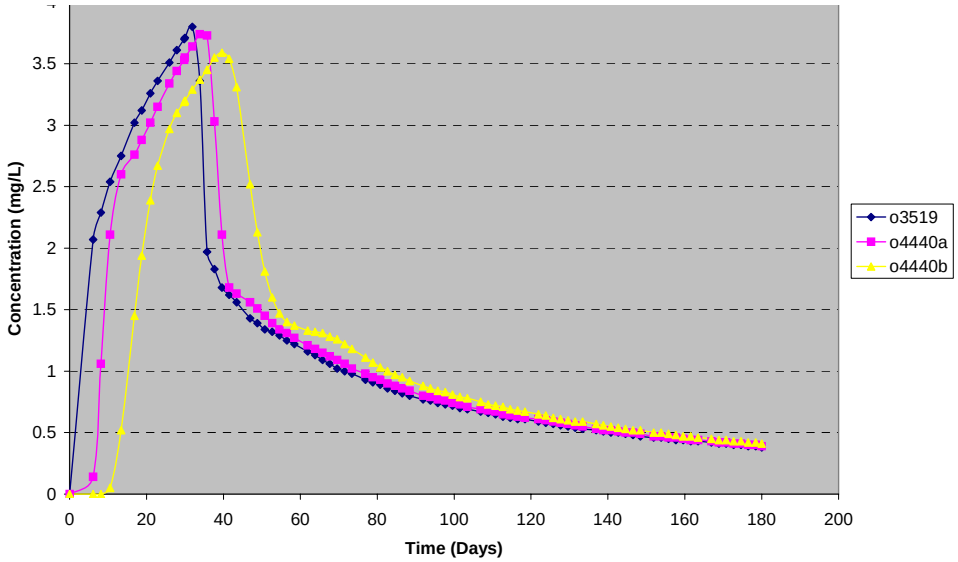


Figure E-3. Bromide Concentrations in Shallow Monitoring Wells NMW-3, NMW-5, NMW-7, NMW-9, and upgradient Well NMW-1 during Tracer Test 1.

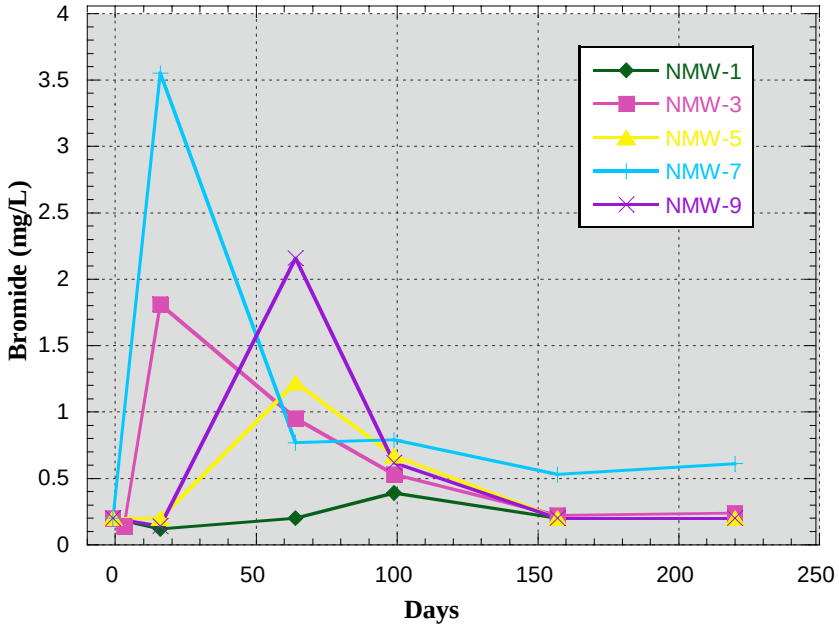


Figure E-4. Model Simulation of Bromide Concentrations in Shallow Monitoring Wells NMW-3, NMW-5, NMW-7, NMW-9, and Upgradient Well NMW-1.

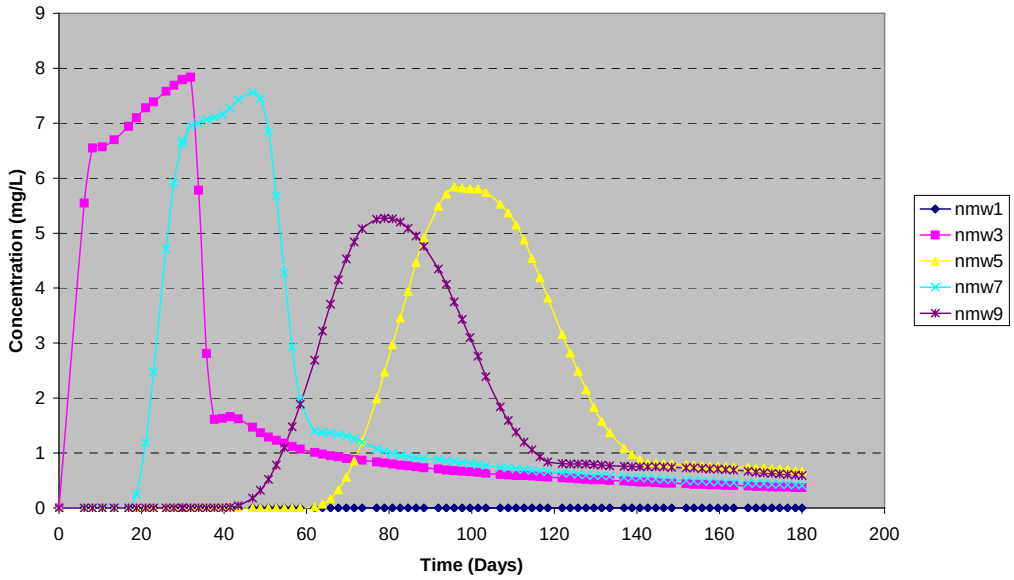


Figure E-5. Bromide Concentrations in Monitoring Wells 3628-3633 during Tracer Test 1.

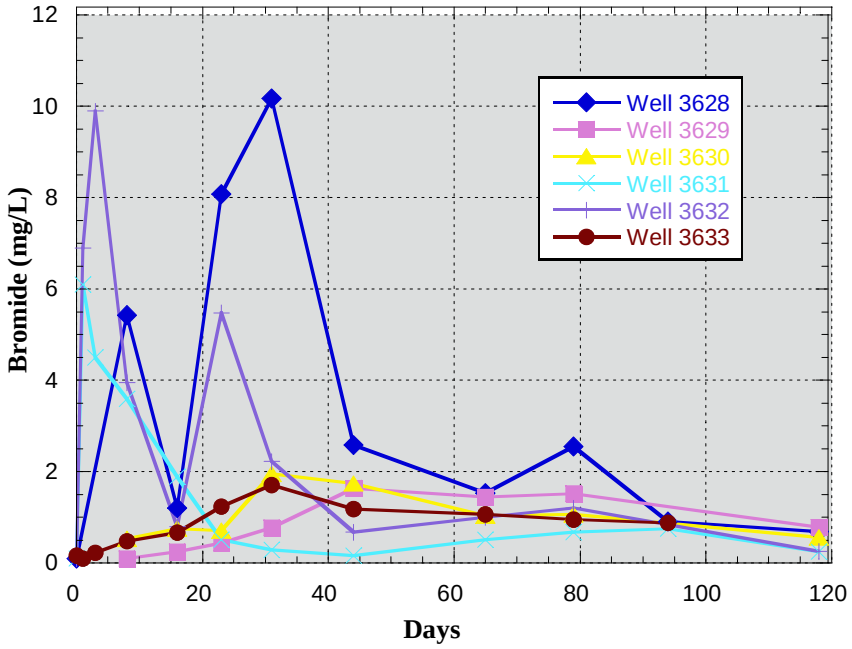


Figure E-6. Model Simulation of Bromide Concentrations in Monitoring Wells 3628-3633.

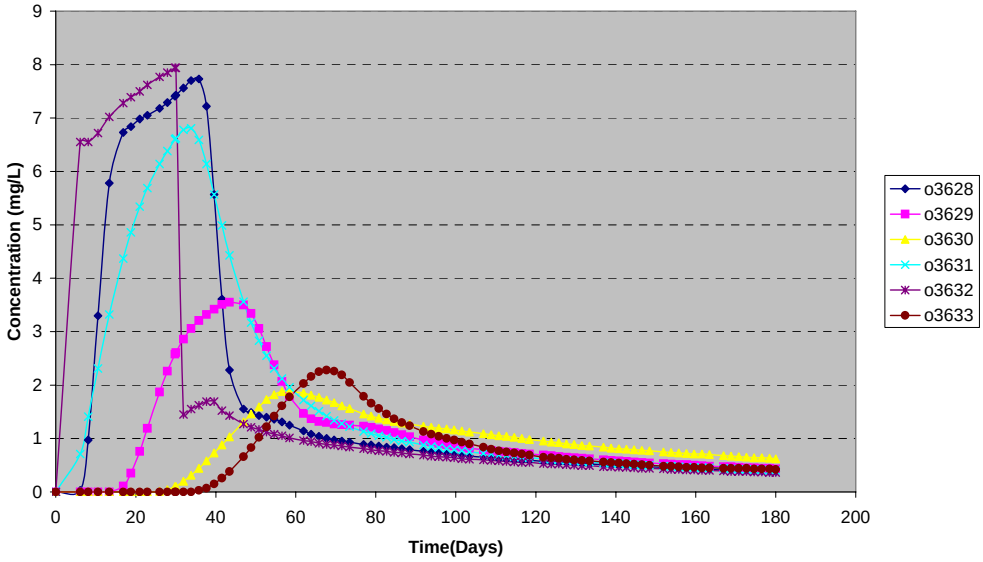


Figure E-7. Bromide Concentrations in Deep Monitoring Wells NMW-4, NMW-8, NMW-10, and Upgradient Well NMW-2 during Tracer Test 1.

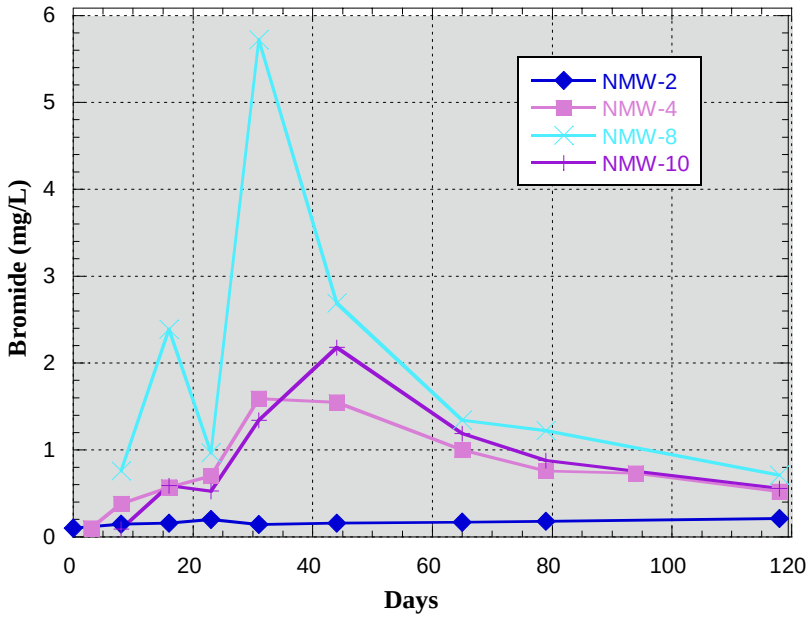


Figure E-8. Model Simulation of Bromide Concentrations in Deep Monitoring Wells, NMW-4, NMW-8, NMW-10, and Upgradient Well NMW-2. Note that Well NMW-6 was not installed.

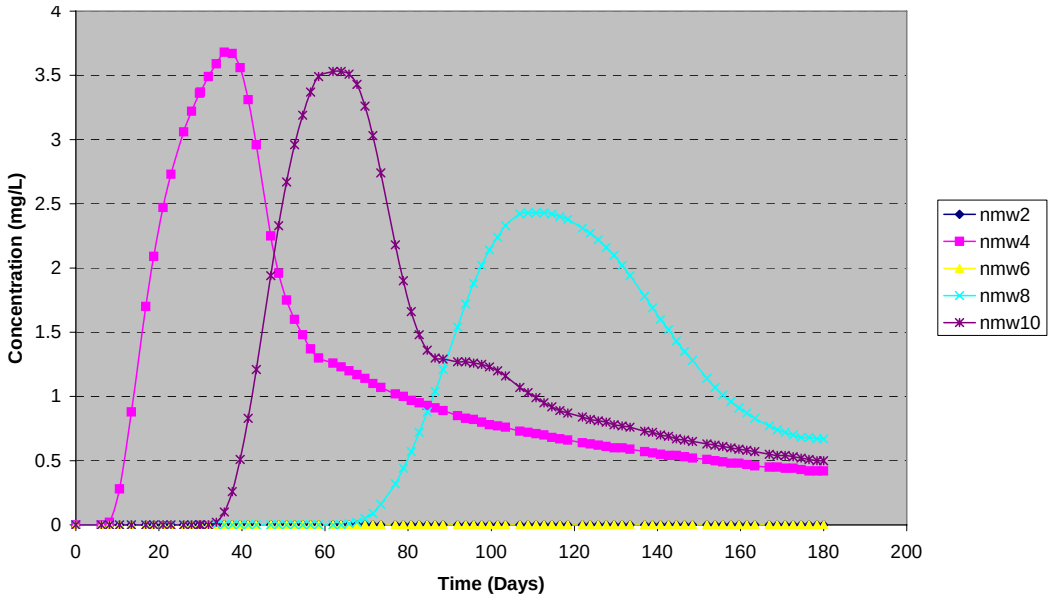


Figure E-9. Bromide Concentrations in Far Downgradient Monitoring Wells 3514 and 3627 during Tracer Test 1.

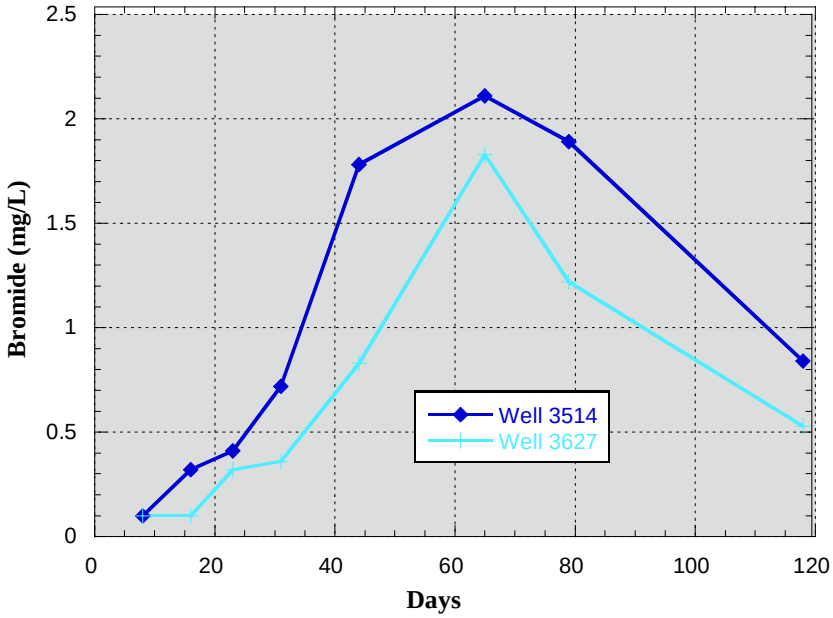
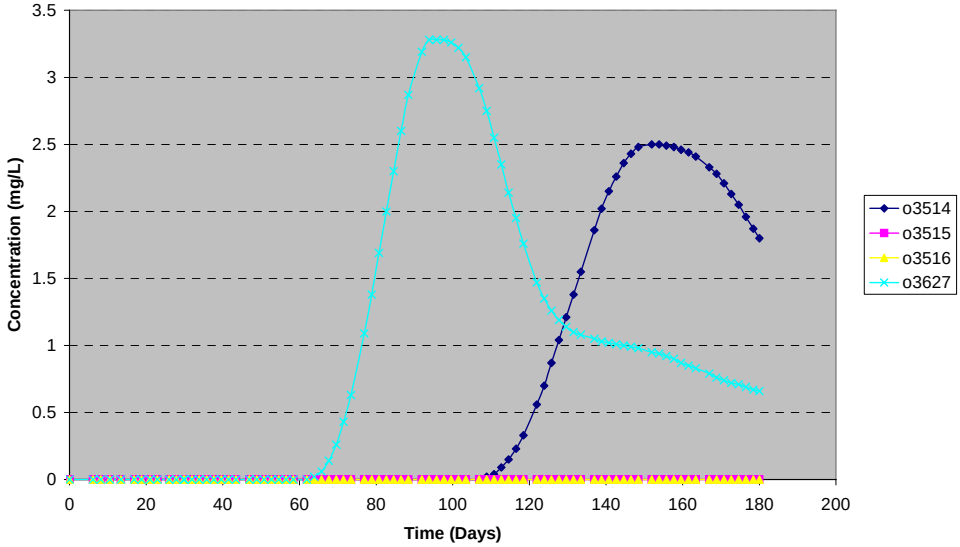


Figure E-10. Model Simulation of Bromide Concentrations in Far Downgradient Monitoring Wells 3514 and 3627. Wells 3515 and 3516 were not samples due to screen depth.



Comparison of Field Tracer Data and Model Simulations from Tracer Test 2 (Tracer Added to d-HFTW)

Figure E-11. Bromide Concentrations in Wells 3519 and 4440 during Tracer Test 2.

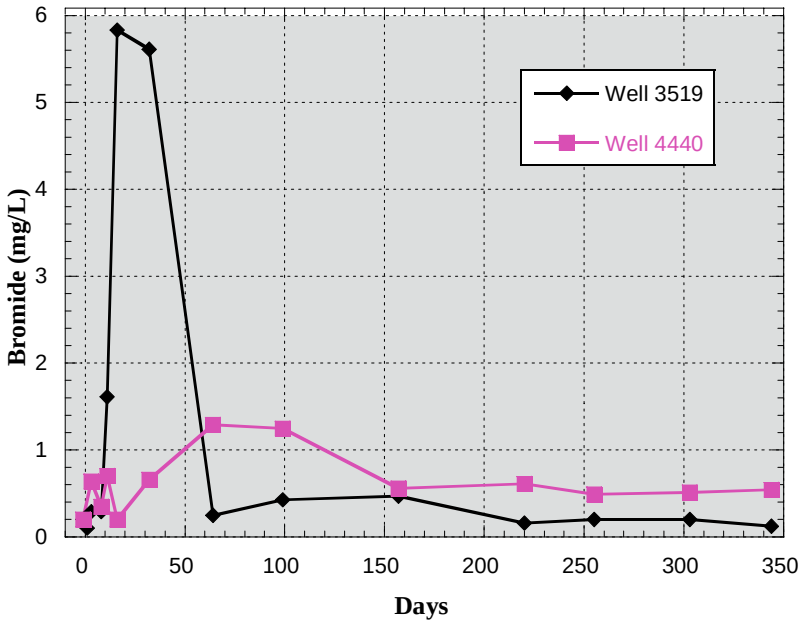


Figure E-12. Model Simulation of Bromide Concentrations in Wells 3519 and 4440. The two symbols for Well 4440 depict simulations at two different screen intervals as this pre-existing well was screened at two depths.

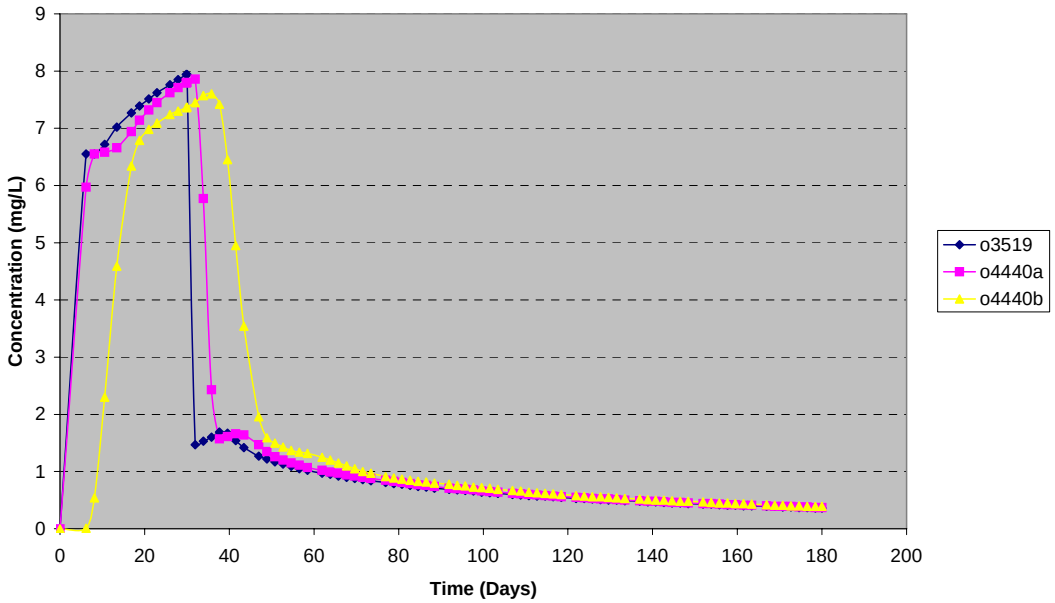


Figure E-13. Bromide Concentrations in Shallow Monitoring Wells NMW-3, NMW-5, NMW-7, NMW-9, and upgradient Well NMW-1 during Tracer Test 2.

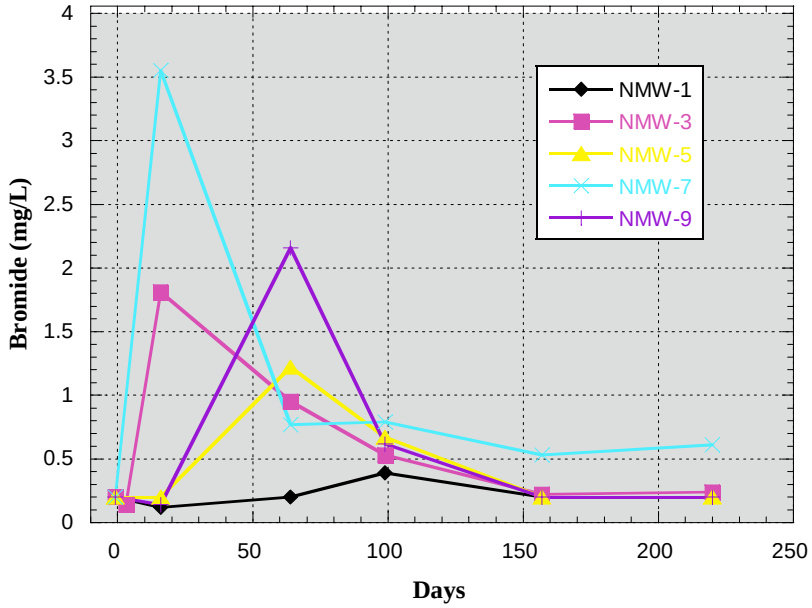


Figure E-14. Model Simulation of Bromide Concentrations in Shallow Monitoring Wells NMW-3, NMW-5, NMW-7, NMW-9, and Upgradient Well NMW-1.

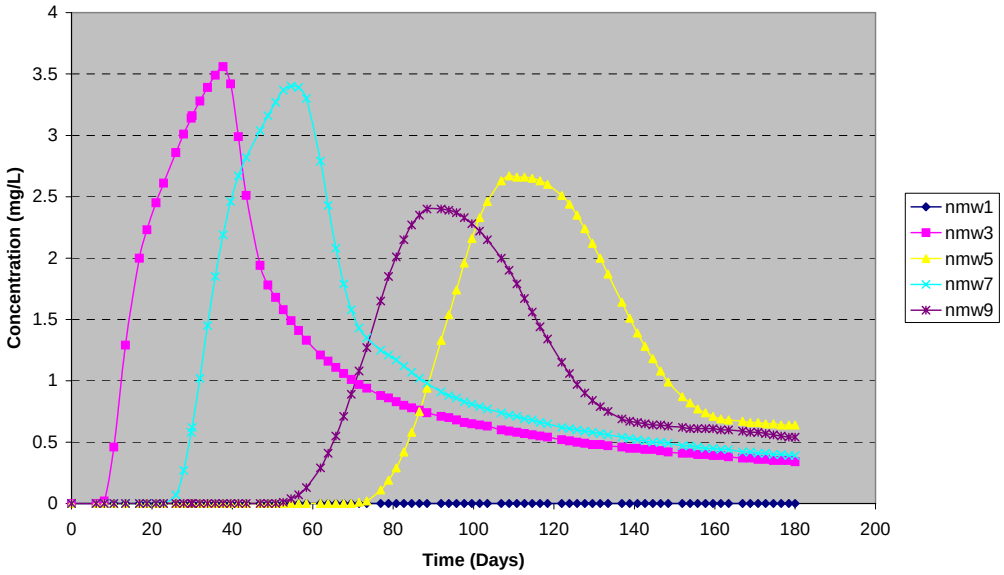


Figure E-15. Bromide Concentrations in Monitoring Wells 3628-3633 during Tracer Test 2.

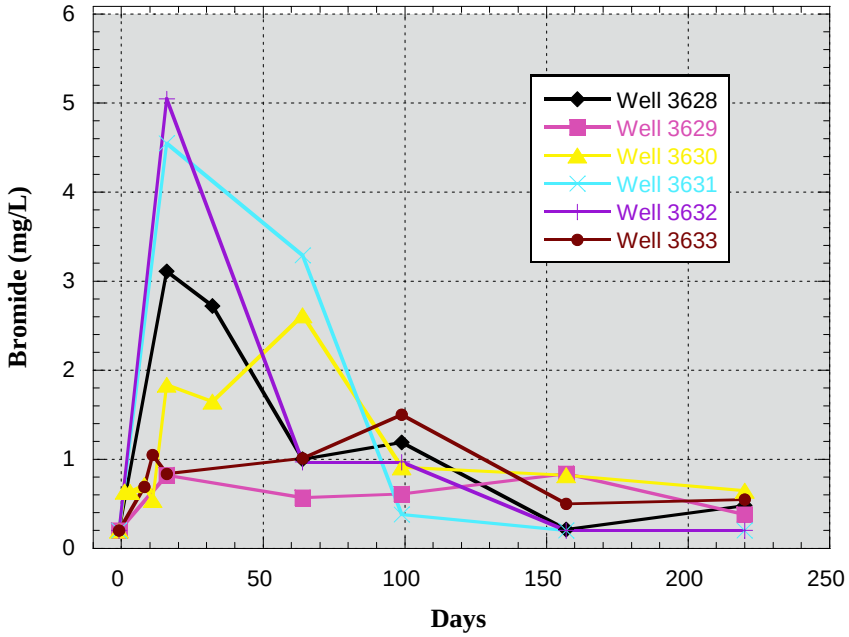


Figure E-16. Model Simulation of Bromide Concentrations in Monitoring Wells 3628-3633.

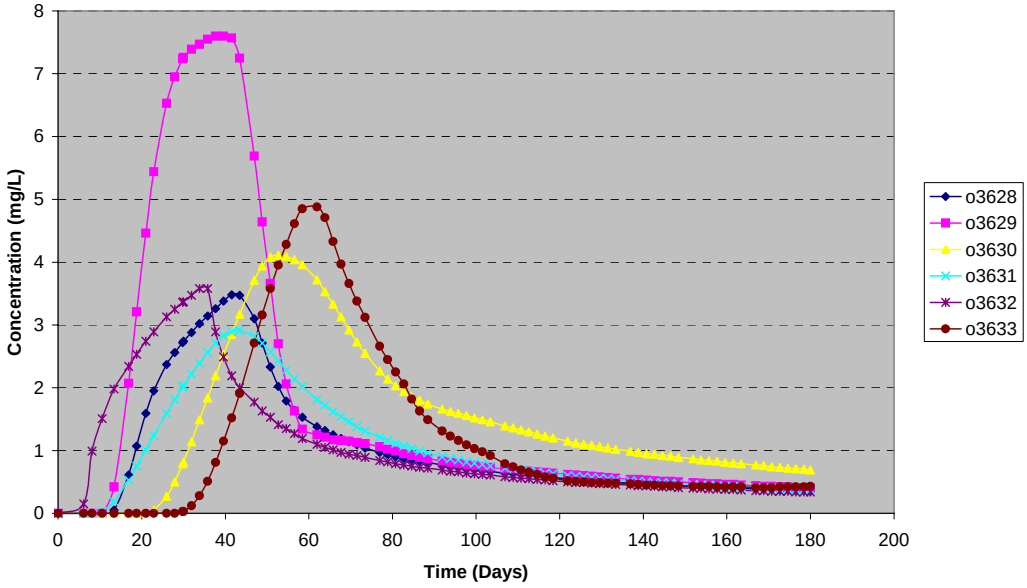


Figure E-17. Bromide Concentrations in Deep Monitoring Wells NMW-4, NMW-8, NMW-10, and Upgradient Well NMW-2 during Tracer Test 2.

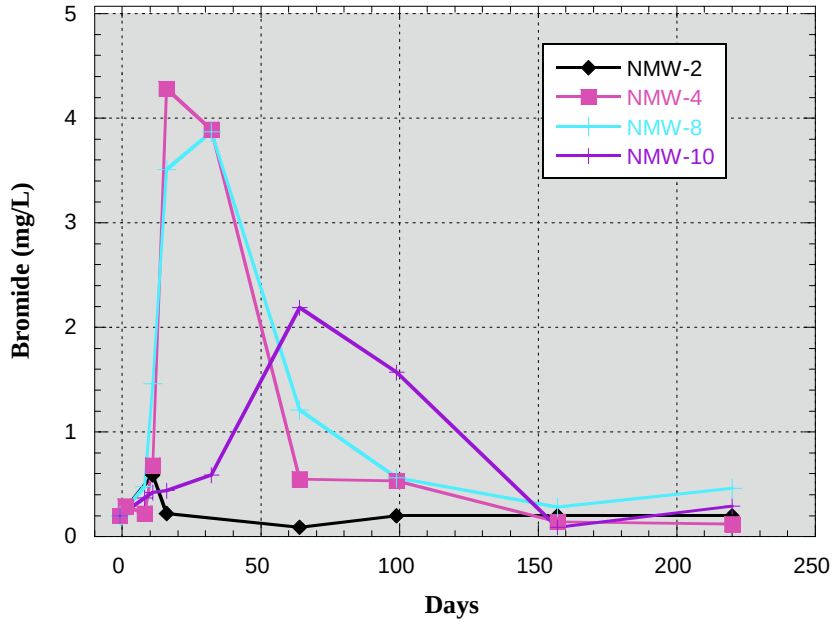


Figure E-18. Model Simulation of Bromide Concentrations in Deep Monitoring Wells, NMW-4, NMW-8, NMW-10, and Upgradient Well NMW-2. Note that Well NMW-6 was not installed.

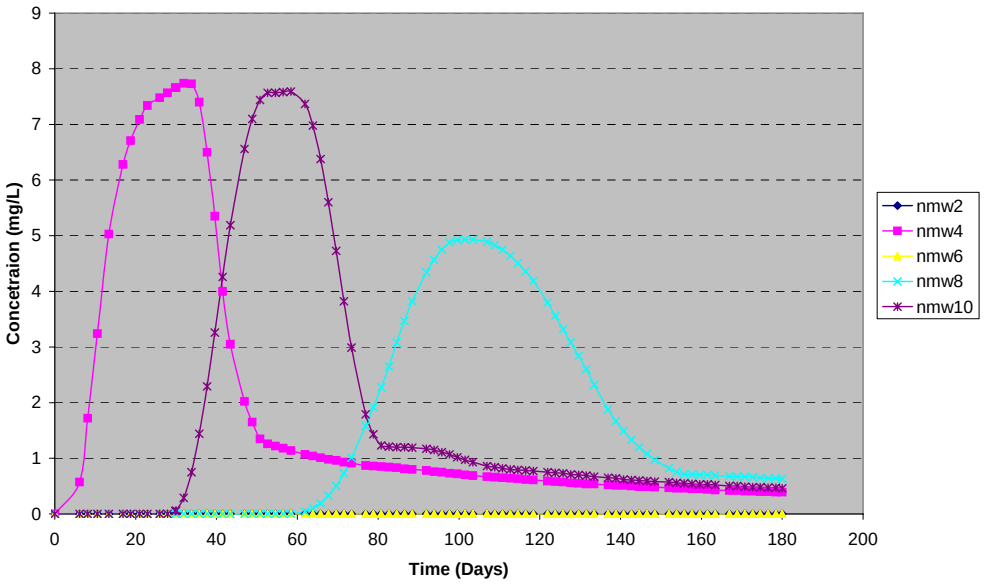


Figure E-19. Bromide Concentrations in Far Downgradient Monitoring Wells 3514 and 3627 during Tracer Test 2.

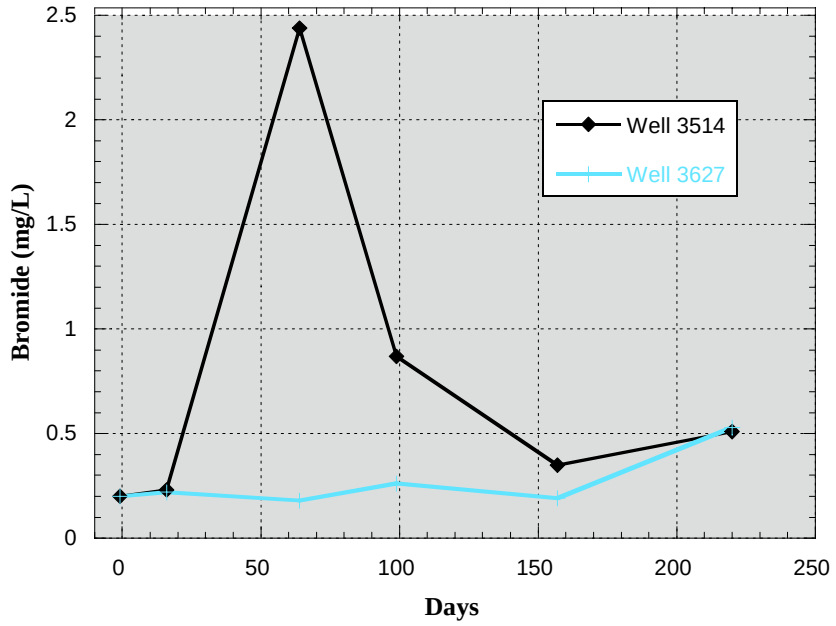
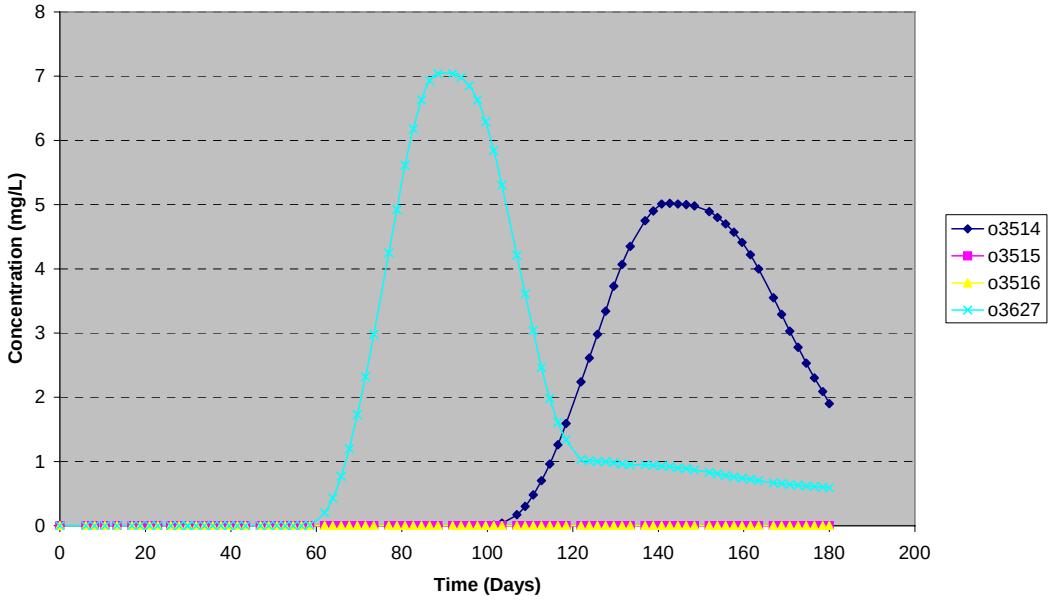


Figure E-20. Model Simulation of Bromide Concentrations in Far Downgradient Monitoring Wells 3514 and 3627. Wells 3515 and 3516 were not samples due to screen depth.



Flow Line Simulations

The flow simulations assume that the HFTWs are screened across layers 2-4 & 7-9 (46-61 ft & 80-100 ft as constructed). The modeled flow is 7 GPM per well.

Figure E-21. Plan View of Demonstration site used in Model Simulations.

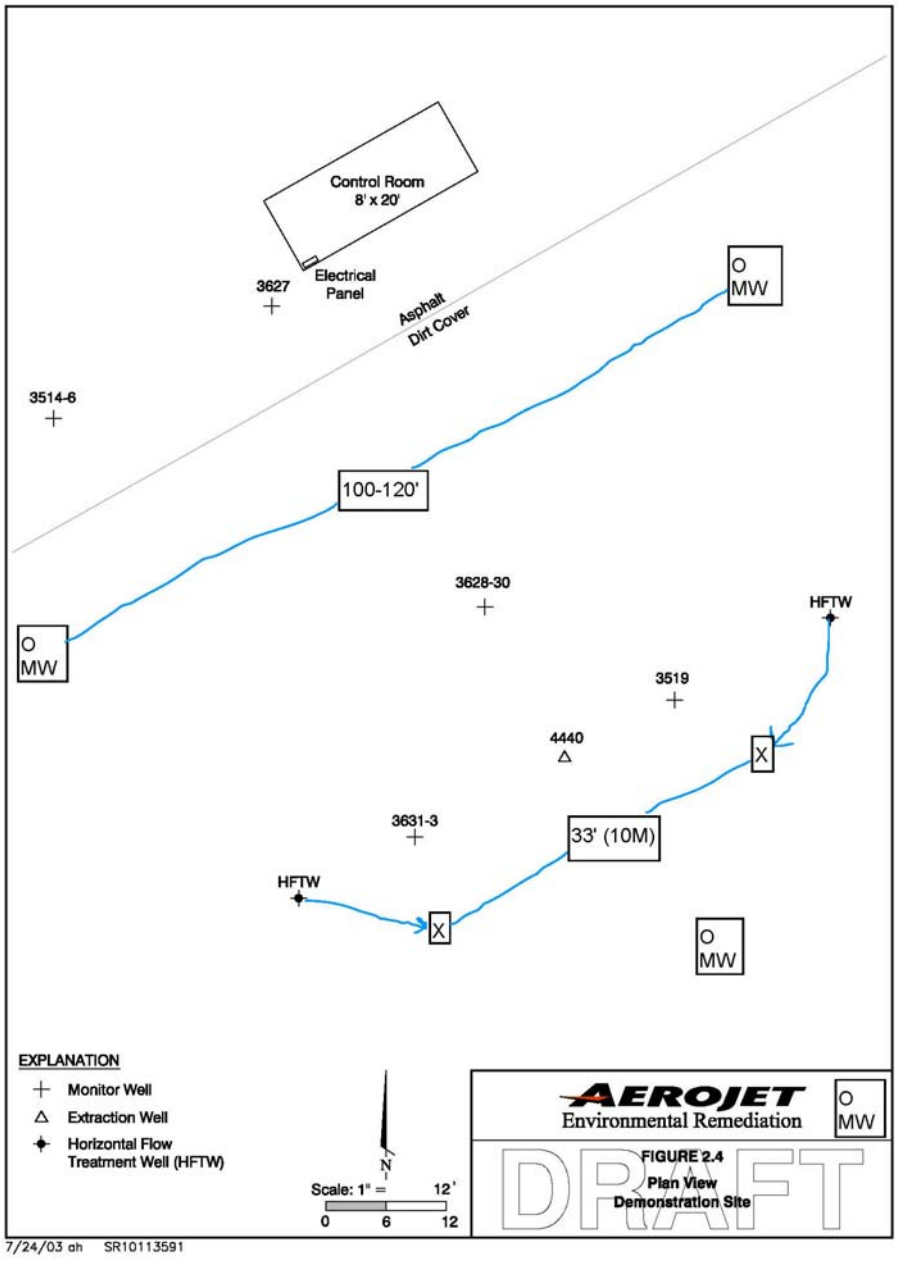


Figure E-22. HFTW Screen Intervals used in Model Simulations

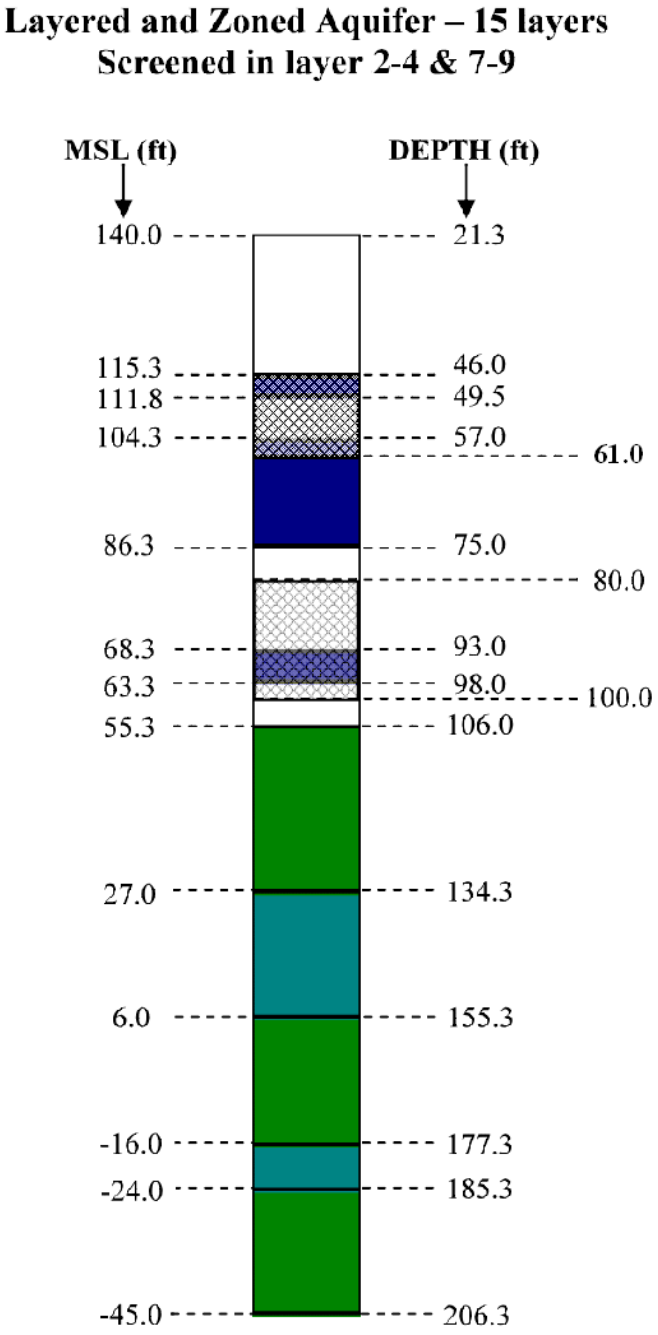
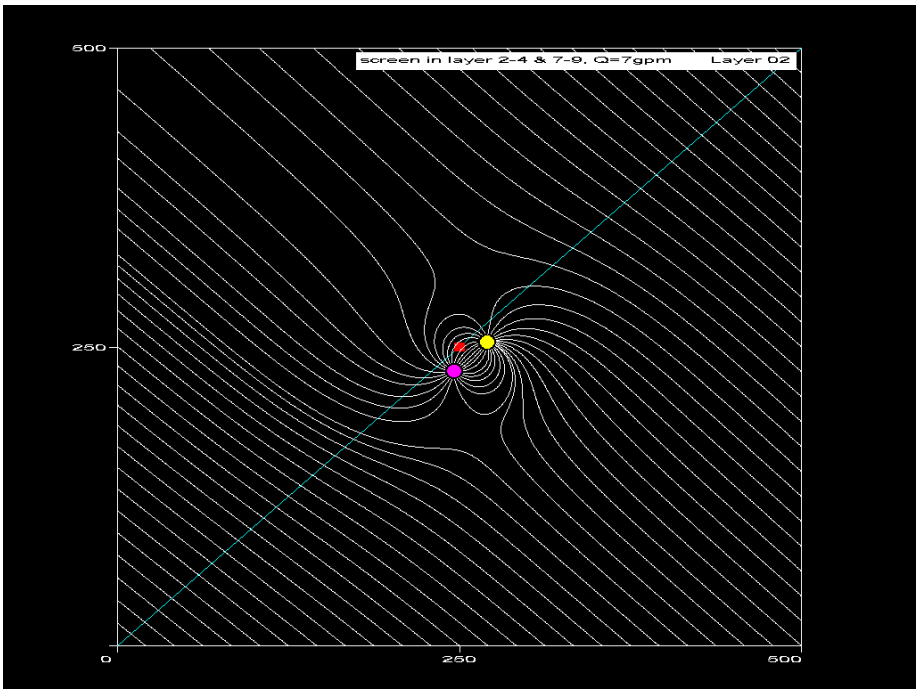


Figure E-23. Streamline Plan View in Layers 1&2. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



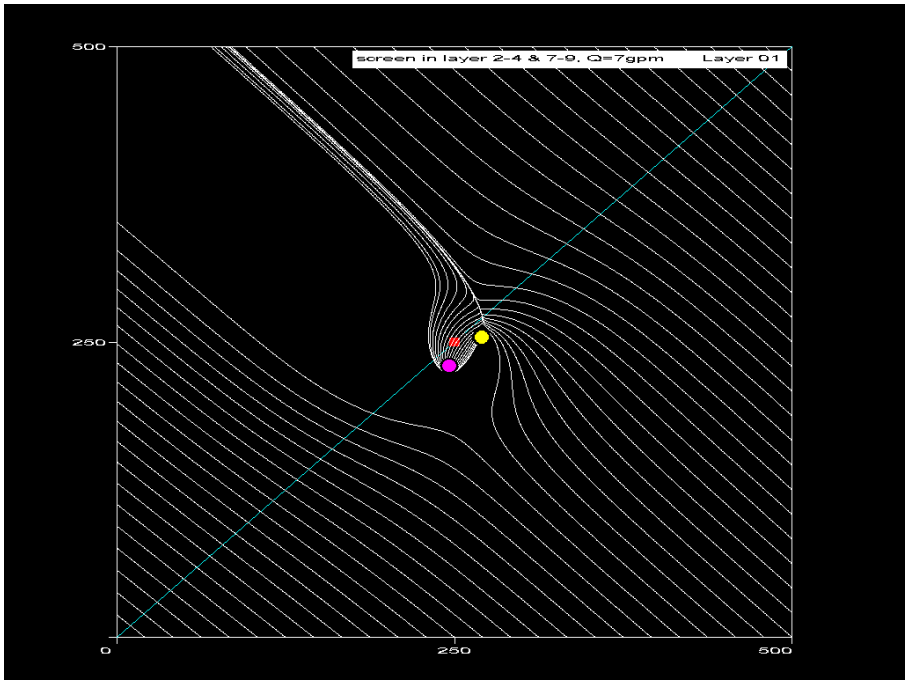
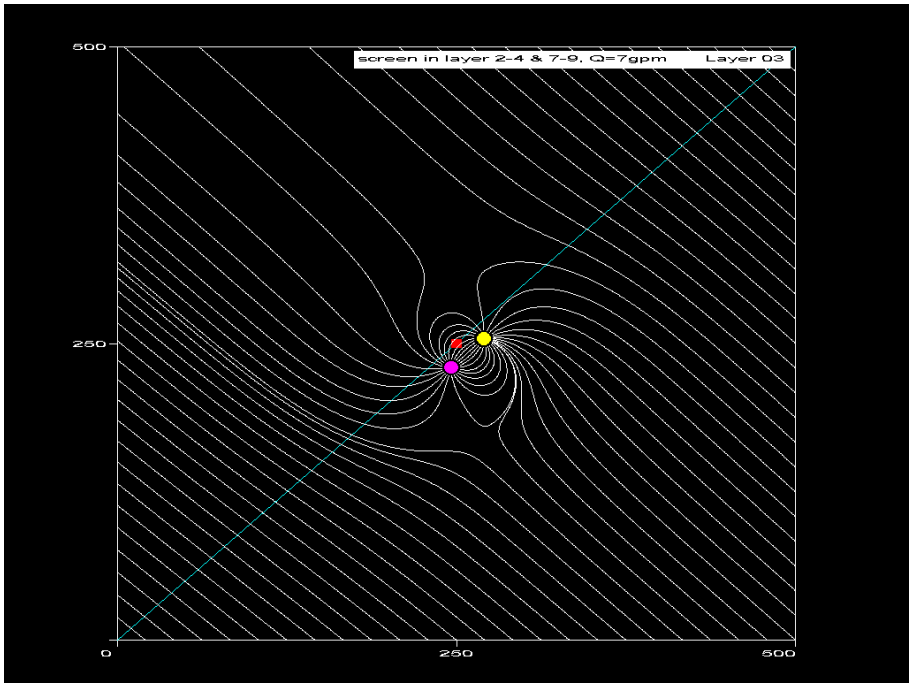


Figure E-24. Streamline Plan View in Layers 3&4. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



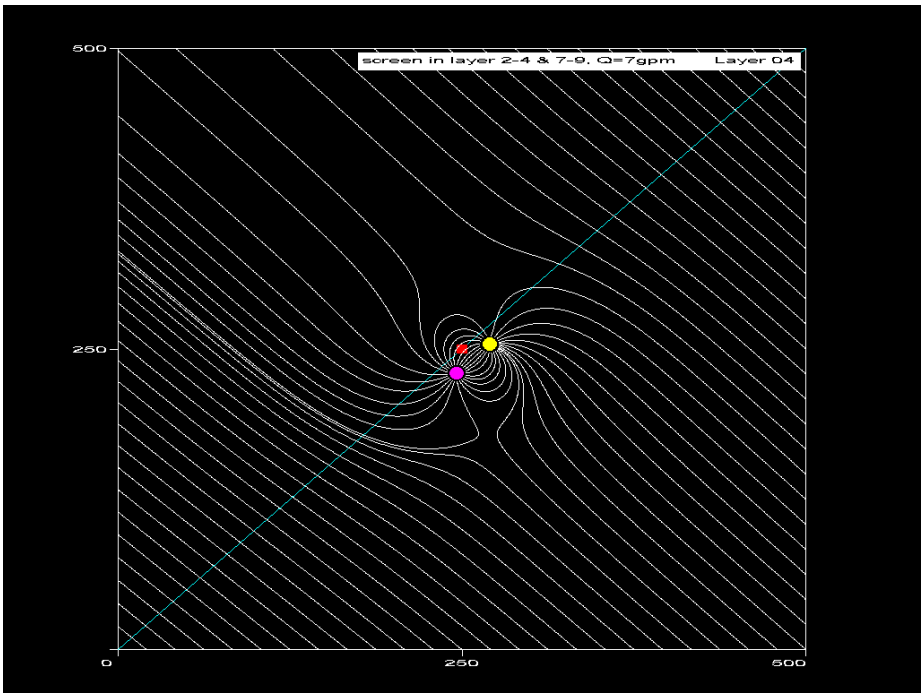
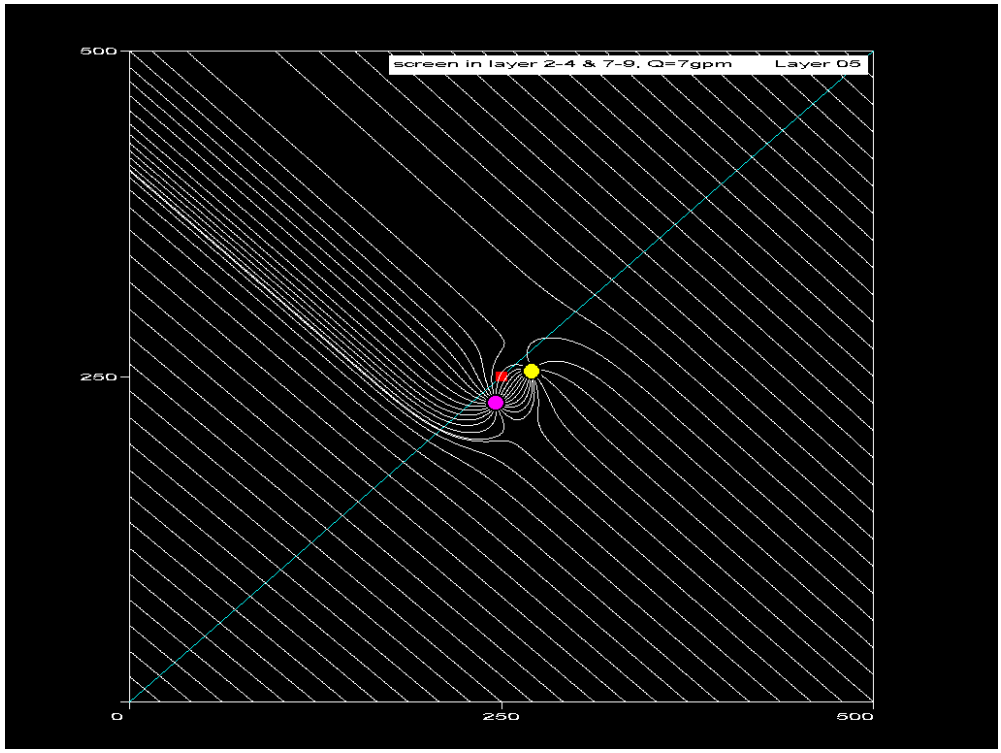


Figure E-25. Streamline Plan View in Layers 5&6. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



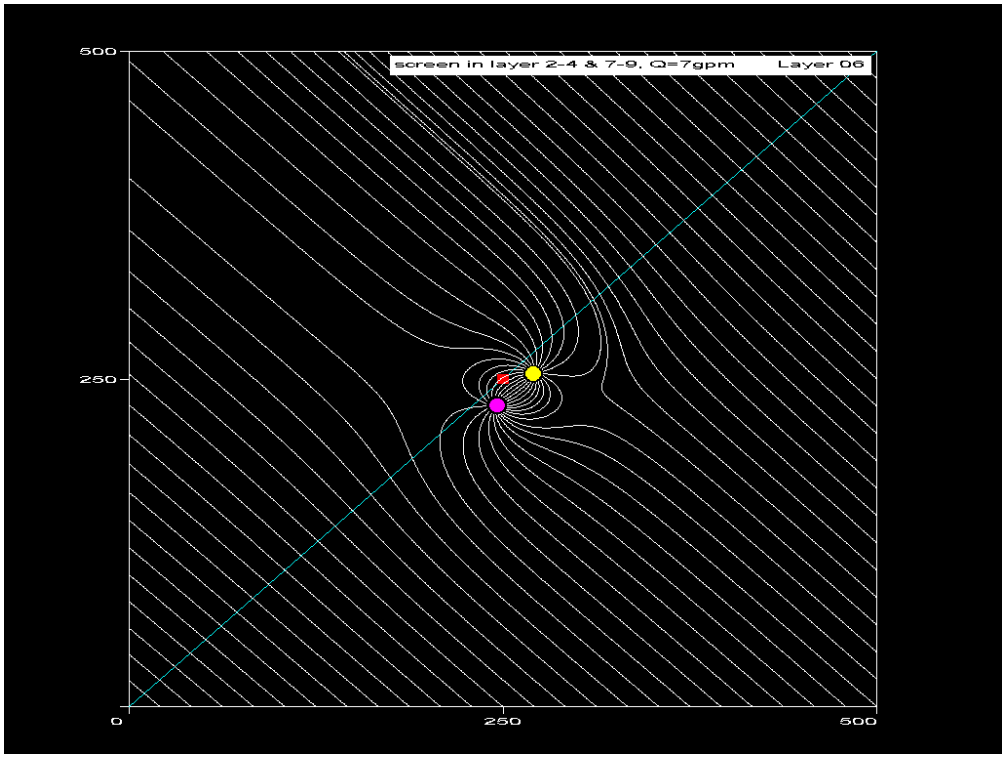
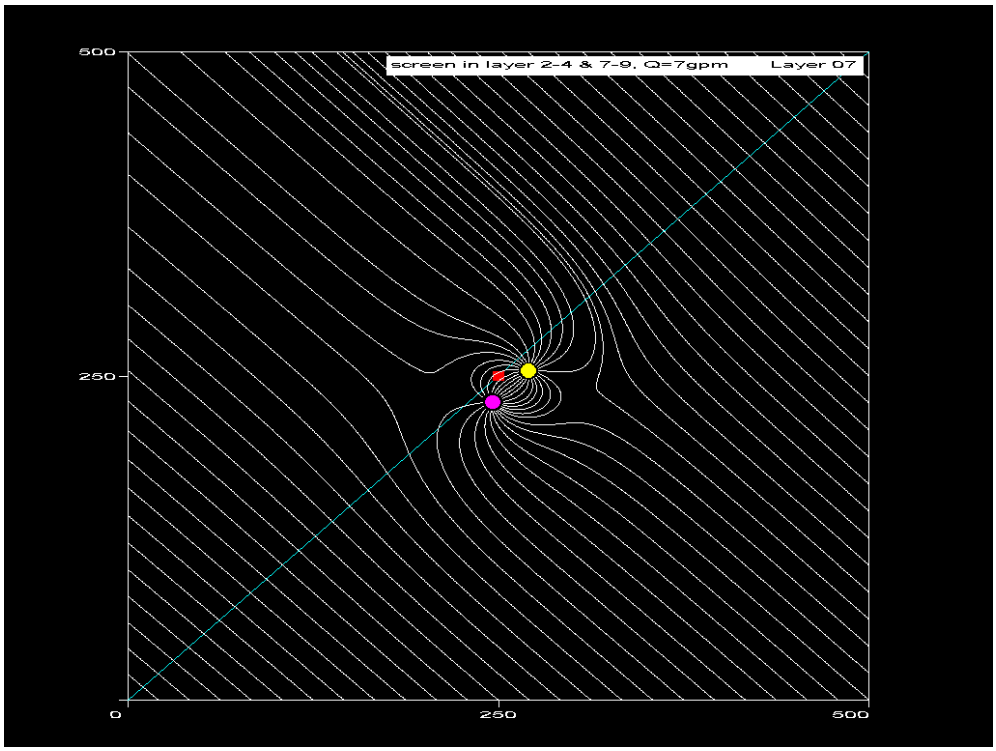


Figure E-26. Streamline Plan View in Layers 7&8. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



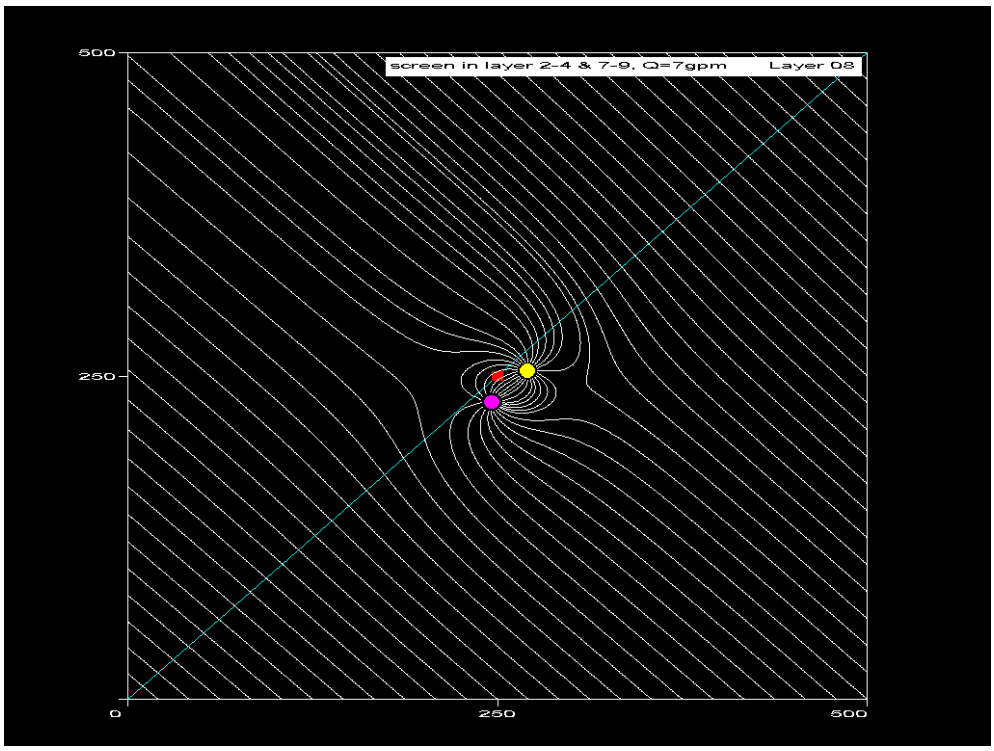
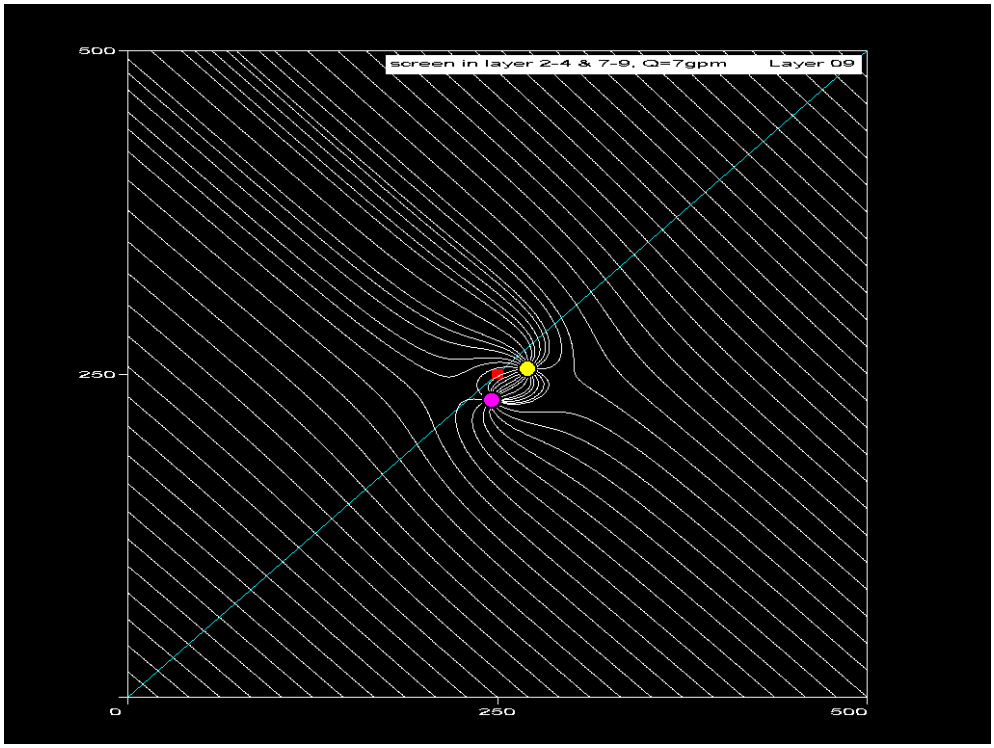


Figure E-27. Streamline Plan View in Layers 9&10. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



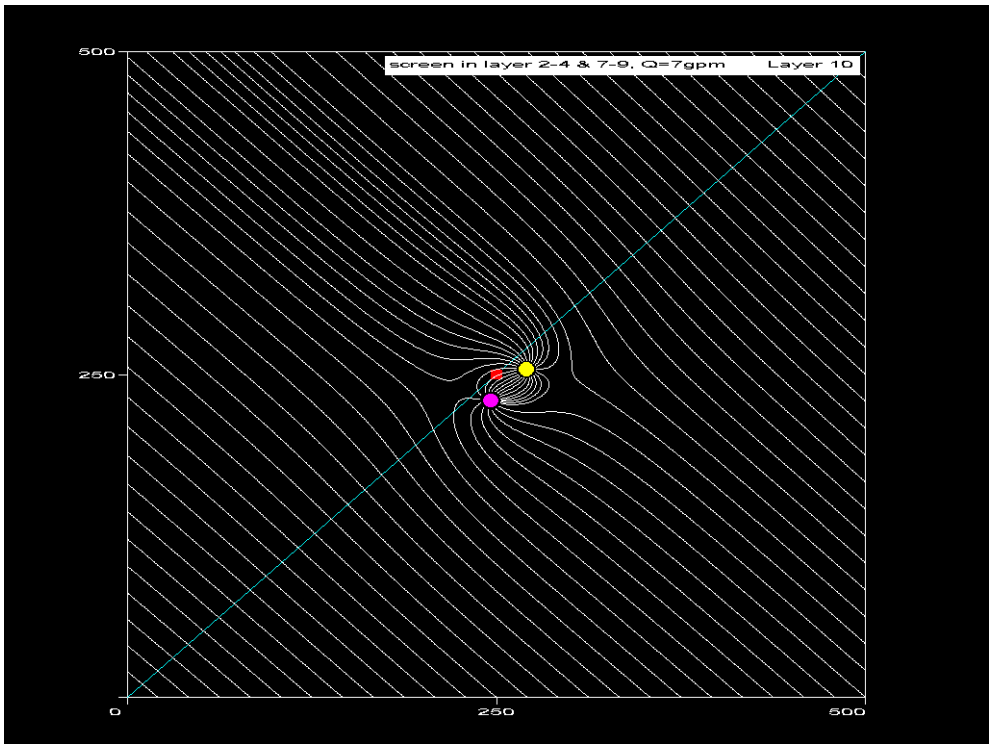
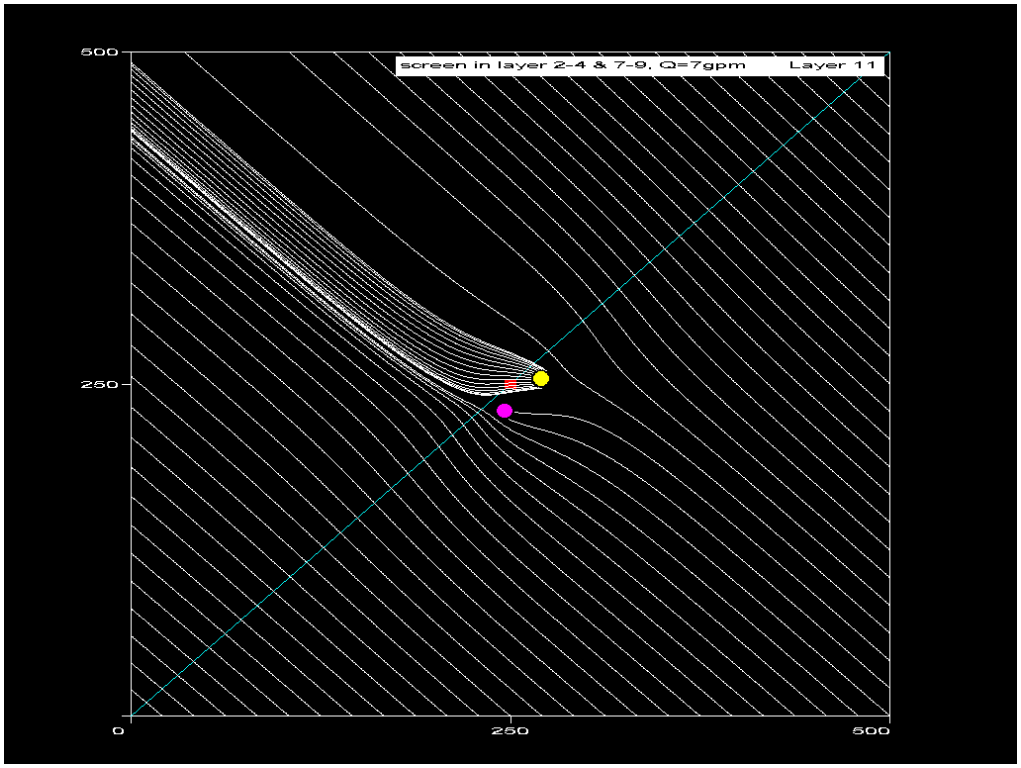


Figure E-28. Streamline Plan View in Layers 11&12. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



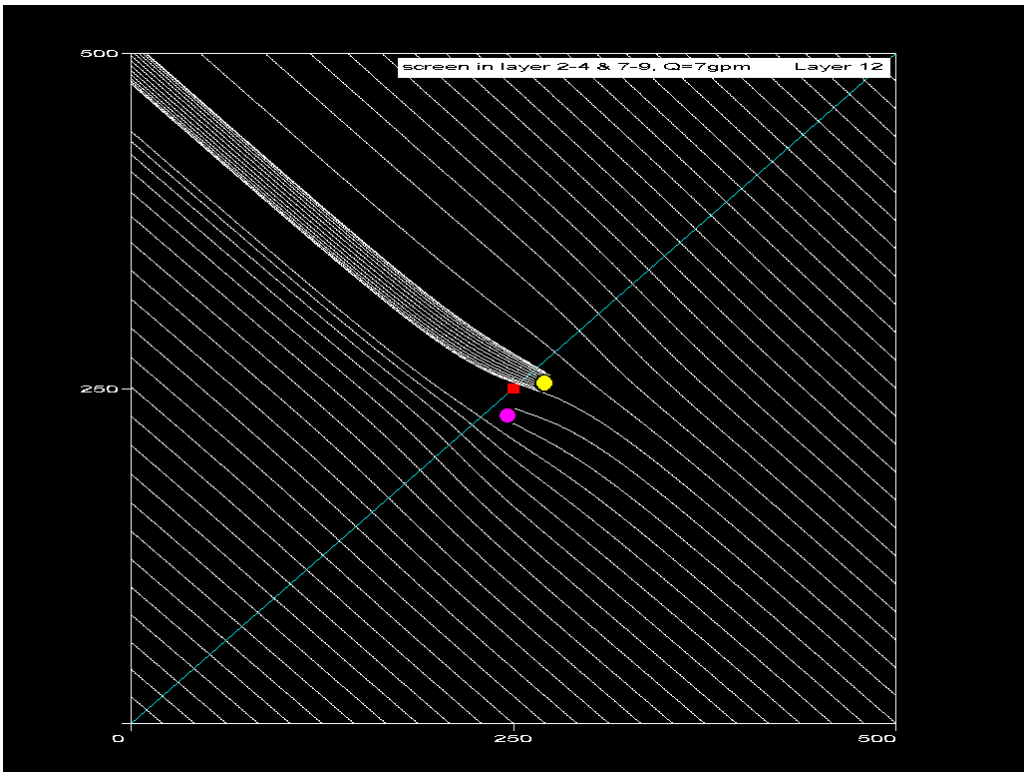


Figure E-29. Streamline Plan View in Layers 13&14. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.

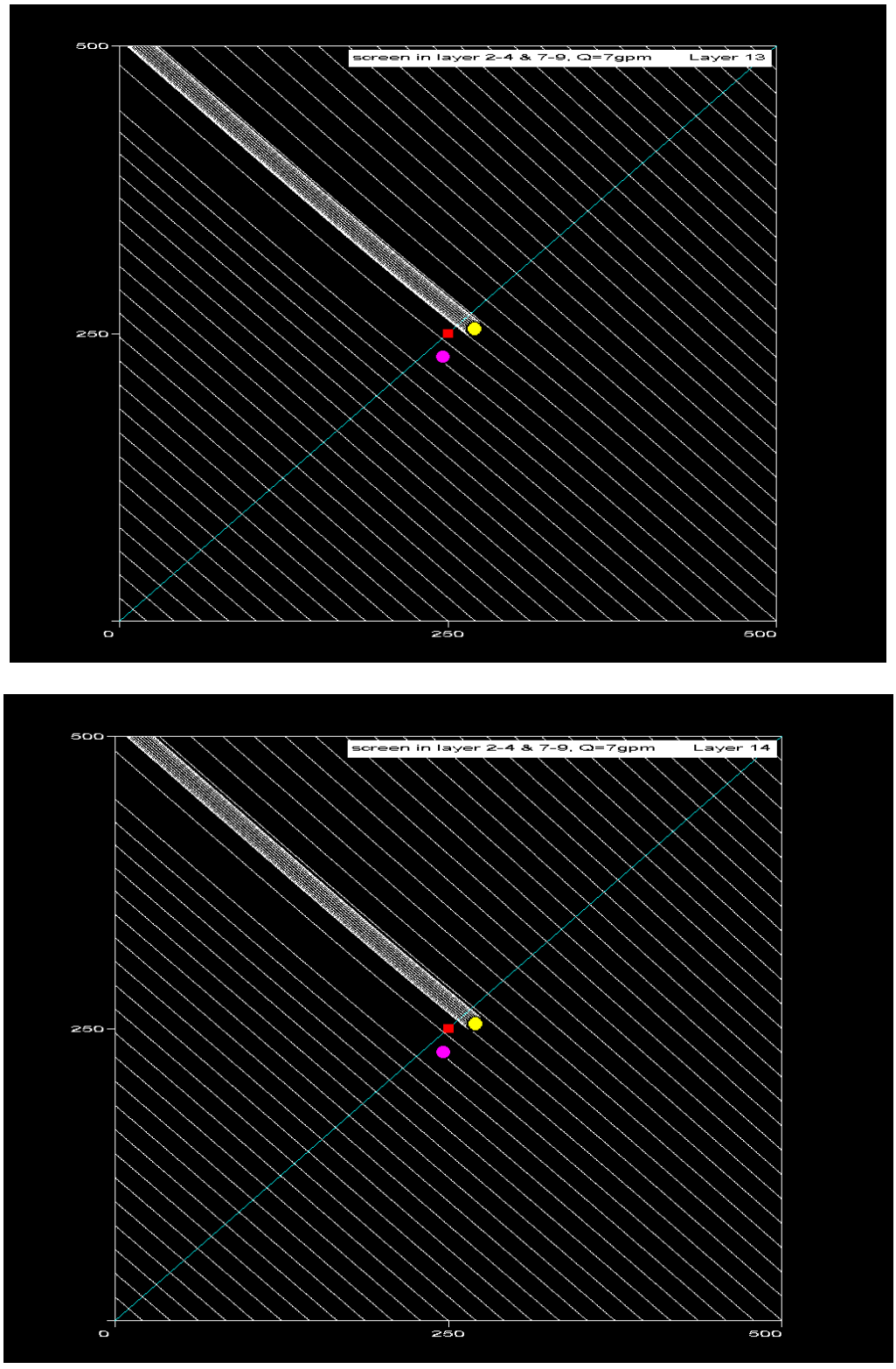
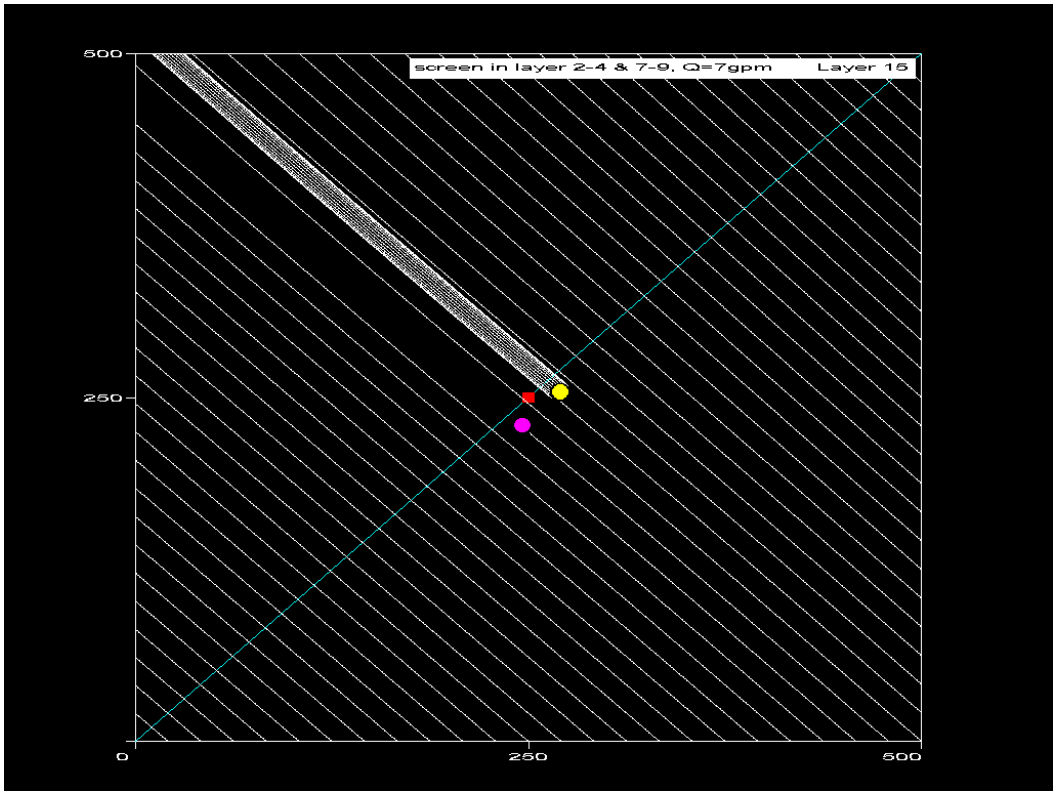


Figure E-30. Streamline Plan View in Layer 15. Scale is in ft and the layer designation is provided at the top right hand corner of each simulation.



APPENDIX F:

Modeling In Situ Bioremediation of Perchlorate-Contaminated Groundwater

M.S. Thesis by R.E. Secody at AFIT

MODELING *IN SITU* BIOREMEDITION OF PERCHLORATE-CONTAMINATED GROUNDWATER

THESIS

Roland E. Secody, Major, USAF
AFIT/GEM/ENV/07-M13

DEPARTMENT OF THE AIR FORCE
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AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the United States Government.

AFIT/GEM/ENV/07-M13

MODELING *IN SITU* BIOREMEDIATION OF PERCHLORATE-CONTAMINATED GROUNDWATER

THESIS

Presented to the Faculty

Department of Systems and Engineering Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering and Environmental Management

Roland E. Secody, BS

Major, USAF

March 2007

AFIT/GEM/ENV/07-M13

MODELING *IN SITU* BIOREMEDIATION OF PERCHLORATE-CONTAMINATED GROUNDWATER

Roland E. Secody, BS
Major, USAF

Approved:

_____//Signed//_____	__16 March 07__
Dr. Mark N. Goltz (Chairman)	date
_____//Signed//_____	__16 March 07__
Dr. Jungi Huang (Member)	date
_____//Signed//_____	__16 March 07__
Maj Jeffrey Heiderscheidt, PhD. (Member)	date

AFIT/GEM/ENV/07-M13

Abstract

Perchlorate-contaminated groundwater is a significant problem for the Department of Defense and the United States Air Force. An innovative technology was recently developed which uses dual-screened treatment wells to mix an electron donor into perchlorate-contaminated groundwater in order to effect *in situ* bioremediation of the perchlorate by indigenous perchlorate reducing bacteria without the need to extract the contaminated water from the subsurface. In this study, a model that simulates operation of the technology is calibrated and validated using 761 days of observational data obtained from a field-scale technology evaluation project. A genetic algorithm was used with the first 113 days of data to derive a set of best-fit parameters to describe perchlorate reduction kinetics for the electron donor, citrate, utilized in the evaluation study. The calibrated parameter values were then used to predict technology performance from day 114 through day 761. Measurements of goodness-of-fit statistics indicate the model appears to qualitatively reproduce the salient characteristics of the observed data when utilizing the new best-fit parameter values. Therefore, it appears the model may be a useful tool for designing and operating this technology at other perchlorate-contaminated sites.

Acknowledgements

There are many individuals I would like to thank for the support they've provided as I've worked to complete this thesis. First, I want to thank my wife and daughter for their love, encouragement and patience as I toiled away on the computer working on this thesis. I also owe my sincere gratitude and thanks to Dr. Goltz, whose guidance was incalculable in making this an enjoyable learning experience. Dr. Huang spent numerous hours with me going over the nuances of GMS, genetic algorithms and learning how to use the High Performance Computing Shared Resource Center. Maj. Heiderscheidt was a great resource while getting up and running on GMS and provided valuable insight into modeling. And finally, a gracious word of thanks to all the individuals involved in the ESTCP *In situ* Bioremediation of Perchlorate in Groundwater (ER-0224) Project. For, without their hard work and expertise, none of this would have been possible.

Roland Secody

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MODELING *IN SITU* BIOREMEDIATION OF
PERCHLORATE-CONTAMINATED GROUNDWATER

1.0 INTRODUCTION

1.1 MOTIVATION

The Safe Drinking Water Act (SDWA) serves to protect public health by regulating the nation's public drinking water supplies. The Act authorizes the Environmental Protection Agency (EPA) to set national health-based standards for drinking water to protect against both naturally-occurring and man-made contaminants. The EPA currently regulates over 90 contaminants which may be found in drinking water and also establishes a Contaminant Candidate List (CCL) to identify and list unregulated contaminants which may require future regulation (EPA, 2006). Perchlorate (ClO_4^-) salts have been used in solid rocket fuels, highway safety flares, air bag inflators, fireworks and matches (Trumpolt, 2005) and were first listed on the EPA's CCL in 1998 (EPA, 1998). The EPA uses the Unregulated Contaminant Monitoring Regulation (UCMR) program to collect data for contaminants suspected to be present in drinking water, but that do not have health-based standards established. Since its first listing on the CCL, the EPA reports that 152 public water systems in 35 states have tested positive for perchlorate in water, with over 11 million people exposed to perchlorate at concentrations of 4 ppb (4μg/L) or higher (EPA 2005; NRC 2005). Reported instances of perchlorate detection are indicated on the map in Figure 1.1. It is likely that the extent of perchlorate contamination of water supplies is actually greater than the EPA report indicates, as the report is limited to those instances where a release has been reported or perchlorate has been detected through sampling (GAO, 2005).

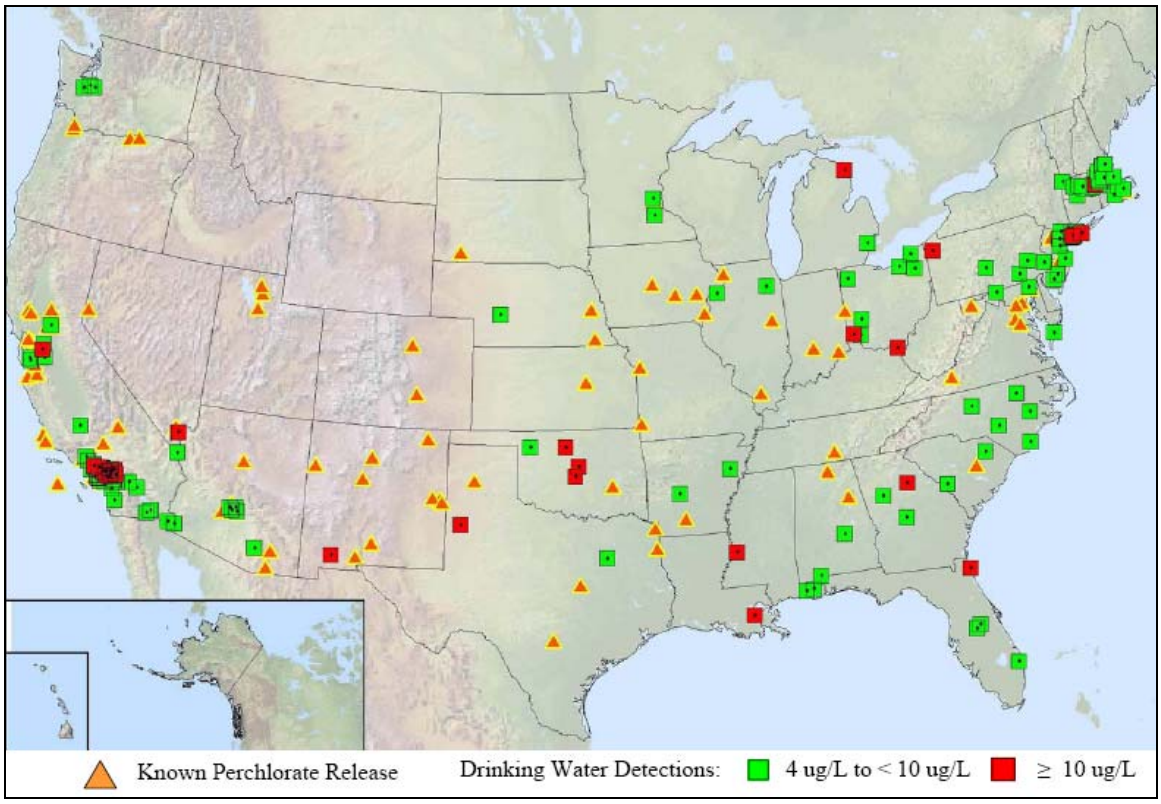


Figure 1.1 Known Perchlorate Releases and Perchlorate Detections under the UCMR Program (Brandhuber, 2005)

Perchlorate is a negatively charged ion that can affect thyroid function through competitive inhibition of the transport of iodide into the thyroid gland. This the only effect that has been consistently documented in humans exposed to perchlorate (EPA, 2005; NRC, 2005). Iodide transport inhibition can lead to iodide deficiencies and decreased synthesis of thyroid hormones, which are critical determinants of growth and development in fetuses, infants and young children. For this reason, the National Research Council (NRC) has identified fetuses, infants and pregnant women as the sensitive populations most susceptible to the adverse effects of perchlorate (NRC, 2005). Sustained changes to thyroid hormone production and fluctuating thyroid stimulating hormone secretions can result in thyroid hypertrophy and hyperplasia, possibly followed by hypothyroidism in people unable to compensate with an increase in thyroid iodide uptake (EPA, 2005).

Following recommendations of the NRC (2005), the EPA adopted a reference dose (RfD) for perchlorate of 0.0007 milligrams/kilogram-day (mg/kg-day) which translates to a Drinking Water Equivalent Level (DWEL) of 24.5 micrograms/liter (μg/L) or 24.5 parts per billion (ppb). The oral RfD is an estimate of a daily oral exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime (EPA, 2006).

Following the EPA's adoption of the RfD, both the Department of Defense (DoD) (DoD, 2006), and the United States Air Force (USAF) (USAF, 2006) published guidance on sampling, analysis, and restoration/remediation requirements for varying levels of perchlorate contamination.

Even with the establishment of EPA's RfD, there are no federal cleanup standards for perchlorate-contaminated groundwater or soil except for site specific standards established under federal statutes such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), and Safe Drinking Water Act (SDWA) (EPA, 2005). In addition, several states as indicated in Table 1.1 have identified state specific perchlorate advisory levels, with Massachusetts going as far as establishing a Maximum Contaminant Level (MCL) of 2 μg/L, which DoD organizations in the state must comply with for Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site remediations (DoD, 2006; USAF 2006).

Table 1.1 State Advisory Levels for Perchlorate (ADEQ, 2007. EPA, 2005; CDHS, 2007; Mass DEP, 2006; NDEP, 2006)

State	Advisory Level	Comment
Arizona	14 μg/L	1998 health-based guidance level; based on child exposure; following EPA established RfD, state task force formed to investigate possibility of developing water quality standard for perchlorate
California	6 μg/L – public health goal (PHG) for perchlorate in drinking water	California Department of Health Services has proposed an MCL of 6 μg/L; currently in regulatory process
Massachusetts	2 μg/L	MCL for drinking water and waste site cleanup established in Jul 06
Maryland	1 μg/L	
New Mexico	1 μg/L – only for monitoring	Drinking water screening level
New York	5 and 18 μg/L	5 μg/L for drinking water planning; 18 μg/L for public notification
Nevada	18 μg/L – public notice standard	For contaminated groundwater
Texas	17 and 51 μg/L	17 μg/L for residential protective cleanup level (PCL); 51μg/L for industrial/ commercial PCL

If remediation of perchlorate-contaminated groundwater is required, a variety of treatment technologies are available as summarized in Table 1.2. Treatment technologies

can be categorized as either destruction or removal and as either *ex situ* or *in situ*. Destruction technologies transform the contaminant into less harmful compounds, while removal treatments simply concentrate the contaminant (typically in a different phase). The concentrated contaminant then must be managed, either through additional treatment or disposal (EPA 2005). *Ex situ* technologies involve bringing the contaminant to the surface for treatment, while *in situ* treatment occurs in place, i.e. in the subsurface (ITRC, 2005). Italicized treatment technologies in Table 1.2 are identified as still being in the experimental/research phases. Of the numerous remediation technologies available, bioremediation has been identified as having the greatest potential for perchlorate treatment (Logan, 2001; Urbansky, 2002); hence much current research focuses on *ex situ* and *in situ* bioremediation (EPA, 2005).

Table 1.2 Perchlorate Treatment/Remediation Technologies (EPA 2005, ITRC 2005)—Italics Indicate Innovative Technologies

	Destruction	Removal
Ex situ	Bioreactors Composting *Catalytic Gas Membrane* *Electrochemical Reduction* *Zero-Valent Iron Reduction under Ultraviolet Light*	Ion Exchange Liquid Phase Carbon Adsorption (GAC) Reverse Osmosis Electrodialysis *Nanofiltration/Ultrafiltration* *Capacitive Deionization*

In situ	Permeable Reactive Barriers (Fixed Biobarriers/Biowalls) Bioremediation (Mobile Amendments) *Vapor Phase Electron Donor Injection* *Constructed Wetlands* *Monitored Natural Attenuation* *Nanoscale Bimetallic Particles*	Phytoremediation

Perchlorate bioremediation occurs when microorganisms, in the presence of an electron donor and a microbial growth-supporting substrate, reduce perchlorate into chloride and oxygen along the following pathway:

ClO_4^- (perchlorate) → ClO_3^- (chlorate) → ClO_2^- (chlorite) → Cl^- (choride) + O_2 (oxygen)

For *in situ* bioremediation, the electron donor is mixed into perchlorate-contaminated groundwater so indigenous microorganisms can reduce the perchlorate. One innovative method of accomplishing this mixing is to use two dual-screened treatment wells as part of a so-called horizontal flow treatment well (HFTW) system. Figure 1.2 illustrates the operation of a HFTW system, showing how an electron donor may be mixed into perchlorate-contaminated groundwater without the need to pump the water to the surface.

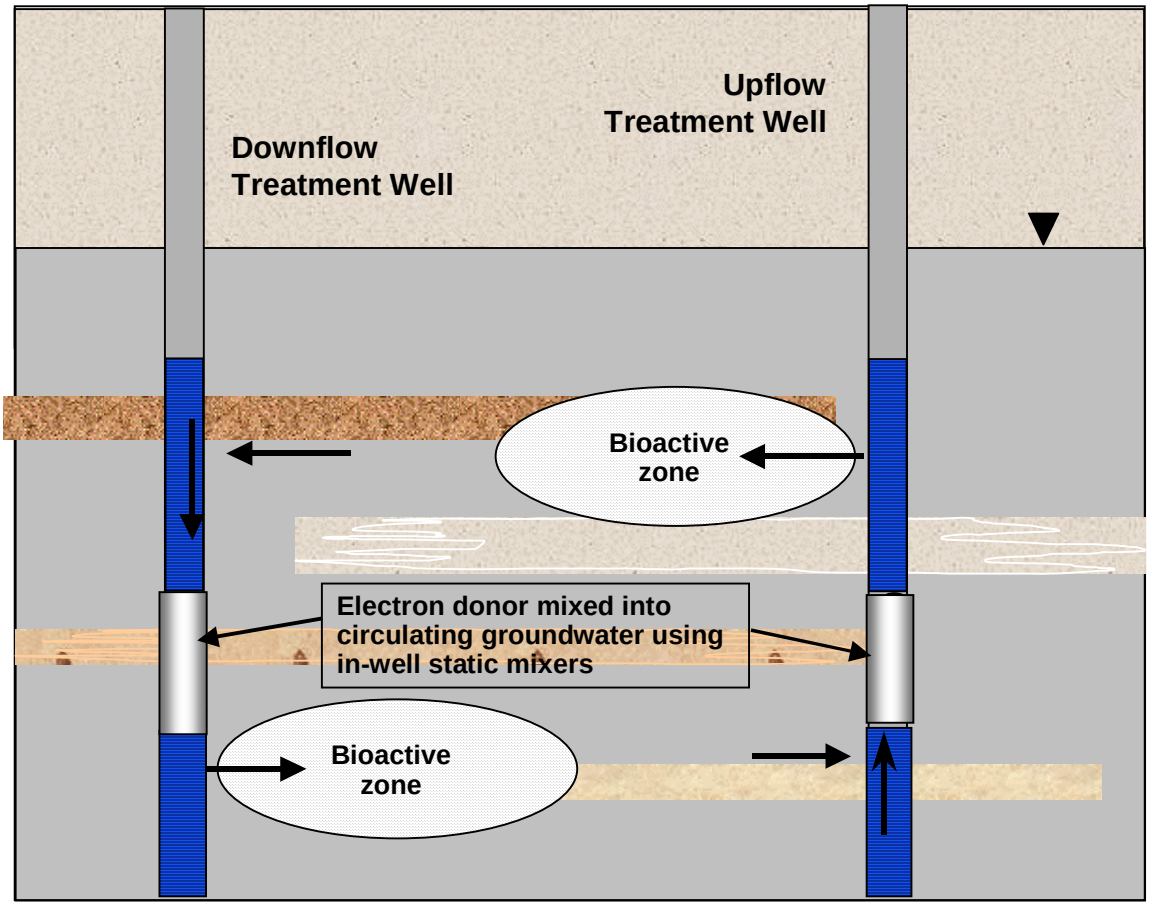


Figure 1.2 Horizontal Flow Treatment Well (HFTW) System

A HFTW system was successfully used to treat trichloroethylene-contaminated groundwater at Edwards AFB (McCarty et al., 1998) and is, as discussed below has been applied to treat perchlorate-contaminated groundwater at the Aerojet Facility in Rancho Cordova, CA (Hatzinger, 2005). The Environmental Security Technology Certification Program (ESTCP), whose goal is to demonstrate and validate promising and innovative technologies that target Department of Defense (DoD) environmental requirements, has identified HFTW systems as having the potential of being widely applicable for *in situ* perchlorate treatment at DoD locations. ESTCP is interested in evaluating HFTWs because of the cost and operational advantages of being able to treat the contaminant in the subsurface without having to pump contaminated water to the surface for treatment. Both the pilot study at the Aerojet site, and this research are parts of an ESTCP-funded

project to evaluate the performance of an HFTW system in promoting *in situ* biodegradation of perchlorate-contaminated groundwater.

Based on the above discussion regarding the prevalence of perchlorate in the subsurface environment, the potential health effects of perchlorate contamination, and regulations mandating cleanup, it seems clear that there is a growing need for remediation technologies to manage perchlorate-contaminated groundwater. *In situ* bioremediation using HFTWs holds promise as a candidate technology. However, in order to facilitate technology transfer and commercialization of this innovative technology, a technology model that can be used to predict performance is extremely useful. Such a model, constructed using data obtained from the field evaluation, may be used by site owners, designers and consultants, and regulators, to optimize a HFTW system.

1.2 EARLIER STUDIES

A previous study was conducted to develop a technology model to mathematically simulate *in situ* bioremediation of perchlorate-contaminated groundwater using HFTWs (Parr, 2002). The technology model is based on a dual-Monod multi-electron acceptor model developed by Envirogen, using acetate as the electron donor, and coupled with a numerical model of advective/dispersive transport of sorbing solutes in the groundwater flow field resulting from HFTW operation (Envirogen, 2002; Parr, 2002).

The technology model was utilized to help design the HFTW system that was installed at the Aerojet Facility. The project investigators used the model to simulate the performance of several HFTW designs. Ultimately, modeling helped the investigators choose such engineered parameters as the treatment well locations, well spacing, pumping rates, and electron donor injection schedule (Shaw, 2003).

Once the design features were specified, a demonstration system was installed in Area D of Aerojet General Corporation's (Aerojet) 8,500-acre Sacramento, California facility that had been used for rocket engine development, testing, and production since 1951. The site selected for the pilot study, as indicated in Figure 1.3, had a large perchlorate plume. Sampling conducted just prior to the HFTW system, showed initial perchlorate concentrations at the demonstration site ranged from approximately 3,100 to 3,600 μg/L.

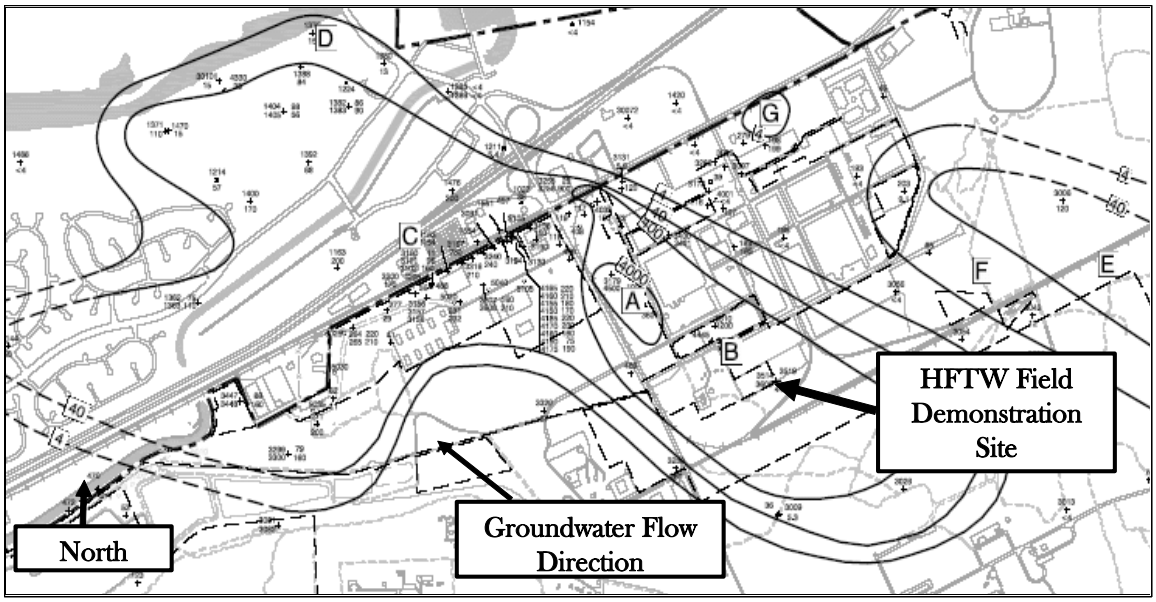


Figure 1.3 Aerojet Site with Perchlorate Isoconcentration Contours Indicated in ppb

The HFTW system was installed in June 2004, and began operating in August 2004. During operation, groundwater samples were collected for analysis of volatile organic compounds (VOCs) (since trichloroethylene (TCE) was present at the site as a co-contaminant), anions, including perchlorate, total iron and manganese, and field geochemical parameters, including pH, dissolved oxygen, conductivity, and redox potential.

1.3 RESEARCH OBJECTIVES:

The main objective of this research is to use the data obtained from the ongoing field trial at the Aerojet facility to calibrate, validate and refine the existing technology model that was used to design the HFTW installation. Specifically, this research will:

(1) Determine how applicable parameters developed in the lab using acetate as an electron donor must be modified to be appropriate for citrate, which was used as the electron donor in the field evaluation.

(2) Determine if the model adequately simulates system performance in the field at the Aerojet facility.

(3) Evaluate the applicability of the HFTW technology under a variety of differing site conditions.

1.4 RESEARCH APPROACH

(1) The literature review will focus on how models have been applied to interpret the results of remediation technology field evaluations and methods utilized for calibration. Questions to be answered include: how models are developed for such evaluations, how data are interpreted, and how can technology models be used to better facilitate technology transfer. The literature review will also address recent developments and current applications of HFTW systems for remediation of other contaminants.

(2) Obtain remediation results from the Aerojet site technology evaluation and compare/contrast field data to model predictions.

(3) Should the model results not match field observations, a determination will be made as to the reason(s) for the discrepancies. Utilizing that information, the technology model parameters will be modified to accurately represent HFTW *in situ* bioremediation operation.

(4) Use the refined model to predict technology performance at other sites, over a range of environmental and operating conditions.

1.5 SCOPE AND LIMITATIONS OF RESEARCH

(1) Calibration and validation of the technology model will be accomplished utilizing field data obtained from the Aerojet project. Thus, model validation will be limited to using data from a single site.

(2) No independent laboratory studies will be conducted as part of this research.

(3) Some limitation of the initial technology model is that various physical and environmental parameters utilized in the model where obtained from external sources and that Parr utilized substrate parameters from various acetate lab studies, whereas the field demonstration utilized citrate as the substrate. Extended maintenance shutdowns of the system and the frequency of sampling may impact validation results.

(4) Due to computational resource and time constraints, a limited number of simulations are conducted. With additional resources, optimization techniques used in the model calibration could be continued.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

This chapter will provide a brief review of perchlorate health effects and regulatory issues associated with perchlorate contamination. A review of the extent to which perchlorate contaminates U.S. groundwaters will be provided along with descriptions of the treatment technologies currently available for remediation, with specific focus on how the innovative Horizontal Flow Treatment Well (HFTW) technology may be applied to effect *in situ* bioremediation of perchlorate-contaminated groundwater. We will also look at development and use of an HFTW technology model to design a pilot study that was conducted to treat perchlorate-contaminated groundwater at the Aerojet site in California.

2.2 PERCHLORATE CONTAMINATION

An excellent oxidizer, perchlorate is used extensively in industry, the Department of Defense (DoD), and the National Aeronautics and Space Administration (NASA). Approximately 90 percent by weight of industrial perchlorate production is utilized in the production of ammonium perchlorate for use as an oxidizing agent for solid propellant rockets and missiles (Trumpolt et al., 2005). Since production began in the United States in 1908, perchlorate has found its way into a diverse array of products. For example, in addition to its use as an oxidizer in rockets and missiles, perchlorate is used in vehicles as an air bag initiator, as a flash powder in photography, in road flares, in matches, in fireworks, as well as in myriad other products (EPA, 2005).

Past management practices during the production, use, and disposal of perchlorate resulted in its release to the environment. Perchlorate is highly soluble and does not appreciably adsorb to soils. It is also kinetically stable under environmental conditions and typically will not react or degrade under ambient conditions (Trumpolt et al., 2005). In addition, biodegradation of perchlorate will not occur unless there are significant

levels of organic carbon present, oxygen and nitrate are depleted and perchlorate-degrading anaerobic bacteria are present. Due to all of these characteristics, perchlorate releases to the subsurface result in dissolved perchlorate plumes that are large, persistent and difficult to remediate (Trumpolt et al., 2005).

2.3 HEALTH RISKS

Perchlorate contamination is a concern because perchlorate competitively inhibits the transport of iodide into the thyroid gland, which may potentially result in adverse health effects. Much recent research has centered on what those health effects are and what concentration levels pose acceptable risks from a regulatory standpoint.

From 1992 through 1998, the EPA published three separate provisional or proposed oral reference doses (RfDs) for perchlorate ranging from 0.00003 mg/kg-day to 0.0009 mg/kg-day. The oral RfD is an estimate of a daily oral exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime (EPA, 2006). In 2002, the EPA published a Draft Perchlorate Risk Assessment which included a mode-of-action model (Figure 2.1) representing a continuum of possible health effects resulting from perchlorate exposure. The model indicated that continued perchlorate exposure ultimately led to birth defects in children and tumors in adults. Based upon their analysis, the EPA proposed an oral reference dose of 0.00003 mg/kg-day, which translates to a concentration in drinking water of 1 μg/L (ppb) as the lowest observed adverse effect level (LOAEL). The LOAEL is the lowest level of a substance that causes statistically and biologically significant differences in test samples as compared to other samples subjected to no substance.

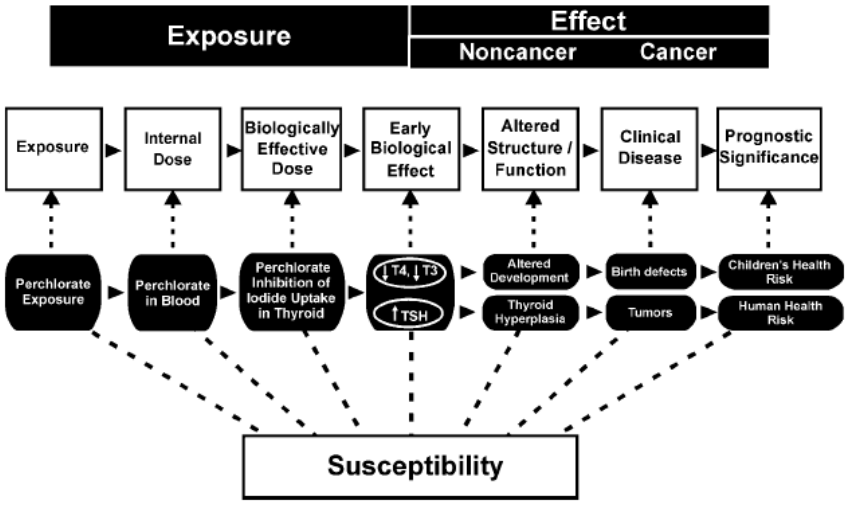


Figure 2.1 Proposed EPA Mode-of-action Model (EPA, 2002)

Following the release of the EPA draft risk assessment report in 2002, differing interpretations of the science associated with perchlorate exposure impacts came to light. In response, in 2003, the Environmental Protection Agency (EPA), the Department of Defense (DoD), the Department of Energy (DOE), and the National Aerospace and Space Administration (NASA) asked the National Research Council (NRC) to independently assess the adverse effects of perchlorate ingestion from clinical, toxicological, and public health perspectives (EPA, 2003). The NRC formed the Committee to Assess the Health Implications of Perchlorate Ingestion. During their review, the committee focused on four main areas: the mode-of action models of perchlorate toxicity, the definition of adverse effect, the point of departure defining the dose-response point that marks the beginning of an adverse effect, and the use of uncertainty factors to derive a reference dose (RfD) for daily oral exposures to perchlorate.

The committee determined there was insufficient evidence to support several causal relationships between perchlorate exposure and adverse effects as noted in Table 2.2, but that there was enough evidence to imply possible associations (NRC, 2005).

Table 2.1 Perchlorate Exposure Causal Relationships (NRC, 2005)

Perchlorate Exposure Health Impacts	Committee Conclusion
Congenital Hypothyroidism	Epidemiologic evidence is not consistent with a causal association between perchlorate exposure and congenital hypothyroidism
Changes in thyroid function in newborns	Epidemiologic evidence is not consistent with a causal association between exposure during gestation to perchlorate in the drinking water at up to 120 ppb and changes in thyroid hormone and TSH production in normal-birth weight, full-term newborns.
Neurodevelopmental outcomes	Epidemiologic evidence is inadequate to determine whether or not there is a causal association between perchlorate exposure and adverse neurodevelopmental outcomes in children
Hypothyroidism and other thyroid disorders in adults	Evidence from chronic, occupational-exposure studies and ecologic investigations in adults is not consistent with a causal association between perchlorate exposure at the doses investigated and hypothyroidism or other thyroid disorders in adults
Thyroid cancer in adults	Epidemiologic evidence is insufficient to determine whether or not there is a causal association between exposure to perchlorate and thyroid cancer
Adversely affect immune system	No evidence for a causative relationship between perchlorate ingestion and any biologically meaningful stimulatory or inhibitory effect on the immune system in rodents, and concludes that the side effects in humans were probably toxic effects of the very high doses of perchlorate given to those patients.

Based upon their review, the NRC proposed a modified mode-of-action model, Figure 2.2. The new model emphasizes that the inhibition of iodide uptake in the thyroid is the only effect that has been observed in humans and is represented in Figure 2.2 as solid arrows. Dashed arrows within the model represent outcomes that have not been clearly demonstrated, but are biologically plausible should the body not be able to adequately adjust to iodide deficiencies (NRC, 2005).

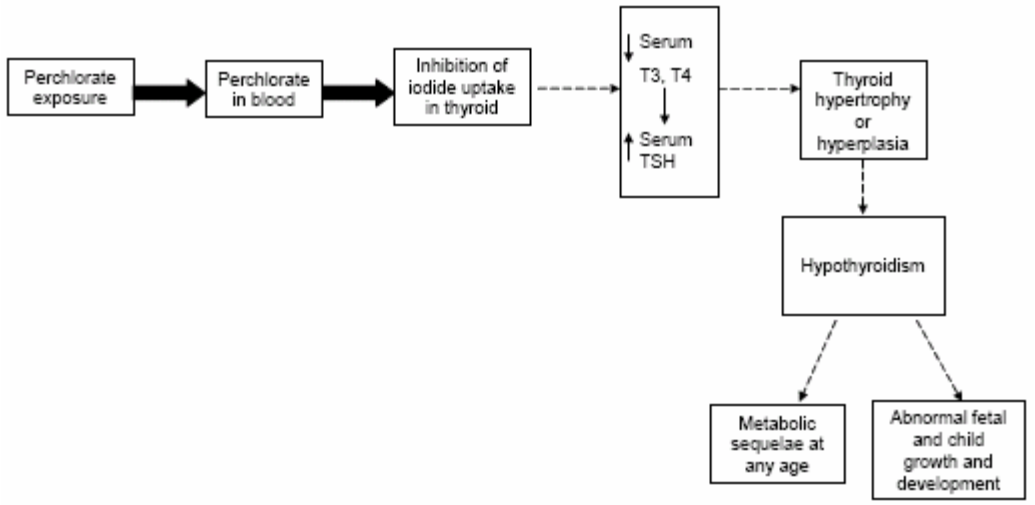


Figure 2.2 Proposed NRC Mode-of-Action Model (NRC, 2005)

Based upon their analysis, the committee decided to provide an RfD recommendation based upon a no observable adverse effect level (NOAEL) as compared to the EPA's RfD which was based upon a lowest observed adverse effect level (LOAEL). A NOAEL represents an exposure level at which there is no statistically or biologically significant difference in the frequency or severity of any effect in the exposed or control populations (EPA, 2006). Thus, by establishing a NOAEL-based RfD, the committee took a more conservative approach than the EPA did (NRC, 2005). The committee's recommendation of an RfD of 0.0007 mg/kg per day should protect the health of the most sensitive populations, defined as pregnant women and their fetuses. A RfD of 0.0007 mg/kg per day is equivalent to 24.5 µg/L per day or 24.5 ppb.

2.4 STATE AND FEDERAL PERCHLORATE REGULATIONS

As indicated in Chapter 1, the EPA reports that 152 public water systems in 35 states have tested positive for perchlorate in water, with over 11 million people exposed to perchlorate at concentrations of 4 ppb (4μg/L) or higher (EPA 2005; NRC 2005). To date, only 9 states have established guidance levels with Massachusetts being the only state to define actual cleanup standards.

The Arizona Department of Health Services (ADHS) has established a Health Based Guidance Level (HBGL) of 14 ppb for perchlorate in drinking water. This level is meant to represent contaminant concentrations in drinking water that are protective of public health during long-term exposures. The HBGLs are not enforceable drinking water standards, but rather are advisory levels identifying concentrations below which contaminants can be present in drinking water and considered safe for human consumption. The Arizona HBGL was established to be protective of children who have higher daily water intake rates and lower body weights (ADEQ, 2004).

The California Department of Health Services (CDHS) has established a Public Health Goal (PHG) and notification level of 6 μg/L which represents the perchlorate concentration in drinking water that poses no significant health risk if consumed for a lifetime, based on current risk assessment principles, practices, and methods (CDHS, 2007). PHGs represent health-protective goals based solely on public health considerations and are not regulatory requirements and as such, there are no consequences to drinking water providers if they cannot meet PHGs. Maximum Contaminant Levels (MCLs), on the other hand, are regulatory drinking water standards that drinking water suppliers must comply with. Once the MCL is established, systems exceeding the MCL are required to notify the CDHS and the public and take steps to immediately come back into compliance. CDHS has proposed an MCL for perchlorate in drinking water of 6 μg/L which is currently making its way through the state regulatory process (CDHS, 2007).

In July 2006, Massachusetts established drinking water and waste site cleanup standards at 2 parts per billion (ppb). The new regulations require most public water systems to regularly test for perchlorate, and if contamination is found to notify the Massachusetts Department of Environmental Protection (MassDEP) of the contamination and conduct appropriate environmental assessment and cleanup. The standard adopted seeks to protect public health, including sensitive populations such as pregnant women, nursing mothers, infants and individuals with low levels of thyroid hormones (MassDEP, 2006).

The Nevada Division of Environmental Protection (NDEP) established 18 ppb as a provisional action level based upon 1999 EPA guidance (NDEP, 2006).

2.5 TREATMENT TECHNOLOGIES

With the widespread perchlorate contamination of groundwater being discovered throughout the United States, as indicated in Figure 1.1, and the increased interest by both federal and state regulatory agencies, a variety of solutions for the treatment of perchlorate contamination have been developed. As indicated in Table 1.2, there are *in situ* and *ex situ* approaches for treating perchlorate-contaminated groundwater, and technologies may be applied that either remove or destroy the perchlorate.

2.5.1 REMOVAL

Typically applied aboveground (*ex situ*), perchlorate removal can be accomplished utilizing anion exchange, filtering or electrodialysis technologies. An early problem with anion exchange was that the ion exchange resins were not selective and removed competing ions along with perchlorate, making them uneconomical. However, ion exchange resins that are selective for perchlorate have been developed to help combat this problem, and currently, anion exchange is the technology that is conventionally used to treat perchlorate-contaminated water (Urbansky, 2002). Filtering technologies such as reverse osmosis or nanofiltration are able to remove perchlorate by forcing the

contaminated water through a filter or membrane that traps the contaminants. Problems with these approaches are that the removal is not selective for perchlorate, and the demineralized water can be corrosive to equipment and piping (Urbansky, 2002). Electrodialysis passes the contaminated groundwater through different membranes while exposing it to an electric field which causes the perchlorate to separate from the water. A problem common to all removal technologies is that perchlorate-contaminated waste is generated which must be treated and disposed of properly, adding complexity and cost to projects (GWRTAC, 2001).

2.5.2 DESTRUCTION

In a review of perchlorate treatment projects, the Ground-Water Remediation Technologies Analysis Center (GWRTAC) found that over 75% of the case studies involved application of destruction technologies (GWRTAC, 2001). Destruction technologies include chemical, electrochemical and biological reduction of perchlorate into its constituent parts; oxygen and chloride.

Chemical reduction of perchlorate is a difficult endeavor because while certain chemical reductants react with perchlorate to reduce it to either chlorate or chloride, only extremely reactive air-sensitive transition metal species, such as ruthenium(II), chromium(II), and titanium(III) have shown any observable redox reactions, and because of the nonlabile properties of perchlorate, any observed redox reactions occur too slowly to be of any practical use (Urbansky, 1998). Electrochemical reduction of perchlorate occurs when an electrical current is applied directly to the contaminated water by a cathode at high potential. This method has challenges of its own which detract from its usefulness; the lengthy time required for the treatment process, electrode corrosion, surface passivation, and natural organic matter adsorption to the electrode surface (Urbansky, 1998).

Of the available technologies utilized for perchlorate remediation, biological degradation has shown the most promise (Urbansky, 1998; Logan, 2001). Figure 2.3 shows that of

the 65 case studies reviewed by the GWRTAC involving perchlorate contamination, 67% focused on biological degradation technologies (GWRTAC, 2001).

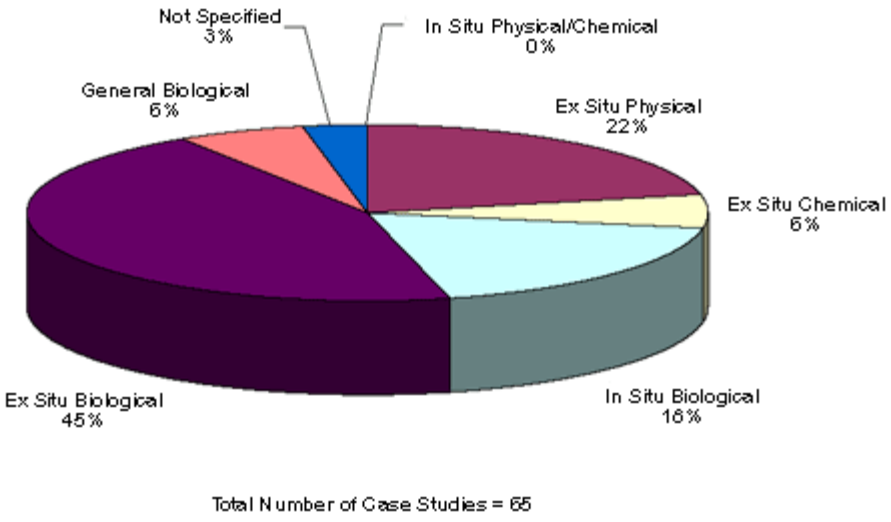


Figure 2.3 General Perchlorate Technology Treatment Types (GWRTAC, 2001)

In biological degradation, perchlorate is used as an electron acceptor by some bacteria for cellular respiration (Logan, 1998; 2001; Coates, 2000). Figure 2.4 presents the pathway used by perchlorate reducing bacteria (PRB) to degrade perchlorate using acetate as an electron donor (Xu et al., 2003). Perchlorate is first reduced to chlorate, then to chlorite, and finally chloride and oxygen.

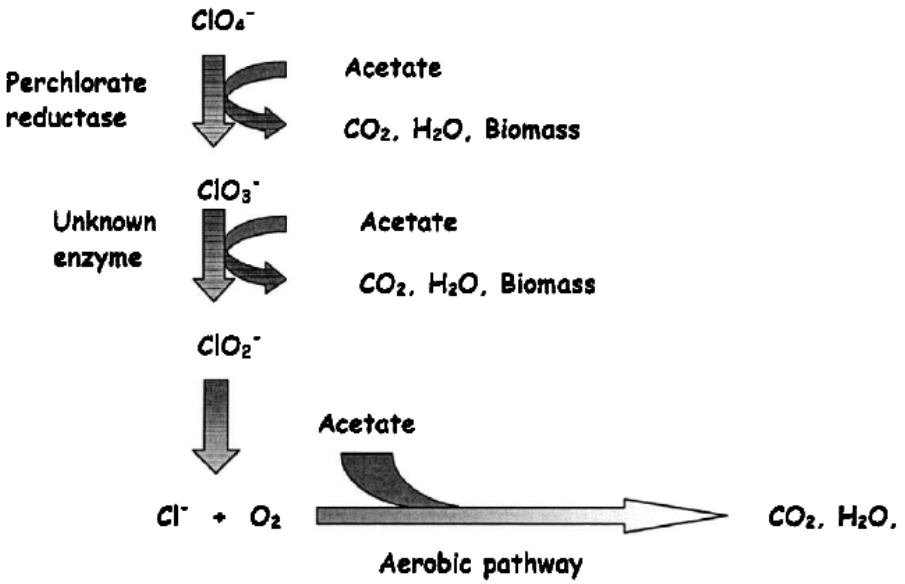


Figure 2.4 Perchlorate Reduction Pathway (Xu et al., 2003 adapted from Rikken et al., 1996)

For both perchlorate and chlorate, reduction does not occur in the presence of dissolved oxygen, meaning that environmental conditions must be anaerobic for perchlorate biodegradation to occur (Xu et al., 2003). It has also be noted that the presence of high concentrations of nitrate partially or completely inhibit perchlorate reduction (Logan, 1998).

2.5.3 *EX SITU* VERSUS *IN SITU* REMEDIATION

As mentioned in Chapter 1, *ex situ* technologies entail extracting the contaminated groundwater to the surface for treatment while *in situ* technologies treat the contaminant in place. Although much past research and technology application has focused on *ex situ* technologies, a review by the Federal Remediation Technologies Roundtable (FRTR), as shown in Figure 2.5, indicates that there's a trend in recent years to deploy more and more *in situ* technologies (Kingscott and Weisman, 2002).

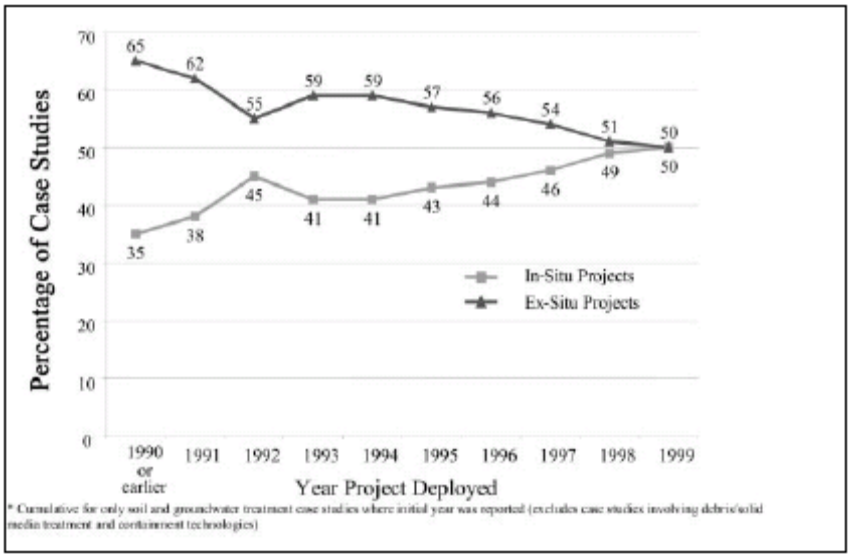


Figure 2.5 In-Situ versus *Ex situ* Treatment (Kingscott and Weisman, 2002)

With *ex situ* treatment technologies, the contaminant is brought to the surface for treatment. This requires significant infrastructure; piping, pumps, filters, tanks, etc., not to mention the costs of pumping the water aboveground. Treating the contaminant *in situ* can reduce or eliminate the aboveground infrastructure and pumping costs (Logan, 2001). As PRBs have been found to be widespread in the environment and are native to many groundwater aquifers, the utilization of *in situ* technologies can avoid the requirement of adding microorganisms to the subsurface (Hatzinger et al., 2002).

In situ biodegradation relies upon indigenous perchlorate reducing bacteria. While perchlorate reducing bacteria are widespread in the natural environment (Hatzinger et al., 2002), as noted earlier, natural degradation of perchlorate is extremely slow, since perchlorate is kinetically stable under ambient conditions (Trumpolt et al., 2005). However, with the addition of an electron donor, the PRB can be stimulated to degrade perchlorate at a faster rate (Hatzinger et al., 2002). A challenge faced in designing an effective and cost efficient *in situ* biodegradation technology is the need to effectively deliver and mix the electron donor(s) into the perchlorate-contaminated groundwater

(Hatzinger et al., 2002). An innovative technology, known as Horizontal Flow Treatment Wells (HFTWs) was developed to meet this challenge.

2.6 HORIZONTAL FLOW TREATMENT WELL (HFTW) SYSTEM

As shown in Figure 1.2, the HFTW system utilizes two treatments wells, each of which has either an upper or lower injection or extraction screen. Looking at two adjacent wells, one well would be operated in an upflow mode and the second in a downflow mode. In the upflow mode, groundwater is extracted from the aquifer through the lower-well screen, mixed with an electron donor and then injected back into the aquifer through the upper-well screen. Operating in a downflow configuration, groundwater is extracted from the aquifer in the upper-well screen, mixed with an electron donor and then injected back into the aquifer through the lower-well screen.

When the amended groundwater is injected into the aquifer, under the anisotropic hydraulic conductivities typically found in aquifers (Christ et al., 1999), the water will flow horizontally toward the adjacent wells' extraction screen. A bioactive zone is established around the injection screens, where perchlorate is reduced by naturally occurring PRB. The two wells operate in tandem, recycling the contaminated groundwater between them. As represented in Figure 2.6, which shows streamlines in the lower aquifer, where the upflow well (u) is an extraction well and the downflow well (d) is an injection well, contaminated water from upgradient is captured by the upflow well and then recycled in the HFTW system (passing multiple times through the bioactive zones). Ultimately, the treated water is injected into the aquifer, where it flows downgradient (Cunningham et al., 2004).

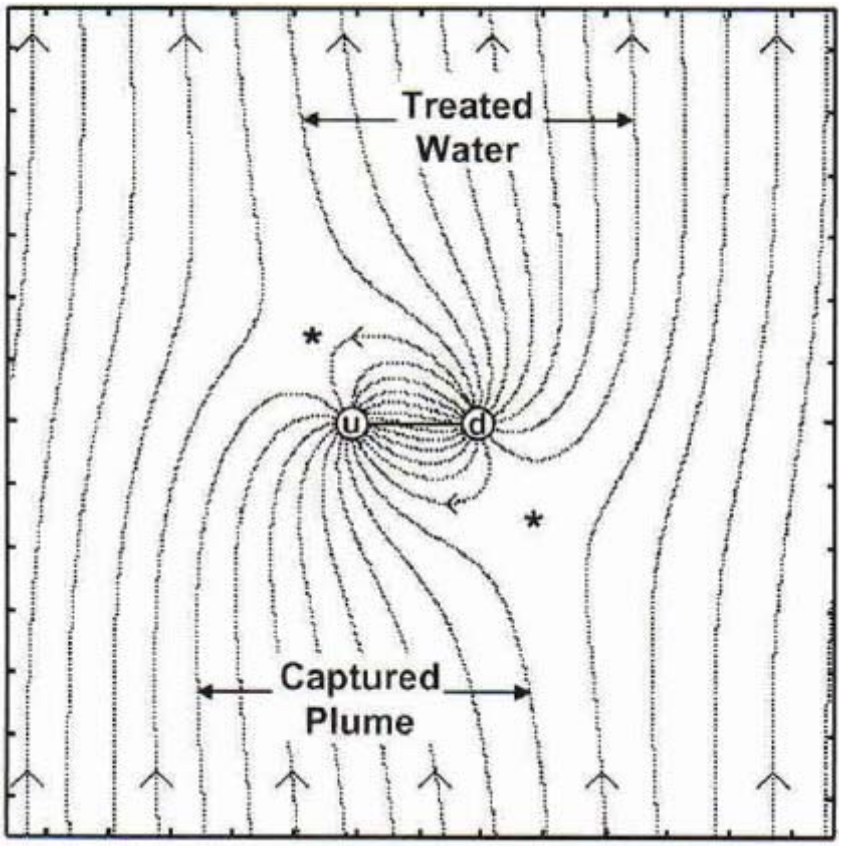


Figure 2.6 Streamlines Representing Groundwater Capture/Recirculation in Lower Portion of an Aquifer Where Upflow Well (u) Extracts and Downflow Well (d) Injects Water. Asterisks Represent Stagnation Points (Cunningham et al., 2004)

HFTWs were selected for use to treat perchlorate-contaminated groundwater at the Aerojet site for a number of reasons. Advantages of recirculating well pairs, or HFTWs, are that they act as an active hydraulic barrier to the flow of contaminated water, but without the need to extract water from the subsurface. The bioactive zones between the wells serve as bioreactors, one each in the upper and lower region of the aquifer. To induce perchlorate biodegradation in the bioactive zones, an electron donor can be efficiently mixed into the contaminated groundwater using mixers installed in the HFTWs (Cunningham et al., 2004), Application of HFTWs to stimulate *in situ* bioremediation by mixing an electron donor into contaminated groundwater was shown to be effective in a previous study by McCarty et al. (1998) where trichloroethylene-contaminated groundwater was successfully treated.

2.7 TECHNOLOGY MODEL

Parr (2002) combined a model that simulates the flow field induced by operation of an HFTW system (Huang and Goltz, 1998) with a submodel that simulates biodegradation of perchlorate by PRB (Envirogen, 2002). The biodegradation submodel uses dual Monod kinetics to simulate perchlorate reduction by PRB in the presence of an electron donor and competing electron acceptors (oxygen and nitrate). As noted earlier in Section 2.5.2, the rate of perchlorate reduction is slowed in the presence of oxygen and nitrate. This is modeled using an inhibition coefficient that slows the rate of nitrate reduction if oxygen is present, and slows the rate of perchlorate reduction if either oxygen or nitrate is present. The rate of perchlorate destruction is also dependent on microbial concentrations as well as the concentrations of both perchlorate and the electron donor (Schwartzenbach et al., 1993). Microbial growth is modeled as a function of the rate of electron donor consumption less biomass decay, which is modeled as a first-order decay process. The model simulates advective/dispersive/reactive transport of the perchlorate, donor, and competing acceptors, while the PRB are assumed to be immobile (Parr, 2002). The parameters utilized in the model, along with a short description, are presented in Table 2.2, while a detailed description of the technology model developed by Parr is provided in Appendix A.

Table 2.2 Technology Model Parameters

Parameter	Definition
k_{max}	Maximum specific rate of substrate utilization (mg donor/mg biomass/day)
K_S^{don}	Donor half saturation concentration (mg/L)
K_S^{oxy}	Half saturation concentration when oxygen (an electron acceptor) concentration is varied and limiting (mg/L)

K_S^{nit}	Half saturation concentration when nitrate (an electron acceptor) concentration is varied and limiting (mg/L)
K_S^{per}	Half saturation concentration when perchlorate (an electron acceptor) concentration is varied and limiting (mg/L)
K_i^{oxy}	Oxygen inhibition coefficient (mg/L)
K_i^{nit}	Nitrate inhibition coefficient (mg/L)
$Y_{biomass}$	Biomass yield per mass of donor consumed (mg biomass/mg electron donor consumed
b	Biomass decay rate (1/day)

2.8 AEROJET PILOT STUDY

The completed technology model was utilized in the design of a HFTW system installed at the Aerojet General Corporation's (Aerojet) 8,500-acre Sacramento, California facility used for rocket engine development, testing and production. The site chosen for the pilot study was contaminated with perchlorate from a former propellant burn area. Samples taken from monitoring wells indicate initial perchlorate concentration levels ranging from approximately 3,100 to 3,600 μg/L (Shaw, 2003).

The objective of the pilot study was to demonstrate and validate the combined use of two innovative technologies; bioremediation of perchlorate-contaminated groundwater through electron donor addition and application of HFTWs to achieve *in situ* mixing of the electron donor with the perchlorate-contaminated water and delivery of the mixture to indigenous PRB (Shaw, 2003). Many of the design parameters for the field

demonstration, including well spacing, pumping rates, and electron donor delivery schedule were selected based on model simulations (Shaw, 2003).

A HFTW system, as shown in Figure 2.7, was installed at the Aerojet site in June 2004. Groundwater at the site is encountered at a depth of 25 to 30 feet bls, with static groundwater at about 30 feet bls. Groundwater flow is towards the northwest with a gradient of approximately 0.017 ft/ft. The HFTW system consisted of two treatment wells installed approximately 10 m apart, oriented so that the line connecting the two wells was approximately perpendicular to groundwater flow. Nineteen monitoring wells were installed surrounding the HFTWs at the locations shown in Figure 2.7. Wells were screened at the depths indicated in Table 2.3. A description of site conditions and details regarding HFTW and monitoring well installation may be found in Shaw (2003). Initial operation and adjustment of the system began in August 2004. Addition of citric acid as the electron donor began on 28 October 2004 and sampling data from monitoring wells were collected and is available for dates through 28 November 2006.

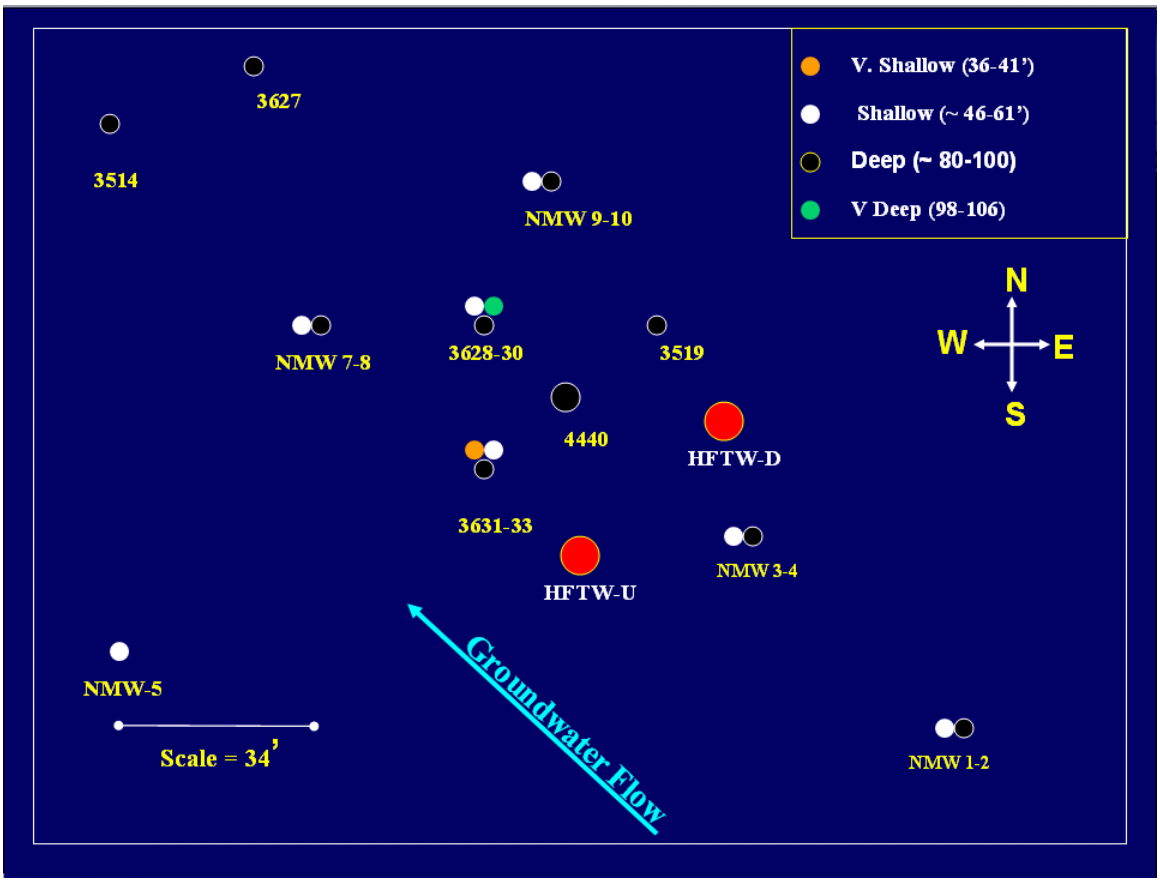


Figure 2.7 Plan View of HFTW and Monitoring Well Layout at Aerojet Site (Hatzinger and Diebold, 2005)

Table 2.3 Monitoring Well Screen Intervals (Shaw, 2003)

Well	Screen Interval (ft bls)
MW3628	52-57
MW3829	80-85
MW3630	96-101
MW3631	36-41
MW3632	52-57
MW3633	98-103
MW3627	75-95
MW3519	78-103
MW3514	77-90

MW4440	75-93 and 98-106
NMW1-2	46-61 and 80-100
NMW3-4	46-61and 80-100
NMW5	46-61
NMW7-8	46-61 and 80-100
NMW9-10	46-61 and 80-100

Initial results shown in Figures 2.8 and 2.9 indicate that the system successfully degraded perchlorate, and that within the first three months, perchlorate levels in the shallow/very shallow monitoring wells (screened between 36 and 61 ft below ground surface) declined by an average of 94% from their starting levels, and 58% in the deep monitoring wells (screened between 80 and 106 ft below ground surface) (Hatzinger et al., 2005).

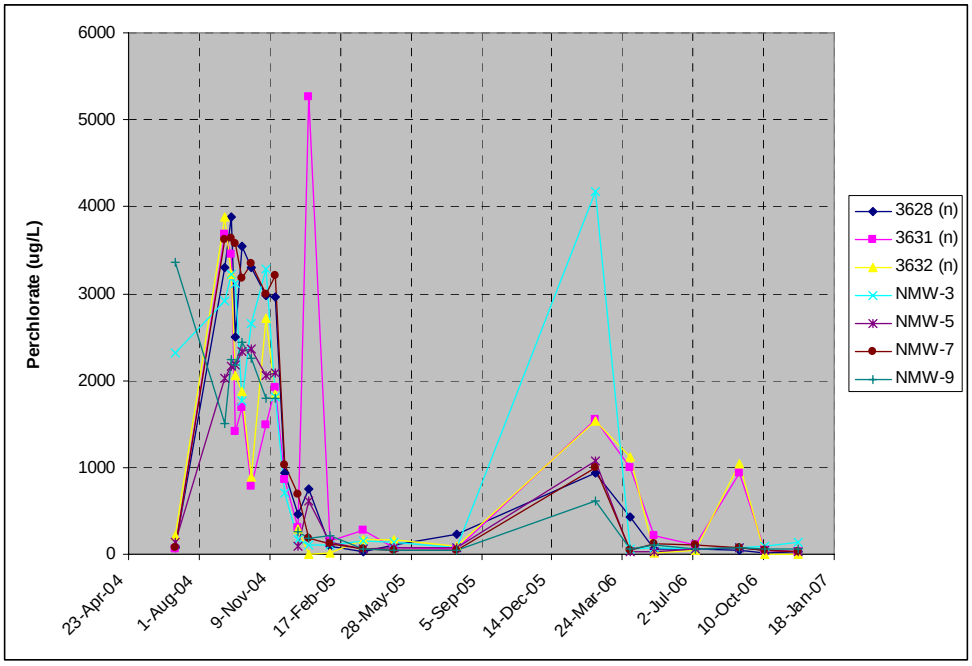


Figure 2.8 Perchlorate Levels in Shallow and Very Shallow Monitoring Wells (Hatzinger and Diebold, 2005; Shaw, 2006)

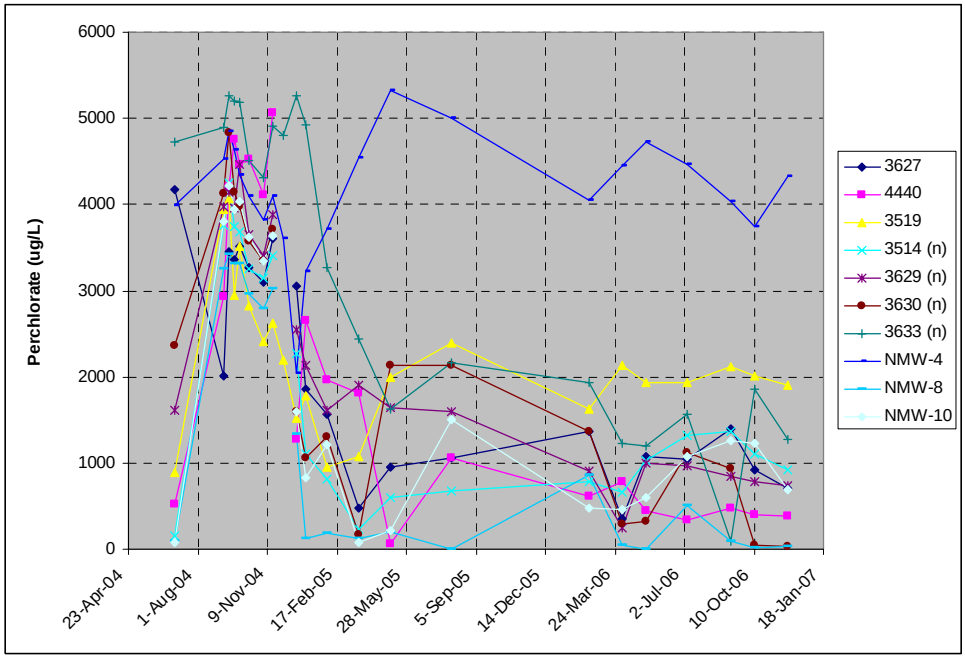


Figure 2.9 Perchlorate Levels in Deep Monitoring Wells (Hatzinger and Diebold, 2005; Shaw, 2006)

2.9 MODEL CALIBRATION/VALIDATION

Anderson and Woessner (1992) put forward that model calibration and verification demonstrate that a model can mimic past behavior while model validation determines whether the model can predict the future (Hassan, 2004). Calibration involves tuning the model by fitting the model results to field or experimental data. Calibration is accomplished by varying parameters, and seeing how parameter changes impact model results. Model validation is the process of using the model to make predictions, and then testing those predictions by comparing them with data, for the purpose of refining, enhancing and building confidence in the model (Hassan, 2004).

2.9.1 GOODNESS-OF-FIT ERROR STATISTICS

In order to calibrate a model, or to assess how well model simulations predict observations, measures of accuracy are required. It is commonly accepted that there is no single best measure of how "good" a model is, and that assessing model accuracy is

necessarily subjective (Collopy and Armstrong, 1992). However, there are a number of goodness-of-fit measures that are used to evaluate model accuracy: mean error (ME) , mean absolute error (MAE), and root mean square error (RMSE). These error statistics (detailed in Equations 2.1, 2.2. and 2.4), require one or more observed values of the dependent variable against which to compare the simulation results.

2.9.1.1 MEAN ERROR (ME)

The ME of a number of observations is found by taking the mean value of the differences between actual (A) and computed (C) values without regard to sign. Because the difference between actual and computed values can be either positive or negative, it is possible that error values can cancel each other out, but the ME remains a valuable statistic because it indicates the bias of the model; whether it over or under estimates the actual values. A positive ME indicates that the model is consistently high in its prediction while a negative ME means that the model is consistently low in its predictions versus actual data. ME values closer to zero are desired.

$$ME = \frac{\sum_{t=1}^{n}(A_t - C_t)}{n} \tag{2.1}$$

2.9.1.2 MEAN ABSOLUTE ERROR (MAE)

In contrast to the ME, the MAE takes the absolute value of the differences between actual and computed values. Thus, the MAE considers all the errors present in the simulation, therefore providing an average prediction error.

$$MAE = \frac{\sum_{t=1}^{n}|A_t - C_t|}{n} \tag{2.2}$$

2.9.1.3 ROOT MEAN-SQUARED ERROR (RMSE)

One of the most commonly used measures for the average size of errors is the mean square error (MSE) which is computed by taking the average of the squared differences between computed and observed values. By taking the square of the differences, the

error cancelling present in the ME is avoided, but the resulting statistic is no longer in the same units as the values being evaluated. The root mean-squared error (RMSE) is the square root of the mean-squared-error and gives the error value the same dimensionality as the actual and computed values. MSE and subsequently RMSE tend to place more emphasis on larger errors and are a more conservative measure than MAE. The smaller the MSE/RMSE value, the closer the fit is to the observed data.

$$\mathrm{MSE} = \frac{\sum_{t=1}^{n} (A_t - C_t)^2}{n} \tag{2.3}$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{t=1}^{n} (A_t - C_t)^2}{n}} \tag{2.4}$$

2.10 EVOLUTIONARY COMPUTING (EC)

In the past, calibration of models relied on manual trial-and-error methods to optimize model parameters for best-fit results. Automated calibration methods have received much interest because they introduce efficiency and allow quantitative estimation of the quality of calibration (Hassan, 2004). The automation that evolutionary computing and genetic algorithms provide make them the ideal solution to optimize model parameters. Evolutionary computing involves the study of a class of algorithms which are inspired by Darwinian principles of natural selection and molecular genetics (Eiban and Smith, 2003). Eiban and Smith (2003) present what they call the evolutionary computing metaphor, shown in Table 2.4, which equates the process of natural evolution to that of problem solving. They go on to provide a generic definition of natural evolution as follows; a given environment is filled with a population of individuals that strive for survival and reproduction, the fitness of these individuals represents their chances of survival and multiplying. This is very similar to the trial-and-error style of problem solving where a collection of candidate solutions exists, and how well they solve the

problem determines the chance that they will be kept and used as seeds for constructing additional candidate solutions.

Table 2.4 Basic Evolutionary Computing Metaphor (Eiban and Smith, 2003)

Evolution		Problem Solving
Environment	⟷	Problem
Individual	⟷	Candidate Solution
Fitness	⟷	Quality

2.11 EVOLUTIONARY/GENETIC ALGORITHMS (GA)

An algorithm utilizing evolutionary principles is termed an evolutionary algorithm (EA). All evolutionary algorithms are comprised of several components illustrated in flowchart form in Figure 2.10.

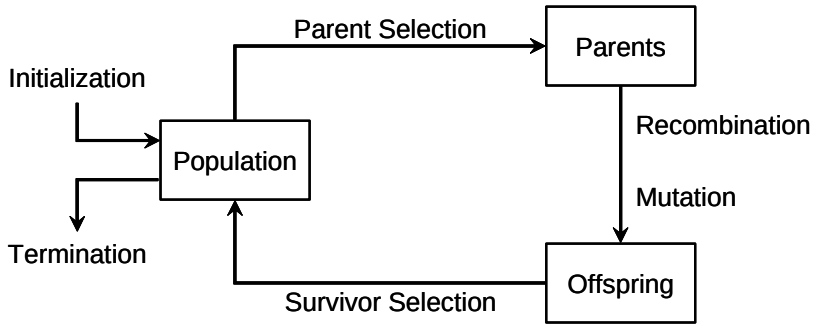


Figure 2.10 General Scheme of an Evolutionary Algorithm (Eiban and Smith, 2003)

This flowchart outlines how an evolutionary algorithm works (Eiban and Smith, 2003). Once a population is created, individuals are selected from the population to serve as parents for new offspring. Through mutation and recombination (defined below) parent characteristics are used to produce offspring, which hopefully have "better" traits, and are therefore fitter, than their parents. One individual is said to be fitter than another if it produces a result that has a higher value of the objective function (assuming the goal is to

maximize the objective function). During survivor selection, fitter individuals are chosen to reproduce as parents, thereby increasing the overall fitness of the population.

2.11.1 GENES/CHROMOSOMES/INDIVIDUALS

Individuals consist of a set of genes (parameter values), which make up a chromosome. A chromosome is a set of parameters that represent a solution to the problem under consideration. An individual is characterized by its chromosome.

2.11.2 OBJECTIVE FUNCTION

As noted above, the objective function forms the basis for determining which candidate solution (individual) should be selected for reproduction (Eiban and Smith, 2003). For example, when using a GA to optimize model parameters, the objective function might be the reciprocal of the RMSE, and the fitness of any particular individual will be evaluated by calculating the value of the objective function that results from using the individual's genes (parameter values) in the model.

2.11.3 POPULATION

In a GA, the role of a population is to hold the candidate solutions, or chromosomes. Individuals within a population do not change, but as individuals are replaced, the population changes and adapts.

2.11.4 PARENT SELECTION

To generate offspring two parents must be selected from the population and in EC, selection is generally accomplished randomly by use of probabilities. Selection combined with survivorship/replacement ensures that the population is continually moving towards a better fit against the objective function (Eiban and Smith, 2003).

2.11.5 VARIATION OPERATORS

Variation operators serve the function of creating new individuals from old ones. This can be accomplished via mutation, recombination and survivor selection. All evolutionary algorithms work by combining selection with a mechanism for introducing variations and the best known mechanism for producing variations is that of mutation (Eshelman, 2000), but crossover serves as the dominant function involved with introducing variation into new genotypes (Eiban and Smith, 2003). Crossover occurs when two individuals (parents) are combined to produce an offspring that has traits of both the parents. The idea is that when two parents have strong traits, there is the possibility the offspring will inherit the best of both parents, making a stronger member of the population. As generations advance, the quality of the population increases and eventually produces a candidate solution that minimizes the error between computed and observed values. Replacement occurs when a member of the population is replaced by an offspring of two parents. This can occur either stochastically, where an individual of the population is selected randomly, or deterministically, where an individual is placed in the population based upon their "fitness" using the objective function as an evaluation tool (Eiban and Smith, 2003).

2.11.6 TERMINATION

Once a GA has been started there must be a method to determine when the GA will terminate. In general, there are two ways to terminate the GA; when an acceptable fitness level is achieved or when the model has run for a specified amount of time. In the example of using a GA to determine best-fit parameters for a model, the GA might terminate when the error statistic is acceptably small or after the GA has run for a specified number of generations.

2.12 SUMMARY

We have reviewed the issues associated with perchlorate contamination; its potential health effects and why innovative treatment technologies are needed to deal with the problem. We have seen that *in situ* bioremediation using HFTWs is an innovative approach that may be useful in helping to manage the perchlorate contamination problem, and have discussed the details of a field evaluation of the technology. In the following chapter, we will present a methodology for applying the technology model described in this chapter and Appendix A, in conjunction with a genetic algorithm to calibrate the model, to help interpret the results of the field demonstration.

3.0 METHODOLOGY

3.1 INTRODUCTION

In this chapter, a technology model that simulates the *in situ* destruction of perchlorate-contaminated groundwater using a HFTW system will be evaluated and calibrated against observational data obtained at the Aerojet site in California. The effect of varying individual model parameters on how well simulation results compare to observation data will be evaluated utilizing goodness-of-fit statistics. Using a genetic algorithm (GA), best-fit parameters will be derived to maximize the goodness-of-fit statistic.

3.2 TECHNOLOGY MODEL

Developed by the Environmental Modeling Research Laboratory of Brigham Young University in partnership with the U.S. Army Engineer Waterways Experiment Station, the Groundwater Modeling System (GMS) provides tools for every phase of a groundwater simulation including site characterization, model development, calibration, post-processing, and visualization. Because of its modular design, the user is able to select modules in custom combinations, allowing the user to choose only those groundwater modeling capabilities that are required (EMS-I, 2007). Parr (2002) utilized GMS to develop a model that calculates hydraulic head and groundwater fluxes induced by operation of a HFTW system. These fluxes are then used as input to a fate and transport model which calculates how physical (advection/dispersion) and biochemical (microbially-mediated perchlorate reduction in the presence of competing electron acceptors) processes affect perchlorate concentrations in space and time. A detailed description of the equations utilized in the model is provided at Appendix A.

3.2.1 GROUNDWATER FLOW MODEL

MODFLOW is a three-dimensional finite-difference model in which groundwater flow within an aquifer can be simulated (Harbaugh et al., 2000). In a finite-difference model, a partial-differential equation representing groundwater flow is replaced by a system of simultaneous linear algebraic difference equations, and these equations are solved at a finite set of discrete points in space and time to calculate head values at those points. Layers can be simulated as confined, unconfined or a combination of both and flows from external stresses such as flow to wells can be simulated.

To use MODFLOW, a region to be simulated must be divided into a rectilinear grid of layers, rows and columns. To model the Aerojet site in California, a three-dimensional grid consisting of 35 rows, 35 columns and 10 layers was used to represent a 121.92 meters square by 54.86 meters deep aquifer volume (Figure 3.1). The density of the grid was designed so that a finer level of detail would be provided in the immediate area surrounding the HFTWs.

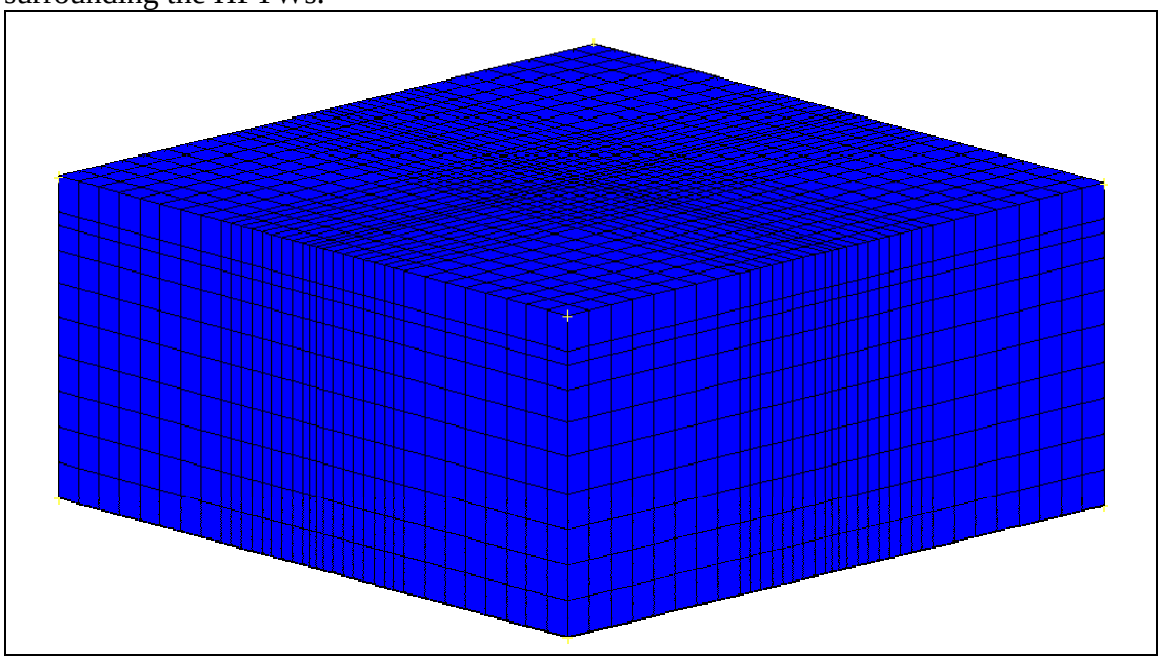


Figure 3.1 MODFLOW Rectilinear Grid

Hydraulic parameters (hydraulic conductivity, transmissivity, specific yield, etc.), boundary conditions (location of impermeable boundaries and constant heads), and stresses (pumping wells, recharge from precipitation, rivers, drains, etc.) are entered into the program. Pump tests were conducted at the Aerojet site to quantify the hydraulic conductivity of the aquifer. Using results for the pump tests, flow modeling and genetic algorithm optimization techniques were used to estimate layer horizontal and vertical hydraulic conductivities, K_h and K_v and specific storage coefficients (S_s) that provided a best-fit of model-simulated drawdowns to measured drawdown data (Hatzinger et al., 2005). For a more detailed description of the site model refer to Parr (2002) and Chosa (2004).

3.2.2 RT3D

RT3D is a software package for simulating three-dimensional, multispecies, reactive transport in groundwater (Clement, 1997; EMS-I, 2007). Initial estimates of the parameters in the biodegradation submodel were obtained directly from laboratory experiments or stoichiometry calculations, while two parameters (k_{max} and b) were fit to data collected during the first 113 days of the pilot study (Envirogen, 2002; Hatzinger et al., 2005). The initial parameters utilized in the technology model are provided in Table 3.1 along with the range of values used to test the model's sensitivity.

Table 3.1 Biological Reaction Parameters (Hatzinger et al., 2005)

Parameter	Original Values	Sensitivity Range Tested
k_{max}	12.5 d-1	0.1, 5, 15, 25
K_S^{don}	93 mg/L	1, 50,150, 200
K_S^{oxy}	1 mg/L	10, 50, 100
K_S^{nit}	180 mg/L	1, 100, 200

K_S^{per}	150 mg/L	1, 100, 200
K_i^{oxy}	3 mg/L	1, 50, 100
K_i^{nit}	25 mg/L	1, 50, 100
$Y_{biomass}$	0.24 mg biomass/mg donor	0.1, 0.15, 0.3, 0.5
b	0.03 d-1	0.001, 0.01, 0.1

The initial parameter values identified in Table 3.1 differ from those used in Parr's model (Appendix A). The differences may be attributed to Parr's use of acetate as the electron donor as opposed to citrate, which was used at the Aerojet pilot study (Hatzinger et al., 2005).

Sampling data obtained before the HFTW system went into operation was extrapolated to the rectilinear grid described in Section 3.2.1 to establish the technology model's initial concentrations of oxygen, nitrate and perchlorate. Concentrations at the southern and eastern boundaries of the grid were held constant. This served as the constant concentration boundary condition, providing a source of contaminants. The average concentrations at the monitoring wells are presented in Table 3.2.

Table 3.2 Average Oxygen, Nitrate, and Perchlorate Concentrations at Aerojet Site on 30 September 2004 (Shaw, 2006)

	Average Concentration (µg/L)
Oxygen	1,370
Nitrate	4,626
Perchlorate	3,307

3.3 ELECTRON DONOR SCHEDULE

Citrate, as the electron donor, was injected into the HFTW system beginning 28 October 04 (day 0). Initial injection rates were based upon previous stoichiometric calculations and technology model simulation results. Injection slug lengths and frequency were varied throughout the operation of the system based upon sampling results. Tables 3.3 and 3.4 represent the electron donor injection schedule utilized during the pilot study from day 0 to day 113 (Huang, 2006). Although the system has been in continuous operation for 761 days with only short work stoppages since its inception, only the first 113 days of operational data are used to calibrate the model parameters. To help validate the model, the model is used to predict observed data from day 114 through 761. Model simulations for days 114 through 761 were based on the same injection rate/concentration and slug length that were used for days 106 through 113.

Table 3.3 Upflow HFTW Injection Schedule

Dates	Days	Injection Rate/ Concentration	Slug Length	Freq (per day)
28 Oct 04 – 13 Jan 05	0 - 77	78.7 ml/min (609 g/L)	20 min	1
13 Jan 05 – 11 Feb 05	77-106	78.7 ml/min (609 g/L)	30 min	1
11 Feb 05 – 18 Feb 05	106-113	78.7 ml/min (609 g/L)	38 min	1

Table 3.4 Downflow HFTW Injection Schedule

Dates	Days	Injection Rate/ Concentration	Slug Length	Freq (per day)
28 Oct 04 – 13 Jan 05	0 - 77	70.0 ml/min (609 g/L)	22 min	1
13 Jan 05 – 11 Feb 05	77-106	70.0 ml/min (609 g/L)	33 min	1
11 Feb 05 – 18 Feb 05	106-113	70.0 ml/min (609 g/L)	33 min	2

3.4 MEASURES OF PERFORMANCE

To evaluate the performance and accuracy of the technology model developed by Parr (2002), concentrations obtained from technology model simulations will be compared against observational data obtained from the HFTW system at the Aerojet site in California. In the analysis, the difference between simulated concentrations and observed values will be calculated and quantified using the error statistics described in Chapter 2. The technology model calibration will include time series plot comparisons and goodness-of-fit statistics to evaluate model performance. The calibration will be used to determine parameter values that result in a best-fit of model simulations to observed data.

There are no criteria which define a "good" value of RMSE or MAE, and as such, the original error values of the technology model as shown in Table 3.5 will serve as the basis for comparisons when evaluating the sensitivity of the model. These error statistics were obtained from the technology model utilizing the initial parameter values shown in Table 3.1, a continuous electron donor injection, and data for oxygen, nitrate, and perchlorate concentrations measured at the site.

Table 3.5 Sensitivity Analysis Baseline Error Statistics

	ME	MAE	RSME
Oxygen	-1.146	1.346	1.672
Nitrate	-1.222	2.048	2.678
Perchlorate	-0.488	1.039	1.566

Sensitivity analyses were conducted by varying the individual parameters in Table 3.1 over the identified ranges, and comparing the error statistics against the baseline statistics to determine if the model simulation improved or degraded. Following the sensitivity analysis, a GA was utilized to determine the parameters that obtain the best-fit between

simulated and observed concentrations. As noted in Section 3.2, observational data from the first 113 days of the study were utilized for calibration of the model.

Table 3.6 shows the error statistics obtained from the technology model utilizing the initial parameter values shown in Table 3.1 and the pulsed electron donor injection schedule detailed in Tables 3.3 and 3.4. These error statistics are used to evaluate changes in model predictions resulting from use of the best-fit parameters.

Table 3.6 Model Performance Baseline Error Statistics

	ME	MAE	RSME
Oxygen	-1.091	1.335	1.656
Nitrate	0.309	1.767	2.172
Perchlorate	0.477	1.227	1.562

Figures 3.2 and 3.3 show plots of simulated (using the technology model with baseline parameters) and observed perchlorate concentrations vs time at two shallow monitoring wells, 3628 (screened 52 – 57 feet below ground surface) and 3631 (screened 36 – 41 feet below ground surface). The shallow monitoring wells correspond with the upper screens of the HFTWs, while the deep monitoring wells coincide with the lower screens. Figure 2.7 shows approximate well locations in relation to the HFTWs.

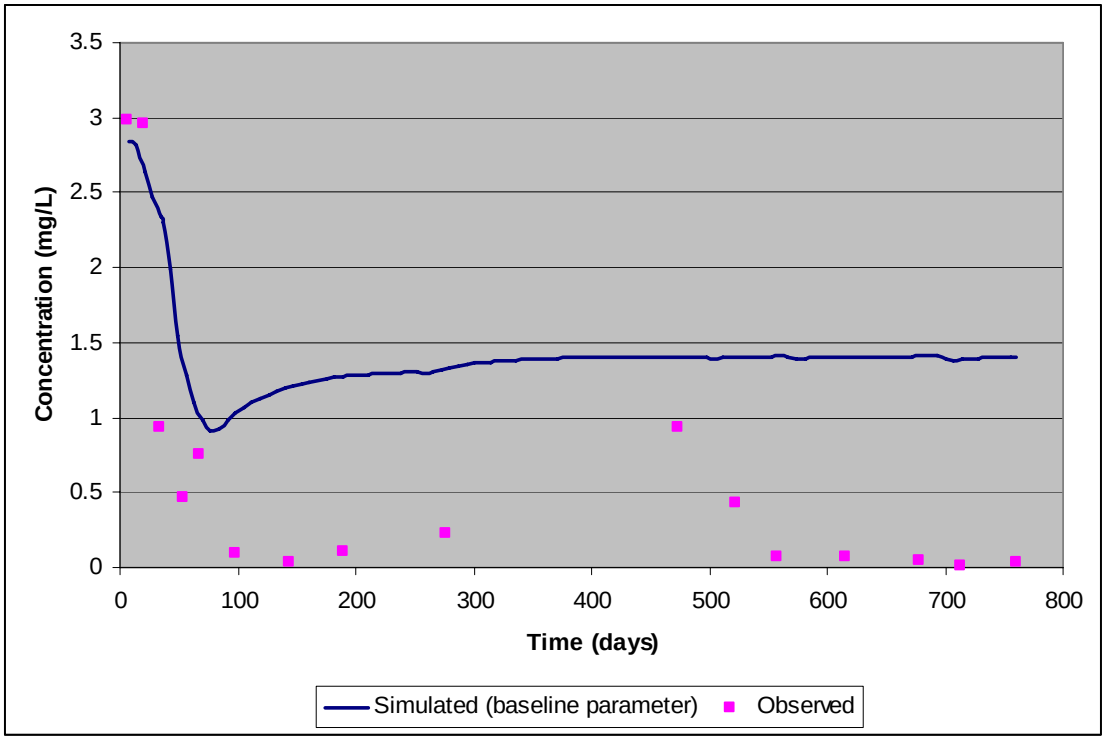


Figure 3.2 Perchlorate Concentration vs Time at Shallow Monitoring Well 3628 (see Figure 2.7 for location)

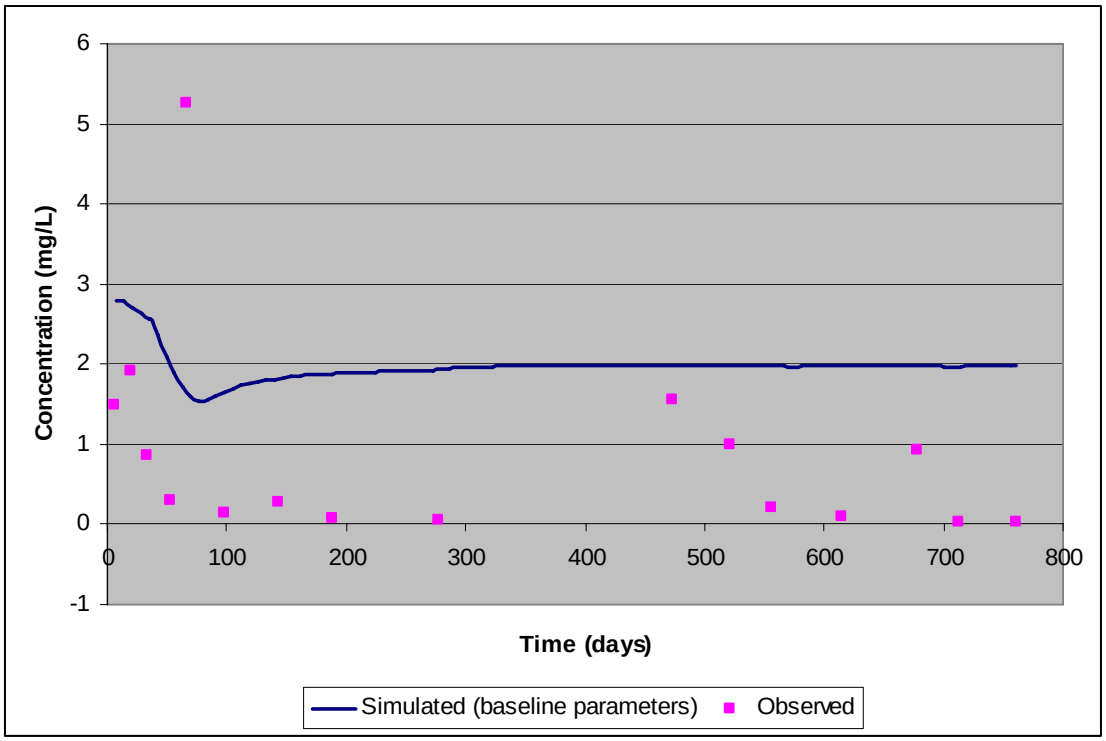


Figure 3.3 Perchlorate Concentration vs Time at Shallow Monitoring Well 3631 (see Figure 2.7 for location)

Figures 3.4 and 3.5 show plots of simulated (using the technology model with baseline parameters) and observed perchlorate concentrations vs time at two deep monitoring wells, 3630 and 3633, which are screened from 80 to 106 feet below ground surface.

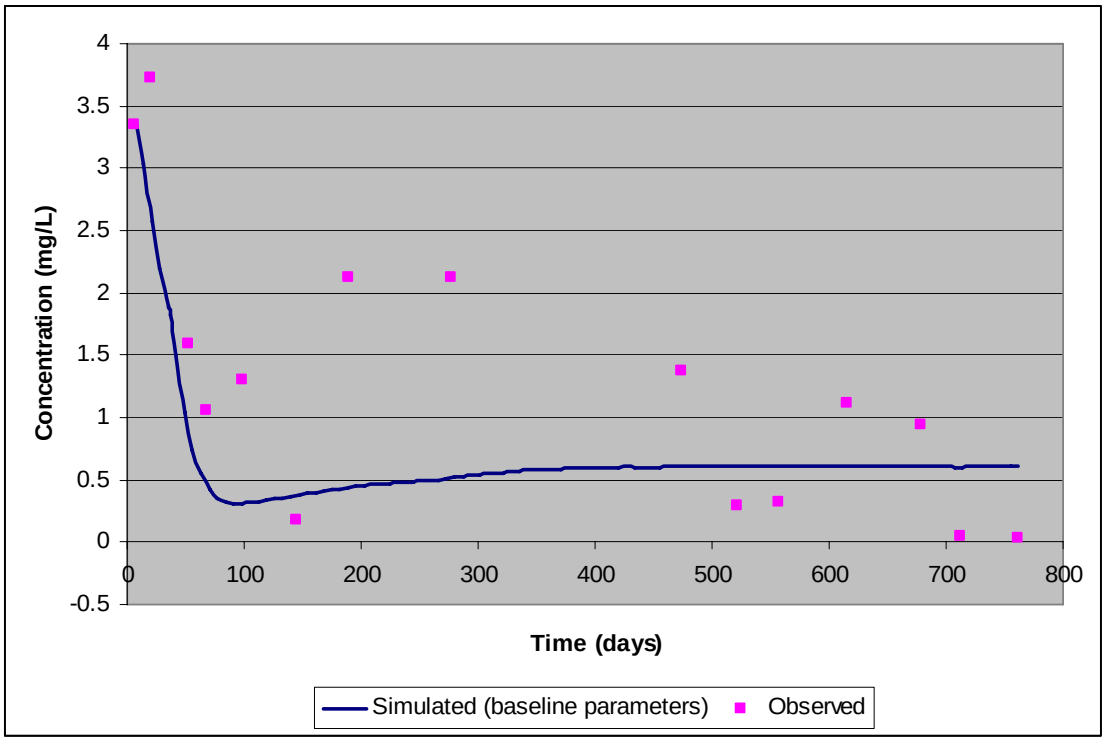


Figure 3.4 Perchlorate Concentration vs Time at Deep Monitoring Well 3630 (see Figure 2.7 for location)

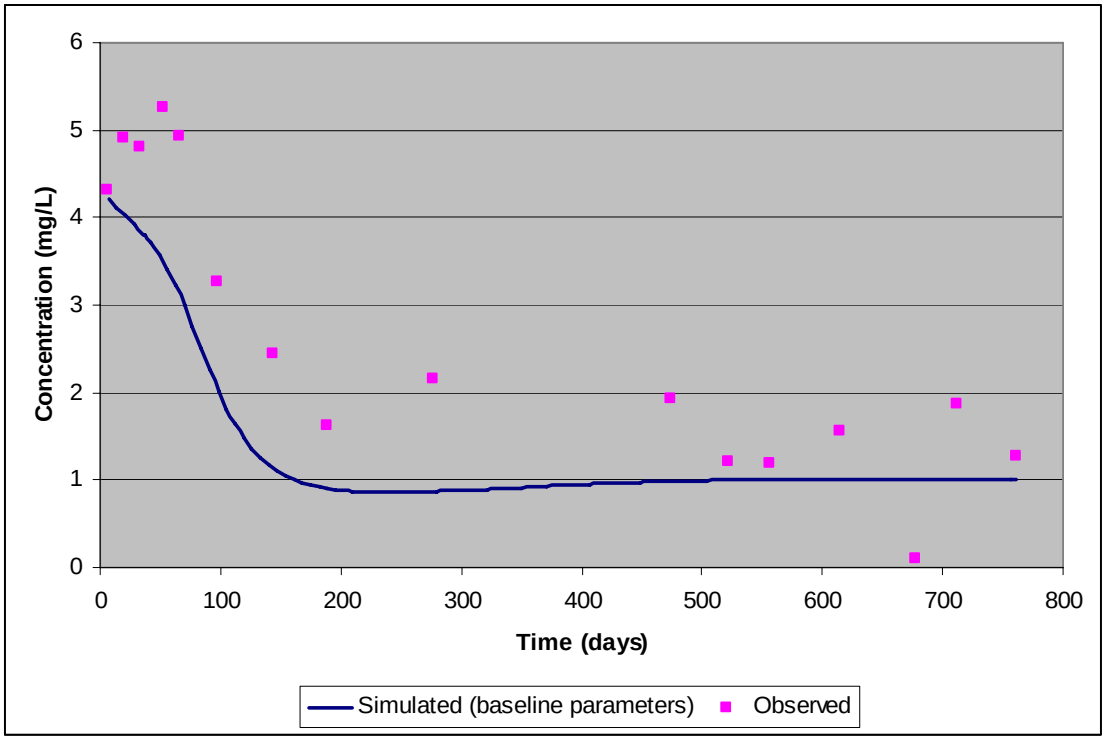


Figure 3.5 Perchlorate Concentration vs Time at Deep Monitoring Well 3633 (see Figure 2.7 for location)

3.5 GENETIC ALGORITHM (GA) CONFIGURATION

As indicated in Chapter 2, GAs are ideal optimization tools. A GA will be utilized in this analysis to determine the model parameters that result in the best-fit of the model to data observed in the first 113 days of the field evaluation. The GA configuration is provided in the following sections.

3.5.1 GA INDIVIDUAL DEFINITION

In reference to the technology model being evaluated, an individual is a set of the nine parameters identified in Table 2.2. In calibrating the model to determine the optimal parameters that best-fit the observed data, those individuals will be varied through use of a GA to minimize the model's error statistics.

3.5.2 GA OBJECTIVE FUNCTION

As mentioned in Chapter 2, a GA requires an objective function to evaluate the candidate solutions. In this study, the first 113 days of the observed oxygen, nitrate and perchlorate concentration data will be used, along with model predictions of those concentrations over the same time period, to calculate the RMSE. The RMSE will be used in a single objective function to be optimized. To frame the error statistic in a form for use in a GA, the RMSE will be inverted, as shown in Equation 3.1, so that the objective function increases as the RMSE approaches zero (Huang, 2006).

$$GA_{Obj} = \frac{1}{1 + RMSE} \tag{3.1}$$

While the RMSE for the goodness-of-fit to oxygen, nitrate, and perchlorate concentrations will be used in the objective function to calibrate the model over the first 113 days of the technology evaluation, individual oxygen, nitrate and perchlorate goodness-of-fit error statistics (RMSE, ME and MAE) will be used to evaluate how well the parameterized model fits the observed data over the entire 761-day technology evaluation period.

3.5.3 POPULATION AND PARENT SELECTION

The population used for this evaluation is set at 30, and parent selection will be accomplished randomly by use of probabilities.

3.5.4 VARIATION

For a genetic algorithm to work, variation must be introduced into the population and reproduction process. The type of GA used in this research is called a MicroGA. MicroGA's method of introducing variation into the population is by use of

recombination, crossover and population regeneration, with no mutation factors applied. The crossover probability to be utilized in this GA is 0.5, meaning that genes from each parent are randomly selected to produce an offspring, with each parent contributing 50% of their genes to the child (Bäck, 2000). As the GA runs, the objective function will cause the population to converge on a set of parameters that provide the highest objective function value. In order to produce fitter (higher scoring) offspring, additional variation must be introduced into the population. This variation is introduced through population regeneration whereby the fittest individual is allowed to reproduce, while the rest of the population is randomly regenerated. With the new population, the GA can continue the recombination and crossover process. Table 3.7 shows the parameter ranges tested with the GA.

Table 3.7 GA Parameter Range

Parameter	Original Values	Range Tested
k_{max}	12.5 d-1	1-50
K_S^{don}	93 mg/L	20-200
K_S^{oxy}	1 mg/L	20-200
K_S^{nit}	180 mg/L	20-200
K_S^{per}	150 mg/L	20-200
K_i^{oxy}	3 mg/L	5-50
K_i^{nit}	25 mg/L	5-50
$Y_{biomass}$	0.240 mg biomass/mg donor	0.01-1
b	0.030 d-1	0.001-0.1

3.5.5 SURVIVOR SELECTION/REPLACEMENT

Replacing members of the population is accomplished via a deterministic method. The candidate that scores highest against the objective function will be placed into the population.

3.5.6 TERMINATION

Due to resource limitations, time constraints and the possibility that the GA could run indefinitely without finding a set of parameters that produced a solution within specified tolerances (Eiban and Smith, 2003), the GA will run for 100 generations.

3.6 DIFFERING SITE CONDITIONS IMPACTS ON TECHNOLOGY PERFORMANCE

To evaluate the effect of differing site conditions on the models results, the Aerojet site model was modified to represent two very different hypothetical sites. The first hypothetical site (Site 1) was homogeneous, with high hydraulic conductivity (50 m/day), and no competing electron acceptors (oxygen and nitrate concentrations set at 0 mg/L). The second hypothetical site (Site 2) was configured to represent a location with high concentrations of competing electron acceptors in a homogeneous, low conductivity (5 m/day) aquifer. To achieve the high concentrations of competing electron acceptors, the initial Aerojet site concentrations identified in Table 3.2 were multiplied by a factor of 10.

4.0 RESULTS AND ANALYSIS

4.1 INTRODUCTION

This chapter presents the analyses that were conducted to determine the sensitivity of technology model results to changes in the model parameters identified in Table 3.7. The chapter also presents the results of the model calibration, obtained by using a genetic algorithm to find the parameter values that resulted in the best-fit of model simulations to concentration data measured during the initial 113 days of the field evaluation at the Aerojet site. The chapter concludes with an analysis of the effect of differing site conditions on simulated technology performance.

4.2 PARAMETER SENSITIVITY ANALYSIS

In this section, we explore the sensitivity of the technology model results to each of the kinetic parameters by varying the parameters identified in Table 3.7. Table 4.1 shows the differences in error statistics obtained by comparing simulations of the model (run for the range of parameter values) with measured data. The differences listed in Table 4.1 are the maximum differences in the error statistic values that were obtained from varying a given parameter. A positive value in the ME column indicates that the error statistic improved as the parameter value increased from low to high. For the MAE and RMSE error statistics, the opposite is true; a positive value indicates the error statistic gets worse as the parameter value increased from low to high.

Table 4.1 Difference in Error Statistics as Parameter Value is Increased from Low to High Values

	Oxygen			Nitrate			Perchlorate		
Parameter	ME	MAE	RMSE	ME	MAE	RMSE	ME	MAE	RMSE
k_{max}	-0.541	0.270	0.281	-3.893	-0.637	-0.363	-2.526	-1.077	-0.658
K_S^{don}	0.014	0.006	0.005	0.199	-0.070	-0.122	0.107	-0.020	-0.047
K_S^{oxy}	0.061	-0.024	-0.030	0.019	-0.005	0.007	0.019	-0.009	-0.009
K_S^{nit}	0.468	-0.457	-0.641	0.233	-0.039	-0.128	-0.246	0.103	0.150
K_S^{per}	0.000	-0.001	-0.001	-0.131	0.045	0.082	0.198	-0.050	-0.083
K_i^{oxy}	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
K_i^{nit}	0.000	0.000	0.000	0.054	-0.023	-0.036	-0.105	0.018	0.044
$Y_{biomass}$	0.002	0.001	0.001	0.027	-0.013	-0.016	0.015	-0.008	-0.008
b	0.006	0.006	0.004	0.799	-0.280	-0.461	0.441	-0.055	-0.160

Table 4.1 shows that the model, as a whole, appears to be most sensitive to the k_{max} and K_s^{nit} parameters, and relatively insensitive to the K_i^{oxy} parameter. Looking at each electron acceptor individually, simulated oxygen concentrations appear to be most sensitive to the k_{max} and K_s^{nit} parameters, and relatively insensitive to all other parameters. Simulated nitrate concentrations appear to be most sensitive to changes in the b and k_{max} parameters, and to a lesser degree, the K_s^{don}, K_s^{nit} parameters. All other parameters impact the technology model's nitrate error statistics to a small degree with the exception of the K_i^{oxy}, which has no impact. Simulated perchlorate concentrations, like oxygen and nitrate concentrations, are most sensitive to changes in the k_{max} parameter, and to a lesser degree K_s^{nit}, and b. Like the other electron acceptors, simulated perchlorate concentrations are insensitive to the K_i^{oxy} parameter.

4.3 MODEL CALIBRATION

A GA, as described in Chapter 3, was utilized to determine the best-fit parameters that would enable the model to fit the observed data from the initial 113 days of the field evaluation. The GA found the set of nine parameter values that maximized the objective function in Equation 3-1. After finding the best-fit parameters, the calibrated model was run to simulate the entire 761 days of field data.

4.3.1 GA OPERATION

The graph of the GA objective function value vs generation number shown in Figure 4.1 indicates how well the GA is performing. As described previously, new offspring are created when crossover and recombination occurs between two parents. Depending on the offspring's objective function value, the offspring is either discarded or replaces a lower scoring individual in the population. As "fitter" offspring are put into the population, the overall fitness of the population gradually improves, as seen by the increasing population average line in Figure 4.1 (note that an objective function value of 1.0 represents perfect correspondence between the measured data and model calculations). Within every generation, there is one individual who has the highest objective function value. These individuals are represented on the graph as the individual maximum line in Figure 4.1. As the population average improves, eventually all individuals converge on a single objective function value and variation must be introduced into the population. When the population is regenerated, as described in section 3.4.4, the objective function value averaged over the entire population sharply decreases (as depicted in Figure 4.1 at generations 25, 48, and 79). Eventually, crossover and recombination improve the fitness of the entire population and the process continues.

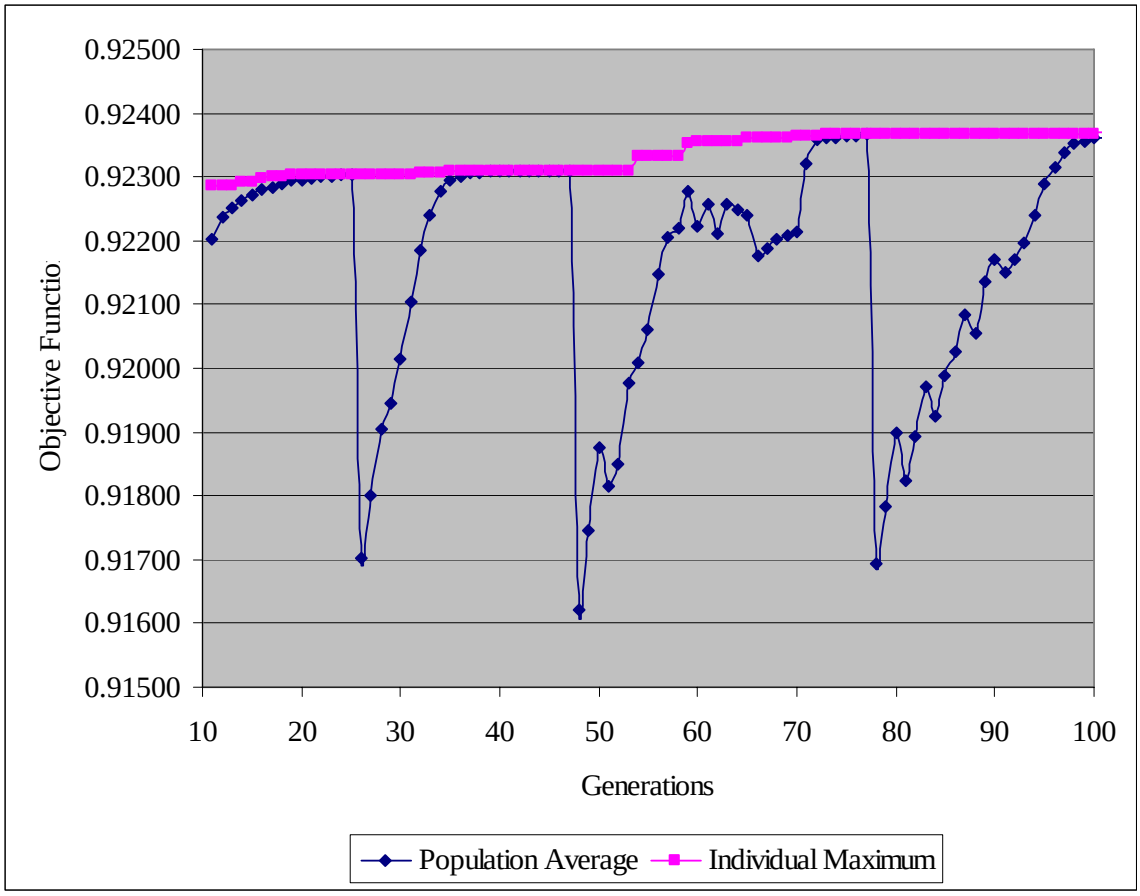


Figure 4.1 Objective function value of most fit individual and population average vs GA generation

4.3.2 CALIBRATION RESULTS

Parameter values calculated at various GA generations are shown in Table 4.2. The parameter values that will be used in subsequent model simulations, which we will refer to as the best-fit values, are the values identified after 100 GA generations. Of the range of values explored by the GA (see Table 3.7), only the best-fit value of K_s^{oxy} was at either the maximum or minimum end of the range (indicating that the best-fit value of Ksoxy may be outside the specified range).

Table 4.2 GA Parameter Values

	Baseline	10 Gen	30 Gen	50 Gen	70 Gen	100 Gen	Units
k_{max}	12.5	23.22	23.22	23.22	7.139	7.188	mg/mg/day
K_S^{don}	93	193.30	137.00	137.30	36.4	36.75	mg/L
K_S^{oxy}	1	186.20	187.60	187.80	184.4	200	mg/L
K_S^{nit}	180	125.60	199.40	198.70	151.1	150.9	mg/L
K_S^{per}	150	67.28	67.24	65.12	53.88	59.41	mg/L
K_i^{oxy}	3	20.61	43.11	43.28	43.66	44.36	mg/L
K_i^{nit}	25	27.22	49.89	49.89	38.05	35.44	mg/L
$Y_{biomass}$	0.24	0.01006	0.01006	0.01000	0.01100	0.01003	mg/mg
b	0.03	0.07938	0.09330	0.09986	0.09996	0.09948	1/day

4.3.3 GOODNESS-OF-FIT ERROR STATISTIC RESULTS

The parameter values in Table 4.2 were entered into the technology model to derive the goodness-of-fit statistics shown in Table 4.3 and Figures 4.2 through 4.4. In early generations, the GA improved the error statistics of the technology model's oxygen concentration calculations but made both the nitrate and perchlorate error statistics worse. As the generations advanced, the perchlorate error statistics began to improve slightly, while the nitrate statistics did not improve compared to their baseline values. Thus, we see that the GA was obtaining calibration parameters that improved the overall fit of the model calculations to the data, but the fit of the model to the concentration data for each of the individual electron acceptors did not necessarily improve with GA generation.

Table 4.3 GA Error Statistic Results

	Oxygen			Nitrate			Perchlorate		
	ME	MAE	RSME	ME	MAE	RSME	ME	MAE	RSME
Baseline	-1.091	1.335	1.656	0.309	1.767	2.172	0.477	1.227	1.562
30 Gen	-0.463	1.011	1.272	0.602	1.860	2.214	0.251	1.267	1.579
50 Gen	-0.451	1.006	1.266	0.642	1.867	2.220	0.260	1.271	1.578
70 Gen	-0.388	0.978	1.231	0.646	1.861	2.204	0.277	1.259	1.559
100 Gen	-0.377	0.975	1.227	0.621	1.865	2.206	0.310	1.267	1.561

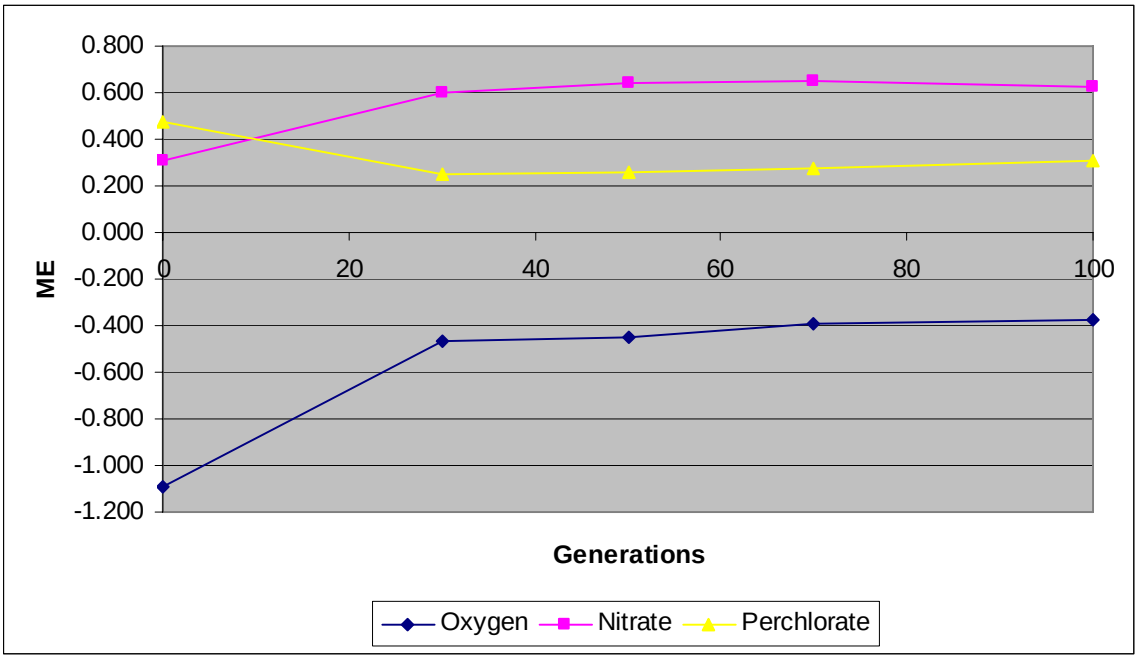


Figure 4.2 Changes in Mean Error over GA Generations

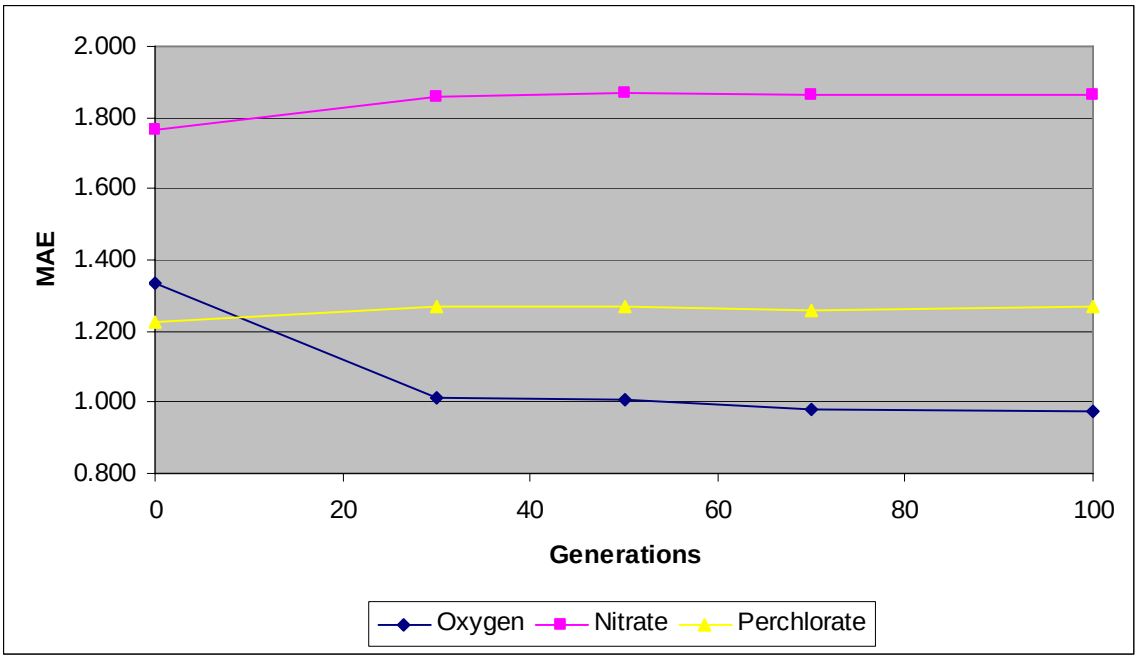


Figure 4.3 Changes in Mean Absolute Error over GA Generations

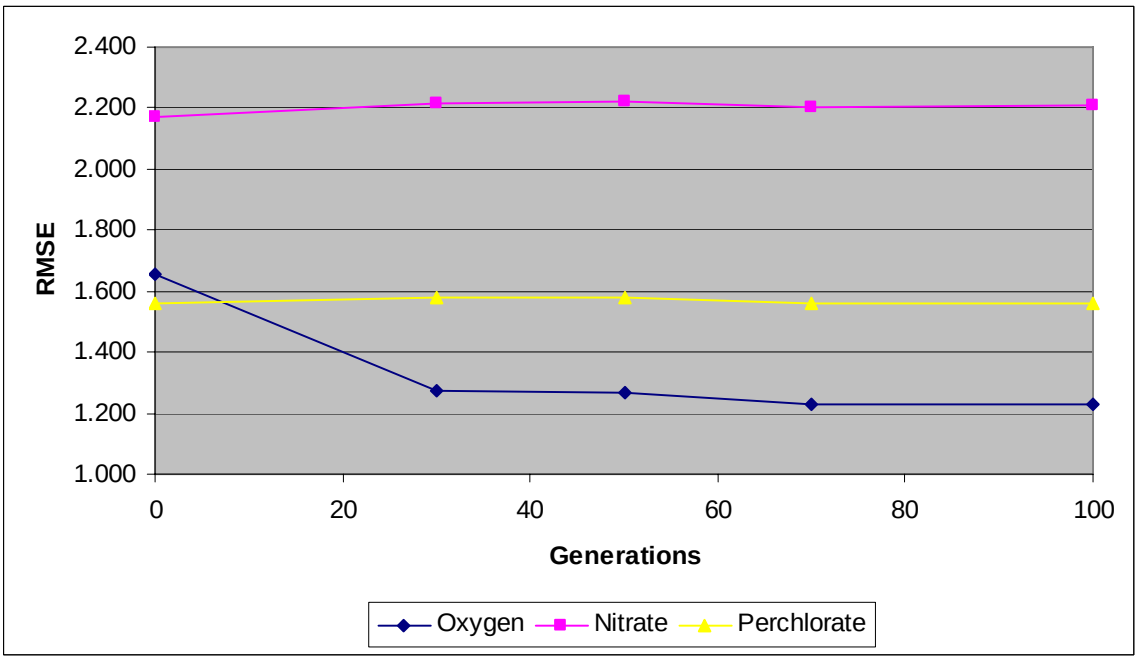


Figure 4.4 Changes in Root Mean-Squared Error over GA Generations

This behavior may be attributed to a combination of the objective function utilized by the GA along with the model structure itself. As described in Chapter 3, the GA maximizes a single objective function (Equation 3.1) based on minimizing the RMSE. The RMSE is

determined by calculating the difference between modeled and measured concentrations for all electron acceptor data, equally weighted. This, coupled with the model structure, where simulated oxygen concentrations affect the nitrate and perchlorate concentrations through competitive inhibition, but not vice versa (Appendix A, Equations A.10 – A.12), results in the GA giving additional weight to fitting the oxygen data.

4.4 BREAKTHROUGH CURVES AT MONITORING WELLS

The best-fit parameters obtained from the GA were used in the technology model to evaluate performance of the model over the entire 761-day period for which data are available. Oxygen, nitrate and perchlorate concentration time series graphs at monitoring wells upgradient and downgradient of the HFTWs are provided for both the shallow and deep parts of the aquifer. A complete set of time series plots for all monitoring wells is provided at Appendix C.

4.4.1 SHALLOW UPGRADIENT MONITORING WELL

NMW3 is a shallow (46-61 ft bls) monitoring well located upgradient of the HFTWs. Figures 4.5 – 4.7 show measured and simulated oxygen, nitrate, and perchlorate concentrations, respectively, versus time at NMW3. We see from Figure 4.5 that using the best-fit parameters improves the model fit for the oxygen data, compared to the baseline parameters. Use of the best-fit parameters results in little improvement for the nitrate or perchlorate simulations. We also note from Figure 4.7 that the perchlorate concentrations at this shallow upgradient well are significantly less than the concentrations predicted by the model.

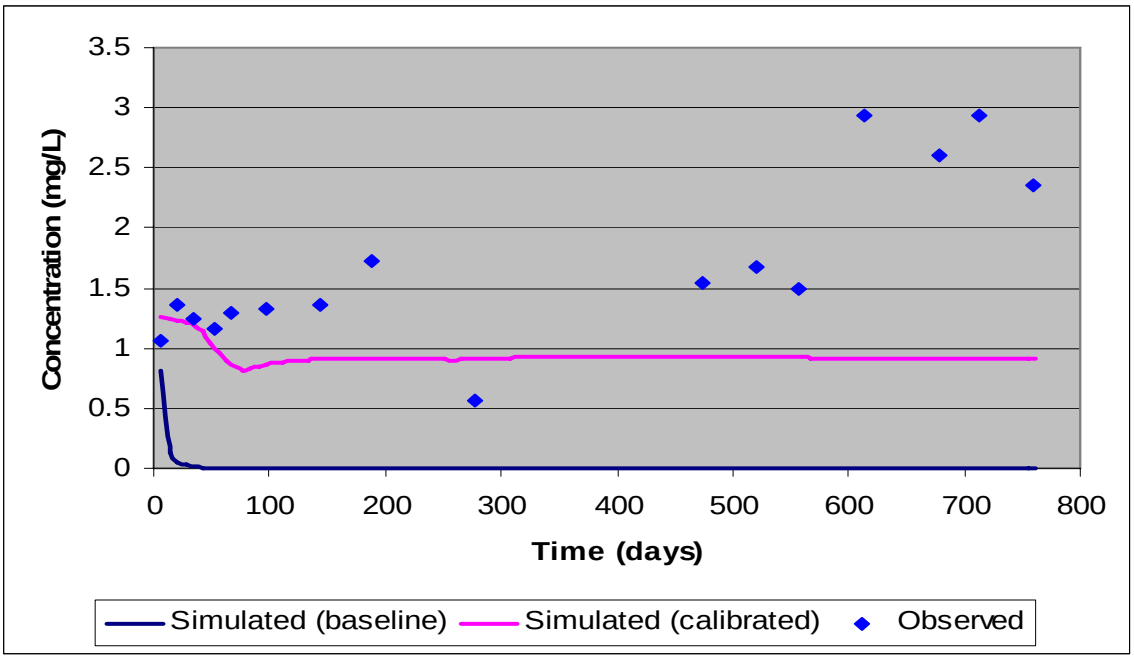


Figure 4.5 Oxygen Concentration vs Time at Well NMW3

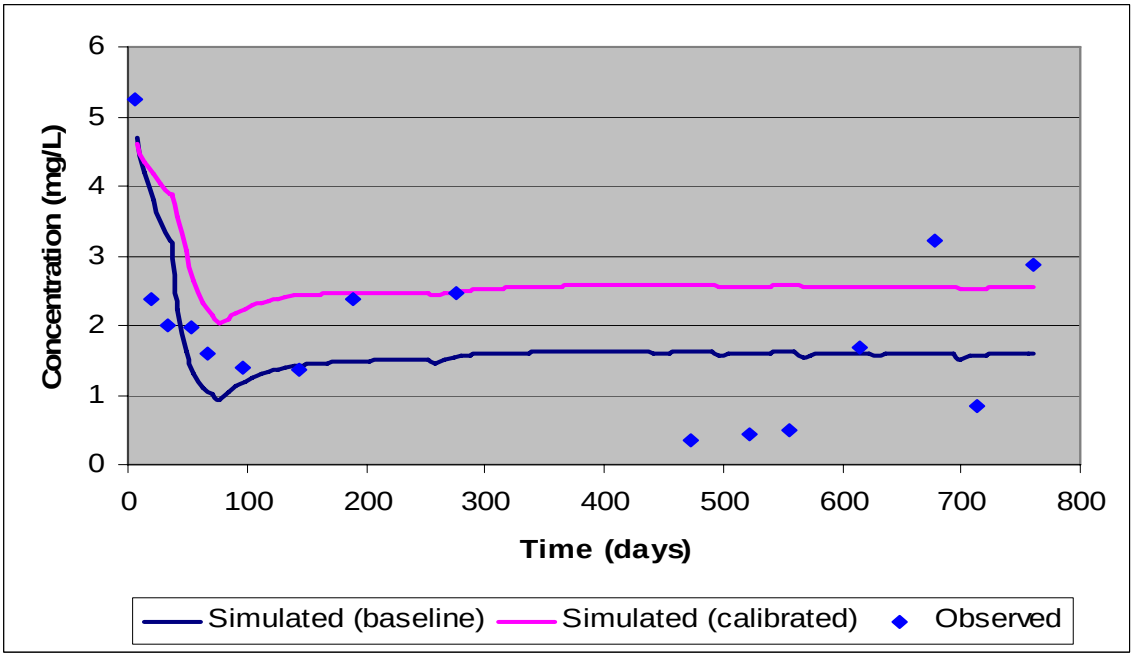


Figure 4.6 Nitrate Concentration vs Time at Well NMW3

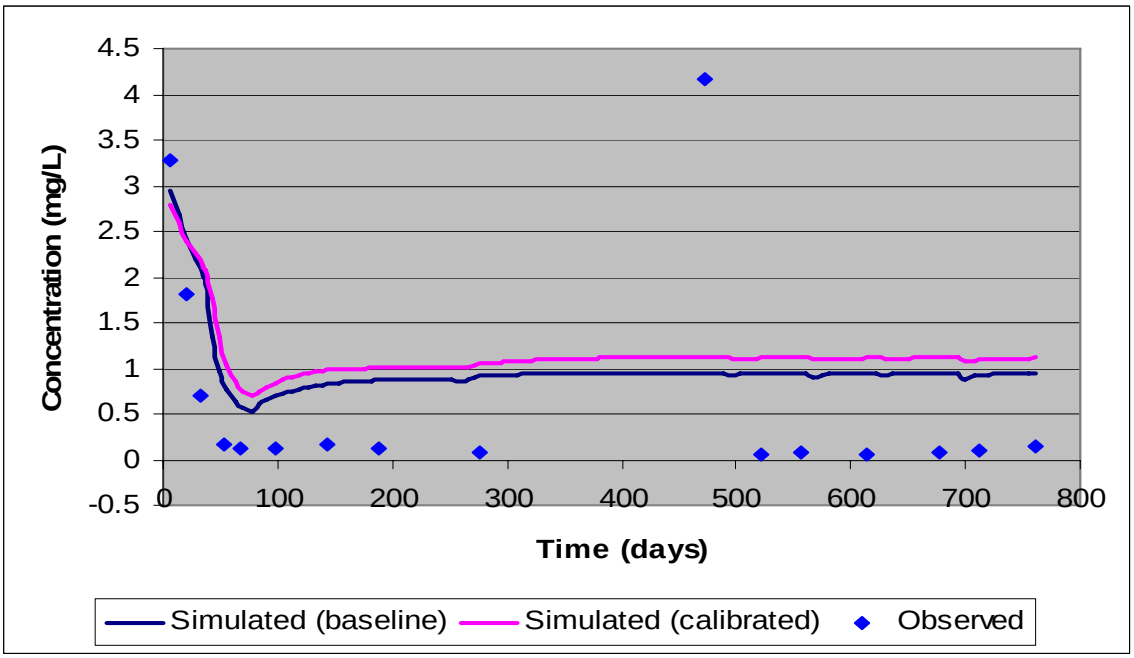


Figure 4.7 Perchlorate Concentration vs Time at Well NMW3

4.4.2 DEEP UPGRADIENT MONITORING WELL

NMW4 is a deep (80-100 ft bls) monitoring well located upgradient of the HFTWs. Figures 4.8 – 4.10 show measured and simulated oxygen, nitrate and perchlorate concentrations, respectively, versus time at NMW4. We see from Figures 4.8 and 4.9 that using the best-fit parameters improves the model's fit for both oxygen and nitrate data, compared to the baseline parameters. Use of the best-fit parameters results in little improvement for the perchlorate simulations. We also note from Figures 4.9 and 4.10 that the measured nitrate and perchlorate concentrations at this deep upgradient well are significantly higher than the concentrations predicted by the model.

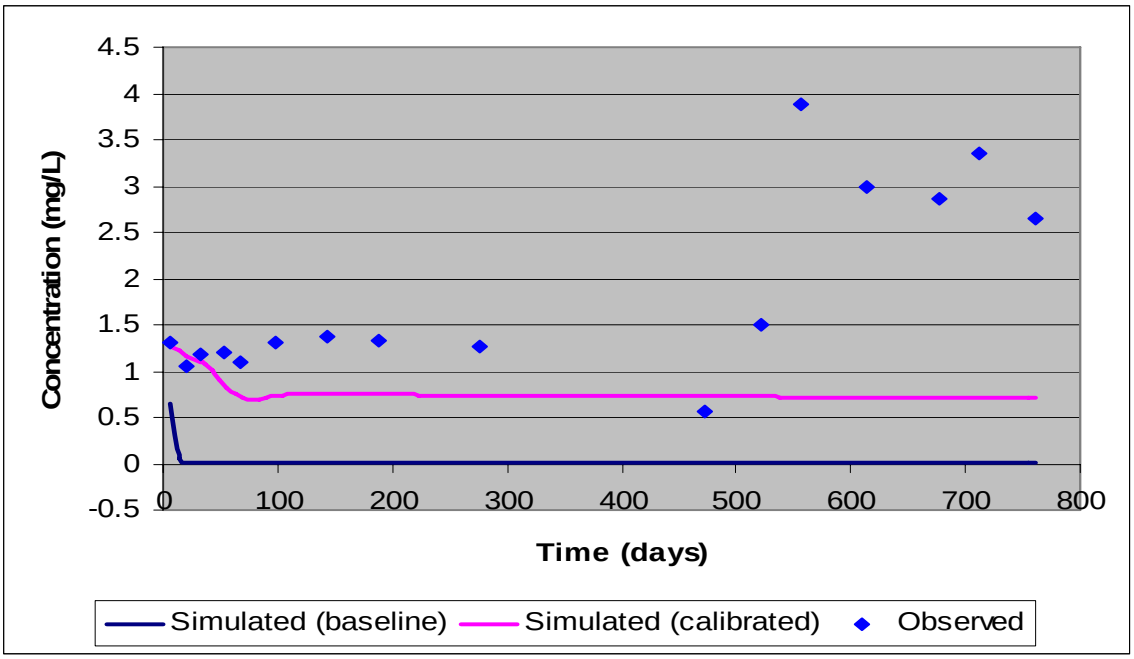


Figure 4.8 Oxygen Concentration vs Time at Well NMW4

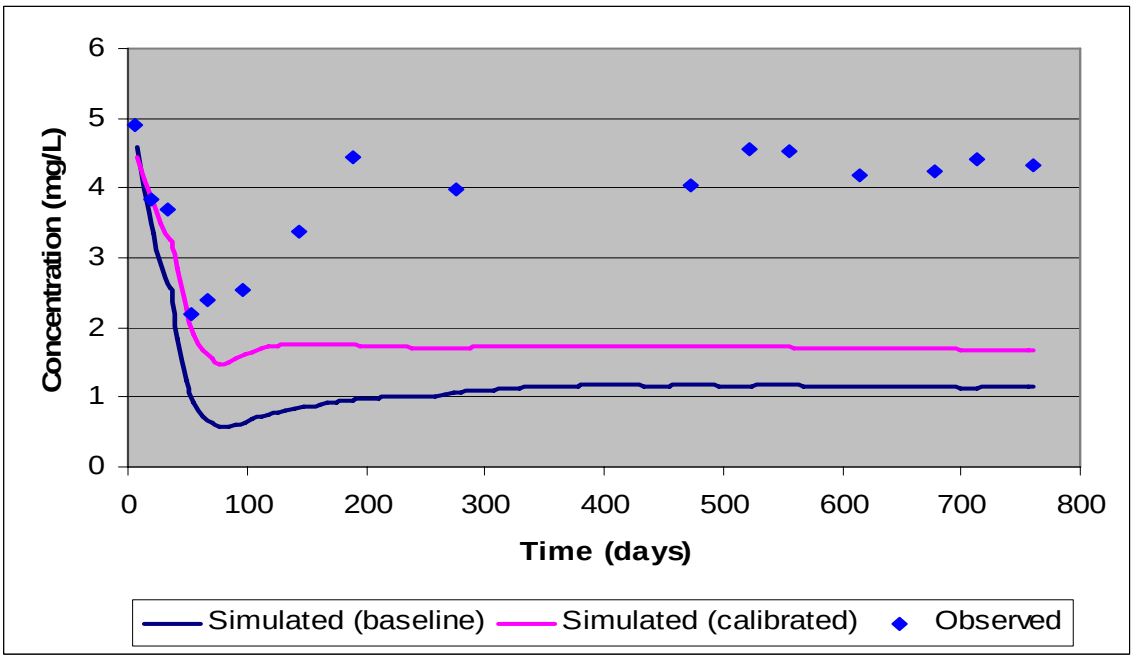


Figure 4.9 Nitrate Concentration vs Time at Well NMW4

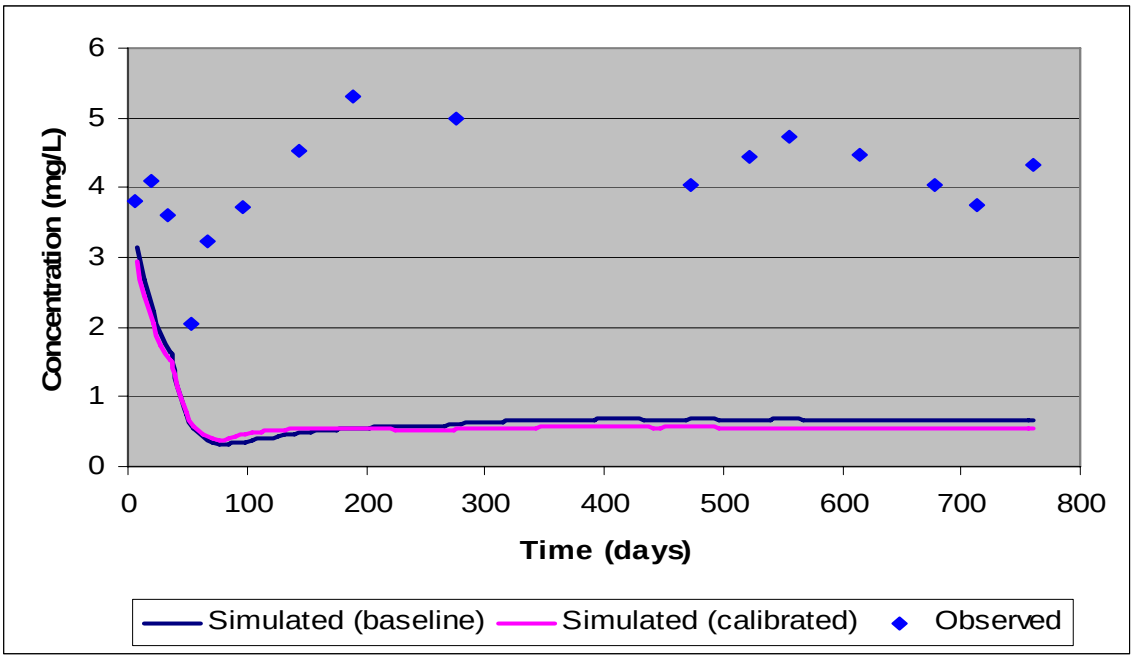


Figure 4.10 Perchlorate Concentration vs Time at Well NMW4

4.4.3 SHALLOW DOWNGRADIENT MONITORING WELLS

Monitoring well 3632 (52-57 ft bls) and NMW7 (46-61 ft bls) are shallow monitoring wells located downgradient of the upflow HFTW. Thus, these wells may be good indicators of the quality of treated water leaving the upflow HFTW. Figures 4.11 – 4.13 show measured and simulated oxygen, nitrate, and perchlorate concentrations, respectively, versus time at monitoring well 3632. We see from Figure 4.11 that using the best-fit parameters improves the model fit for the oxygen data, compared to the baseline parameters. Use of the best-fit parameters results in little improvement for the nitrate or perchlorate simulations. We also note from Figure 4.13 that the measured perchlorate concentrations at this shallow downgradient well are significantly less than the concentrations predicted by the model.

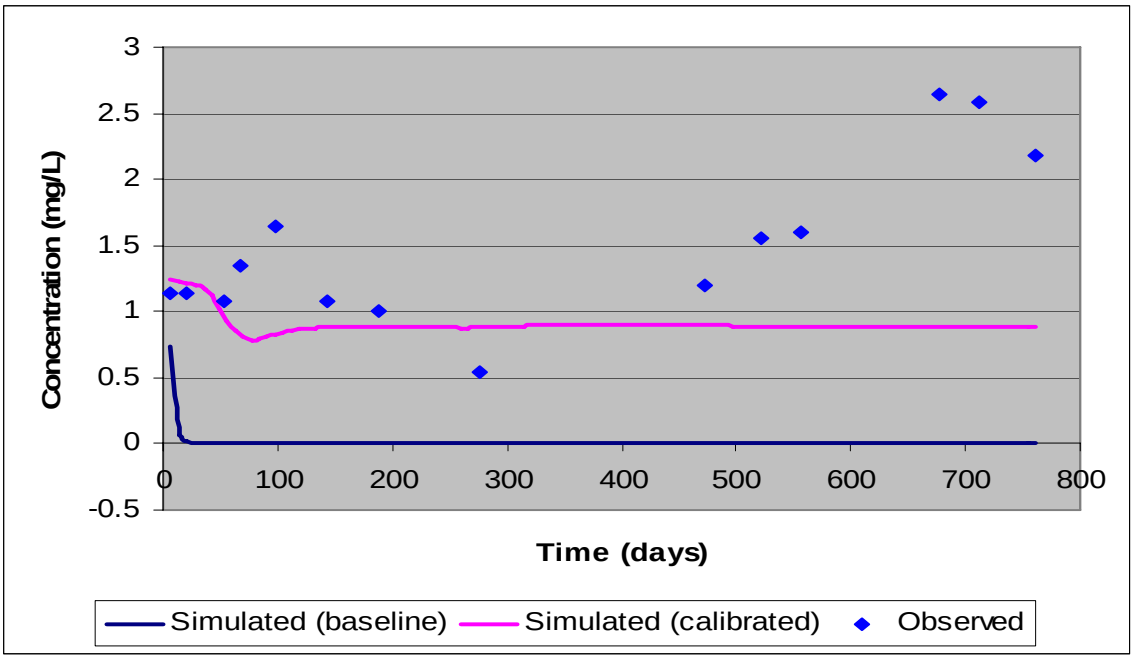


Figure 4.11 Oxygen Concentration vs Time at Well 3632

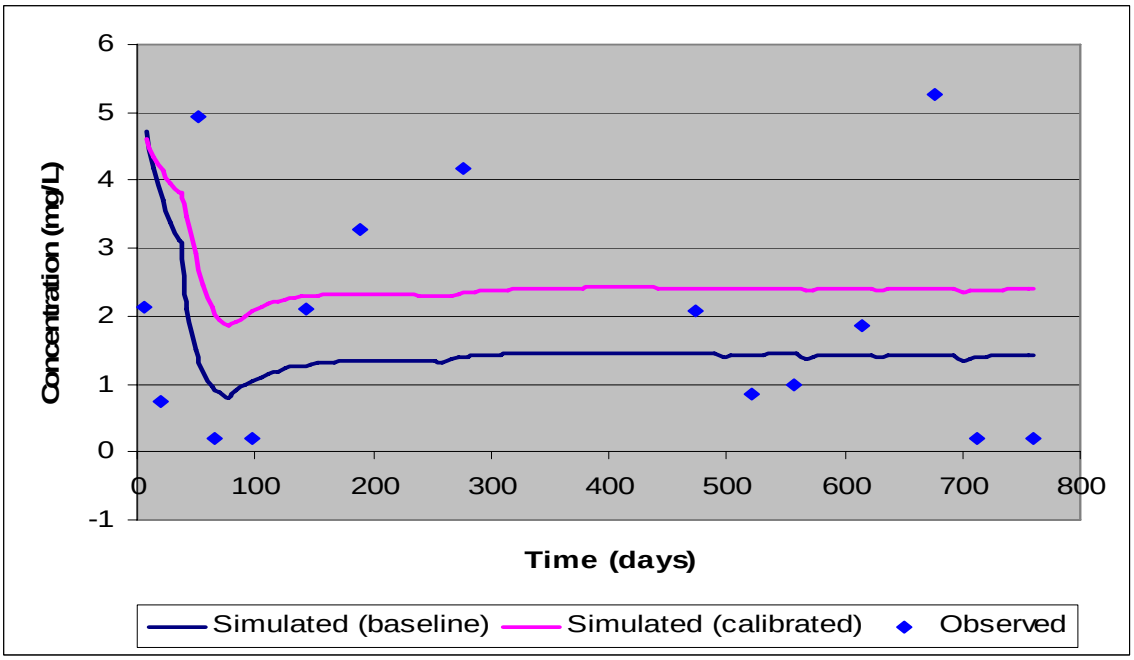


Figure 4.12 Nitrate Concentration vs Time at Well 3632

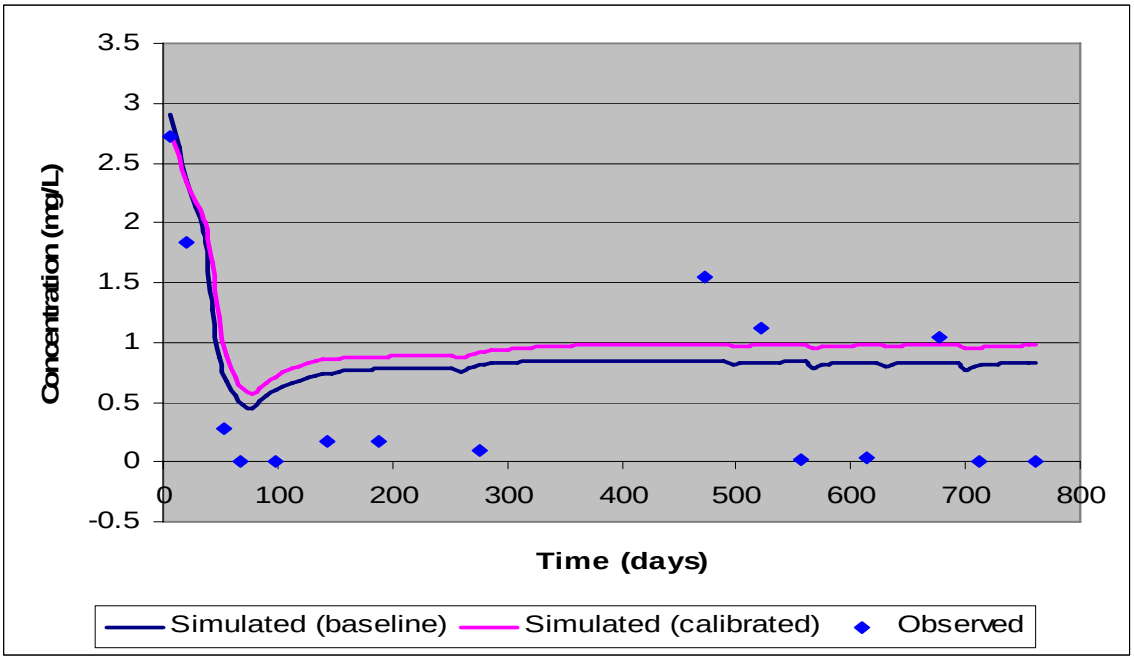


Figure 4.13 Perchlorate Concentration vs Time at Well 3632

NMW7 is a shallow well located further downgradient of the upflow HFTW than 3632. Figures 4.14 – 4.16 show measured and simulated oxygen, nitrate, and perchlorate concentrations, respectively, versus time at NMW7. Figure 4.14 indicates that using the best-fit parameters improves the model fit for the oxygen data, compared to the baseline parameters. Use of the best-fit parameters results in little improvement for the nitrate or perchlorate simulations. We also note from Figures 4.15 and 4.16 that the measured nitrate and perchlorate concentrations at this shallow downgradient well are significantly less than the concentrations predicted by the model.

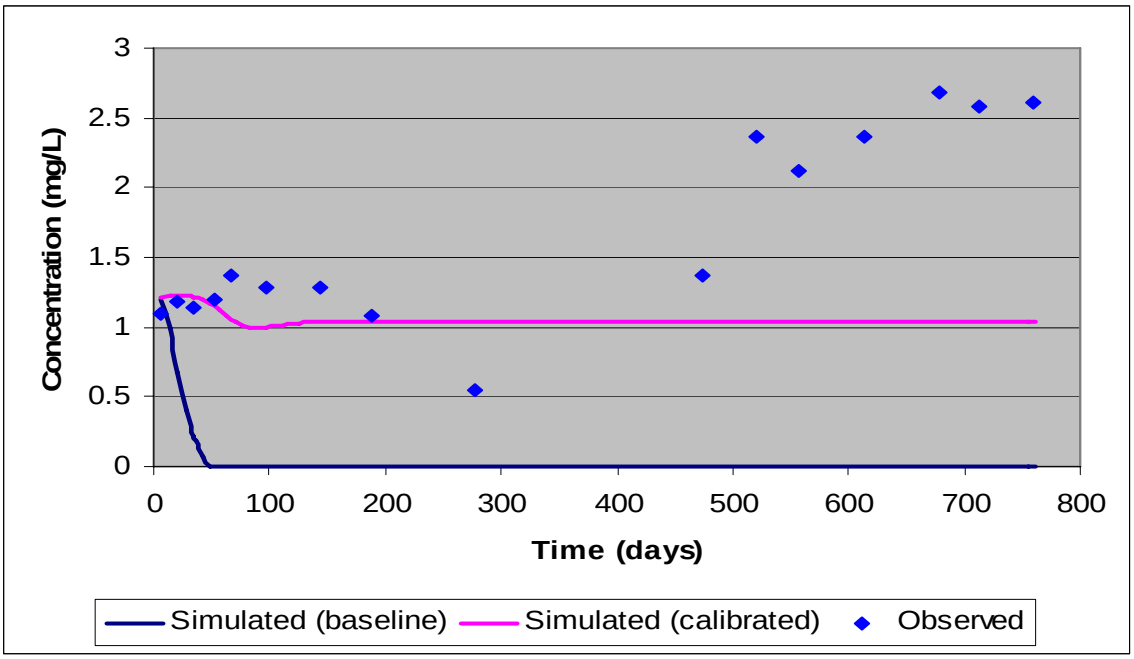


Figure 4.14 Oxygen Concentration vs Time at Well NMW7

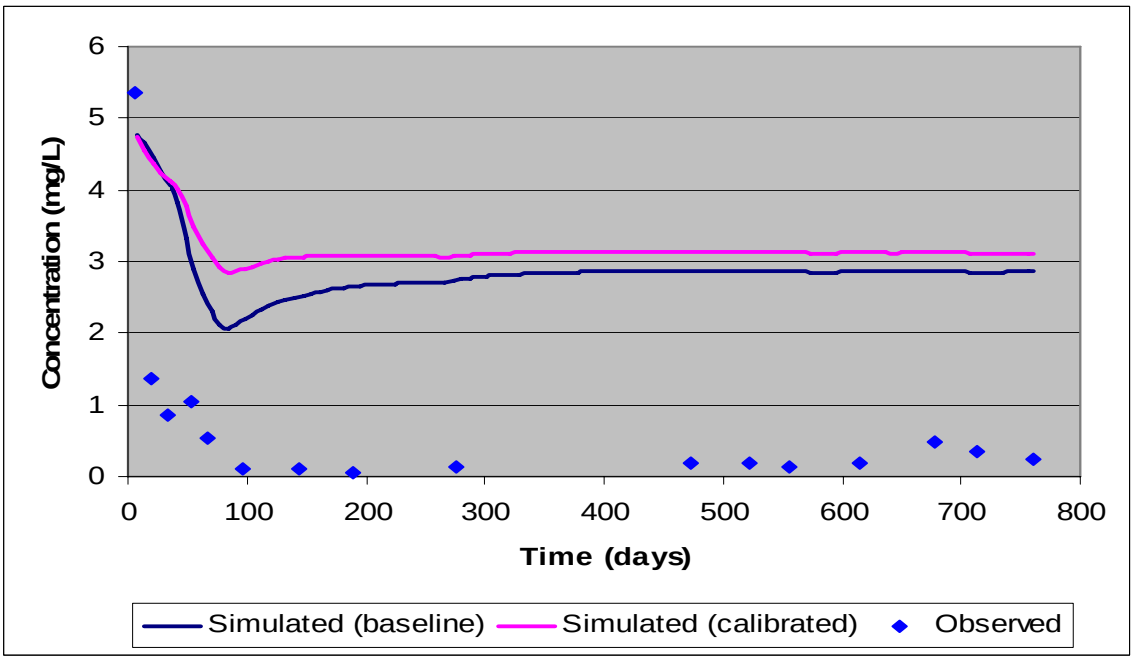


Figure 4.15 Nitrate Concentration vs Time at Well NMW7

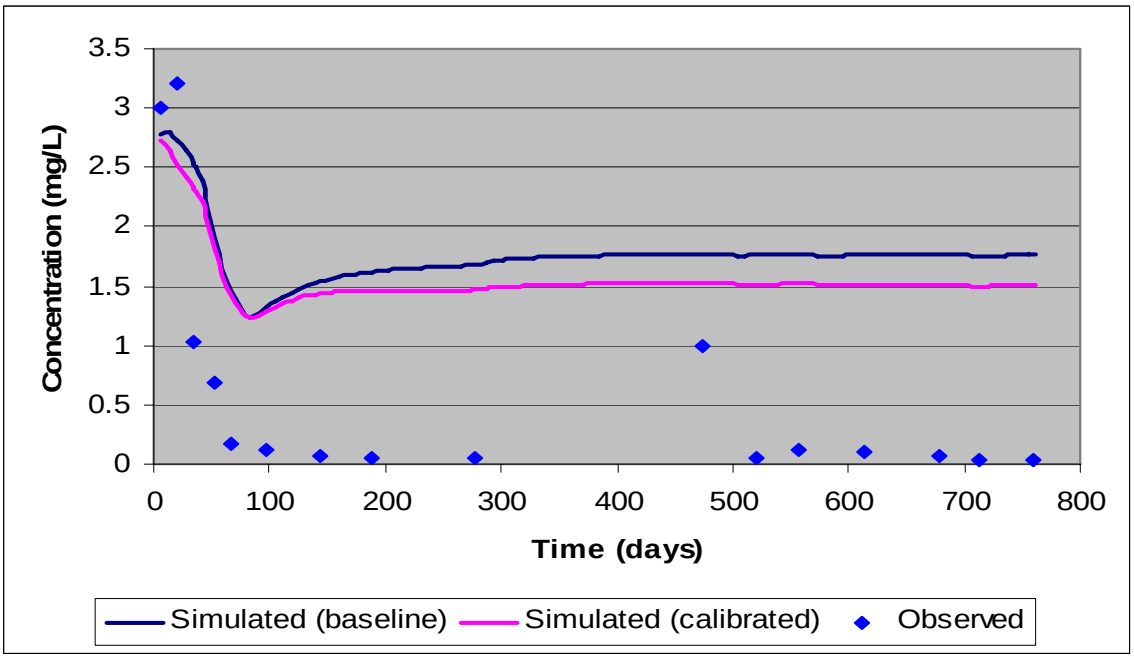


Figure 4.16 Perchlorate Concentration vs Time at Well NMW7

4.4.4 DEEP DOWNGRADIENT MONITORING WELLS

Monitoring wells 3519 (78-103 ft bls) and NMW10 (80-100 ft bls) are deep monitoring wells located downgradient of the downflow HFTW. Thus, these wells may be good indicators of the quality of treated water leaving the downflow HFTW. Figures 4.17 – 4.19 show measured and simulated oxygen, nitrate, and perchlorate concentrations, respectively, versus time at well 3519. We see from Figures 4.17 and 4.18 that using the best-fit parameters improves the model's fit for both oxygen and nitrate data, compared to the baseline parameters. Use of the best-fit parameters results in little improvement for the perchlorate simulations. We also note from Figure 4-19 that the measured perchlorate concentrations at this deep downgradient well are significantly higher than the concentrations predicted by the model.

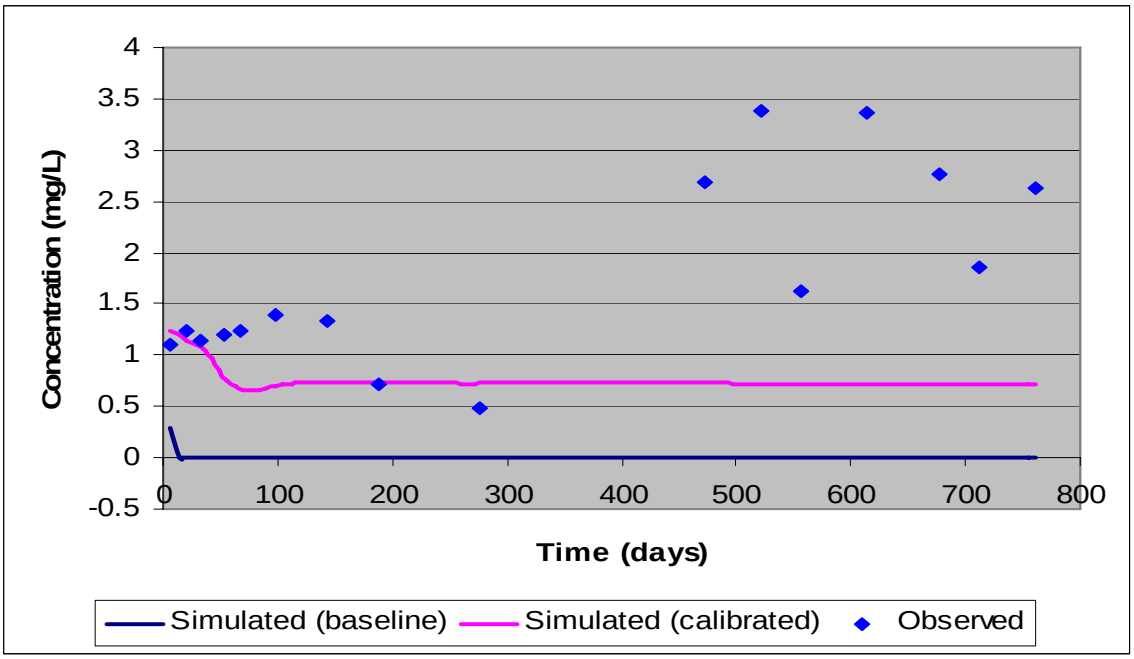


Figure 4.17 Oxygen Concentration vs Time at Well 3519

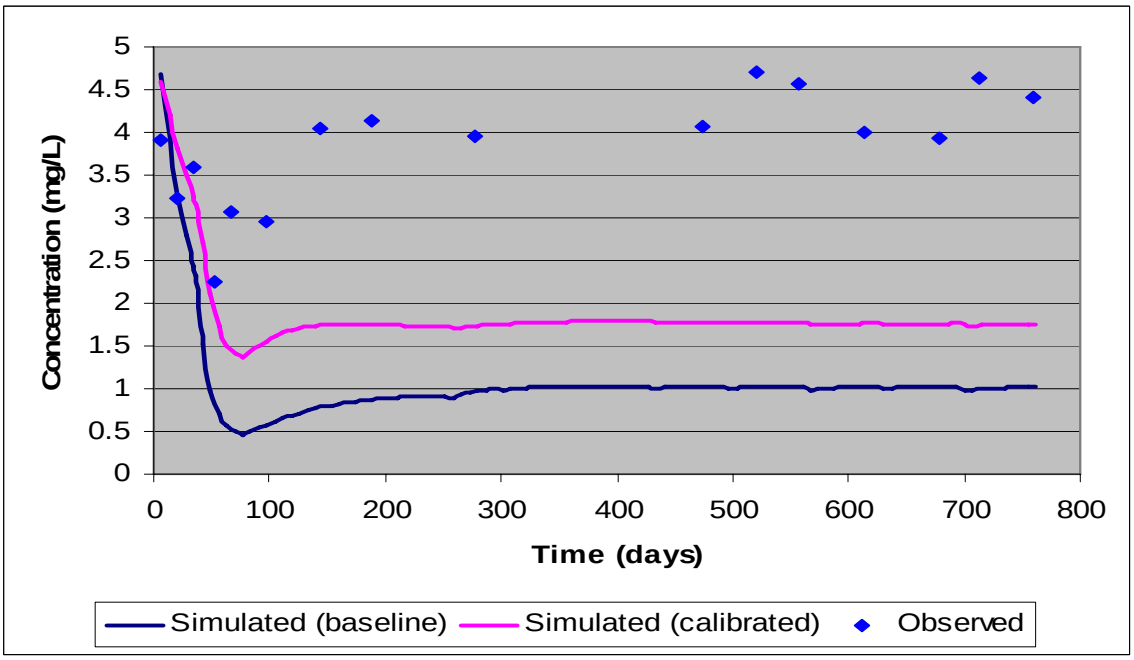


Figure 4.18 Nitrate Concentration vs Time at Well 3519

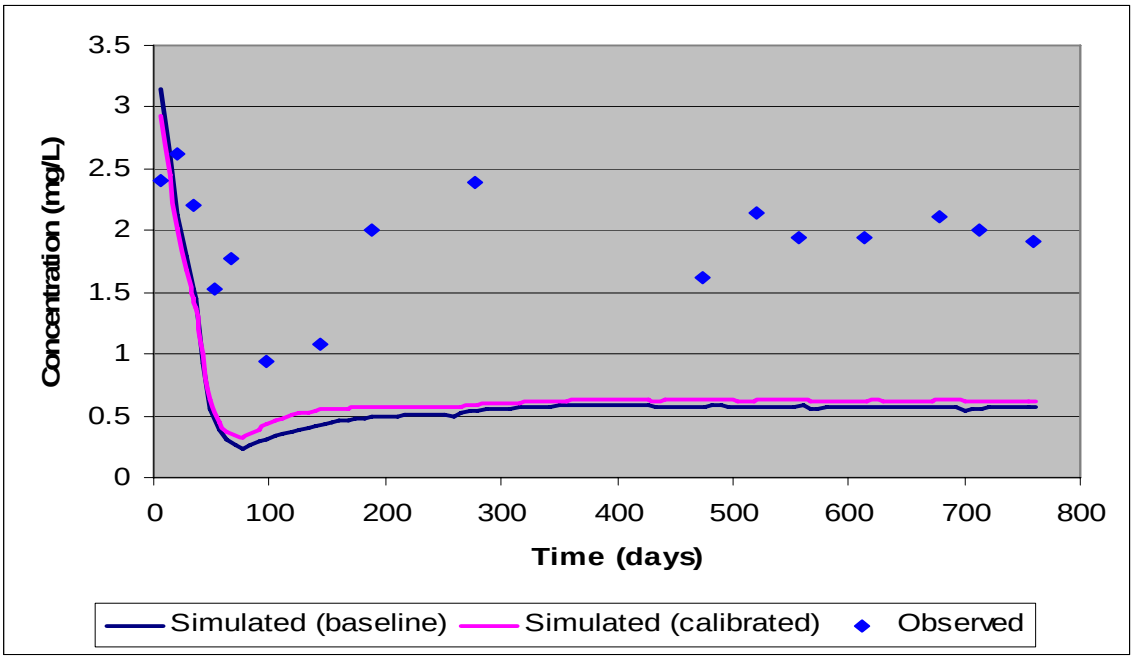


Figure 4.19 Perchlorate Concentration vs Time at Well 3519

NMW10 is a deep well located further downgradient of the downflow HFTW than 3519. Figures 4.20 – 4.22 show measured and simulated oxygen, nitrate, and perchlorate concentrations, respectively, versus time at NMW10. We see from Figure 4.20 that using the best-fit parameters improves the model fit for the oxygen data, compared to the baseline parameters, while Figure 4.21 and 4.22 show little improvement for the nitrate or perchlorate simulations. The model fits to the nitrate and perchlorate concentration data appear reasonable.

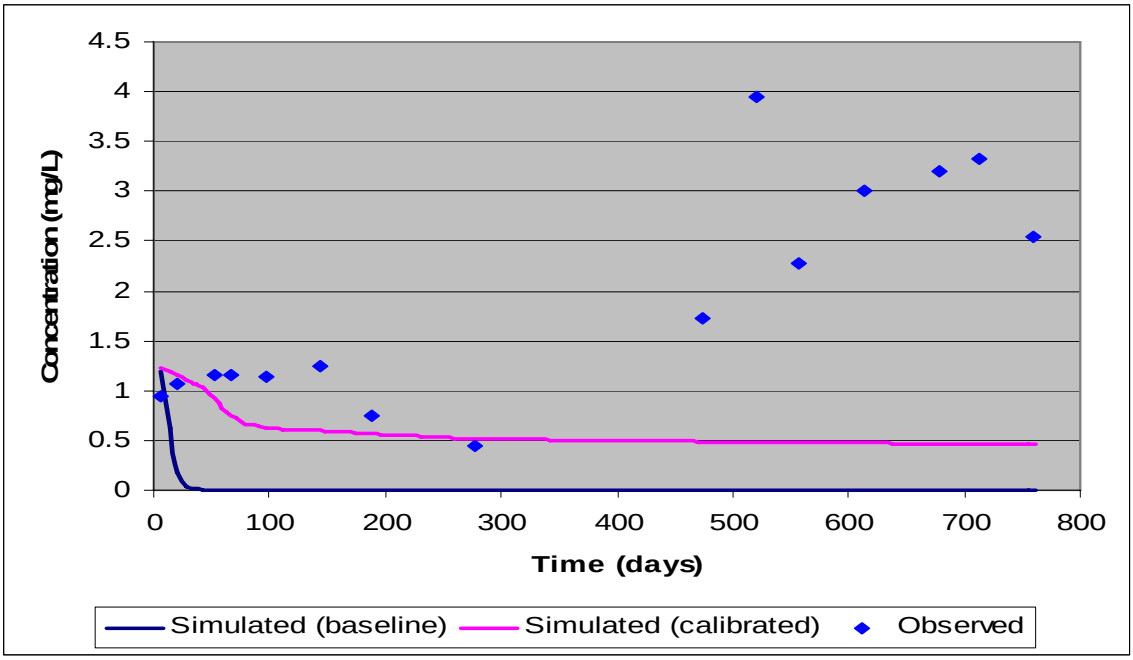


Figure 4.20 Oxygen Concentration vs Time at Well NMW10

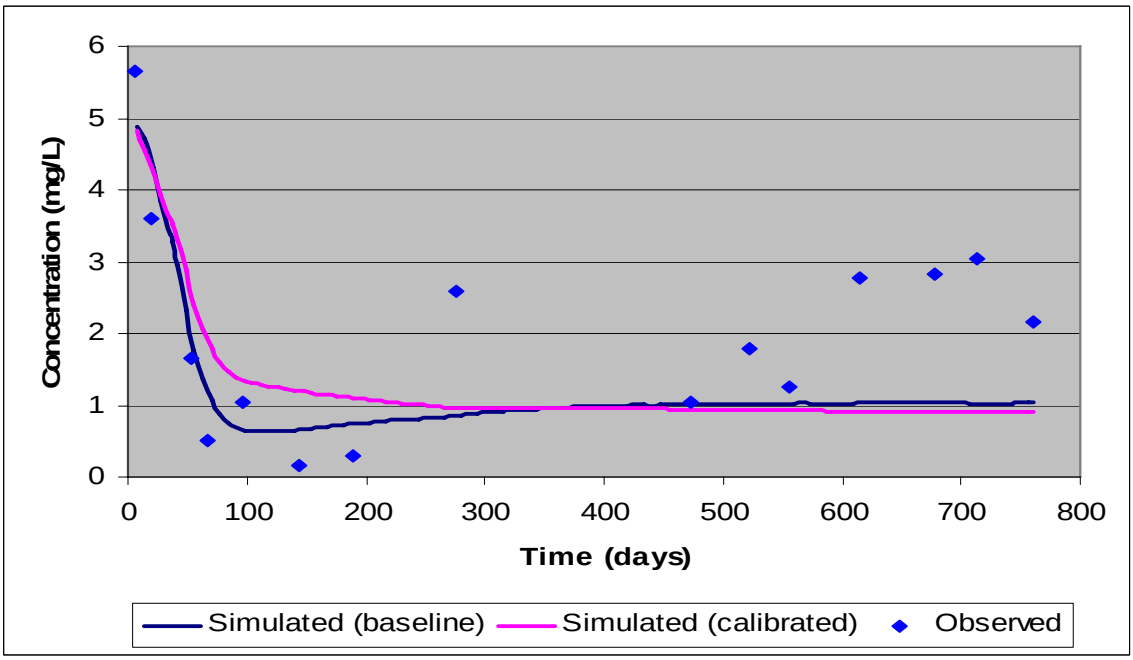


Figure 4.21 Nitrate Concentration vs Time at Well NMW10

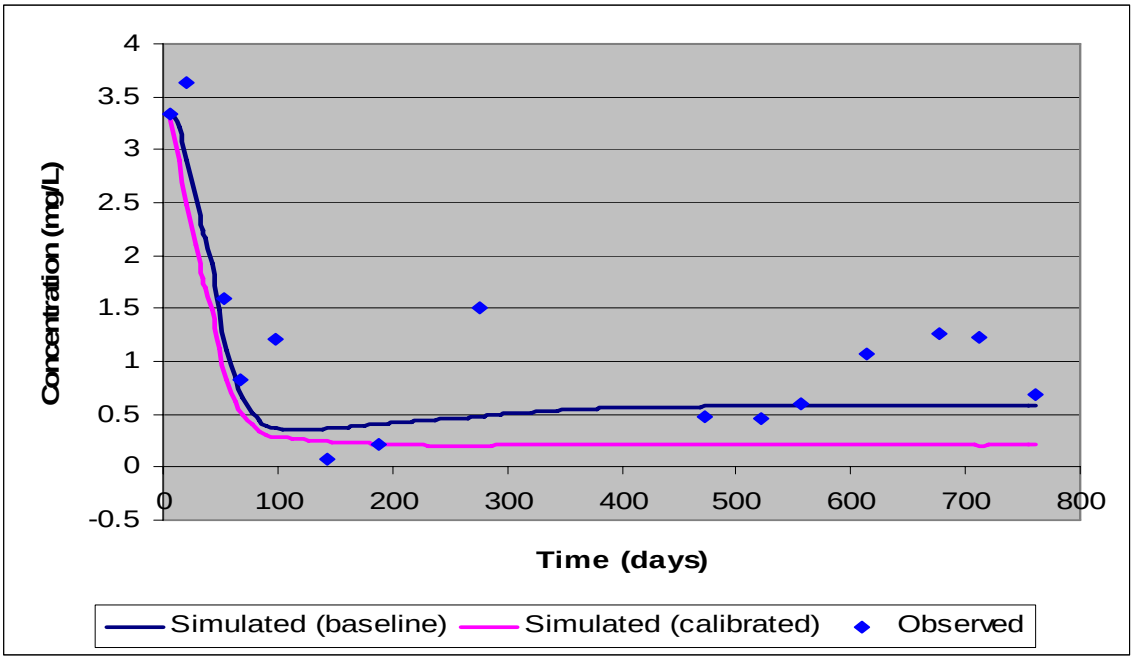


Figure 4.22 Perchlorate Concentration vs Time at Well NMW10

4.5 MODEL APPLICATION TO INVESTIGATE EFFECT OF DIFFERING SITE CONDITIONS ON TECHNOLOGY PERFORMANCE

The best-fit parameters obtained above were utilized in simulations of the technology at the two sites described in Section 3.5 and the results compared with the Aerojet site results. As there are no competing electron acceptors at Site 1, only perchlorate breakthrough curves will be evaluated at the different monitoring wells.

4.5.1 PERCHLORATE CONCENTRATION VS TIME RESULTS

Figures 4.23 through 4.28 indicate that perchlorate concentrations at Site 1 are the highest at all monitoring wells, even though there are no competing electron acceptors present at the site. A potential reason for these results is that due to the high conductivity at the site, the groundwater is flowing through the area so fast that the added substrate is being diluted to the point that an effective bioactive zone cannot be established.

The simulations at all monitoring wells show that the technology performance at Site 2 is generally similar to the performance at the Aerojet site, even with the increased concentrations of electron acceptors and low conductivity. One possible explanation is that the low conductivity of the site is restricting the amount of perchlorate entering the site while at the same time allowing the substrate-amended groundwater more time in the bioactive zones surrounding the HFTWs.

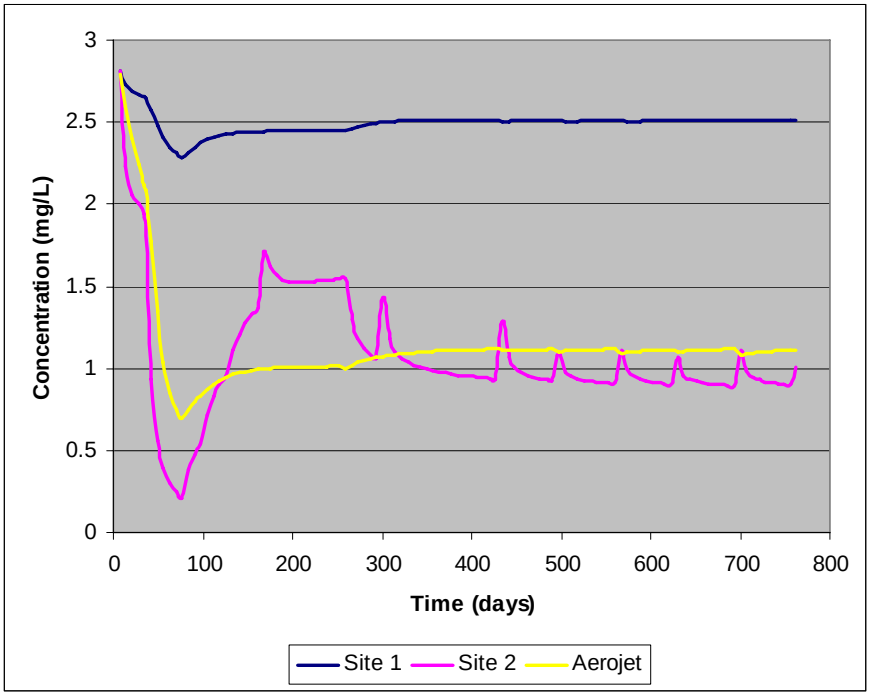


Figure 4.23 Simulated Perchlorate Concentration vs Time at Well NMW3 for Hypothetical Sites 1 and 2 and Aerojet

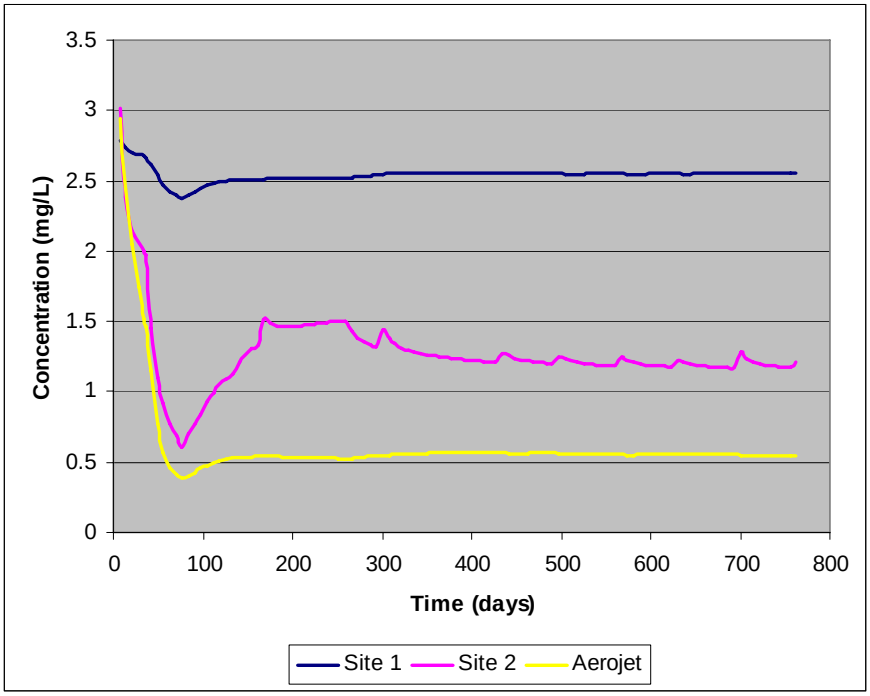


Figure 4.24 Simulated Perchlorate Concentration vs Time at Well NMW4 for Hypothetical Sites 1 and 2 and Aerojet

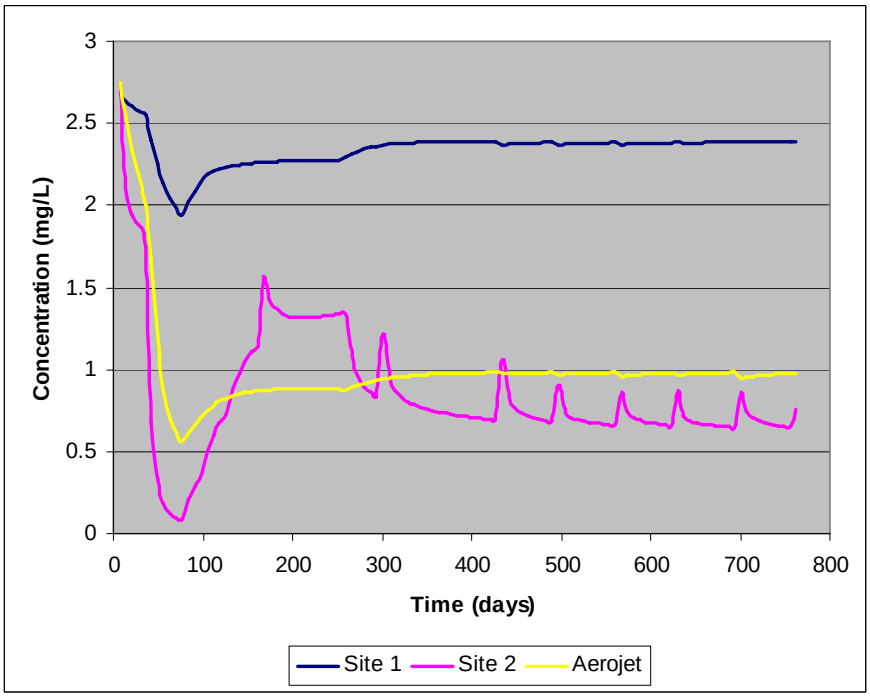


Figure 4.25 Simulated Perchlorate Concentration vs Time at Well 3632 for Hypothetical Sites 1 and 2 and Aerojet

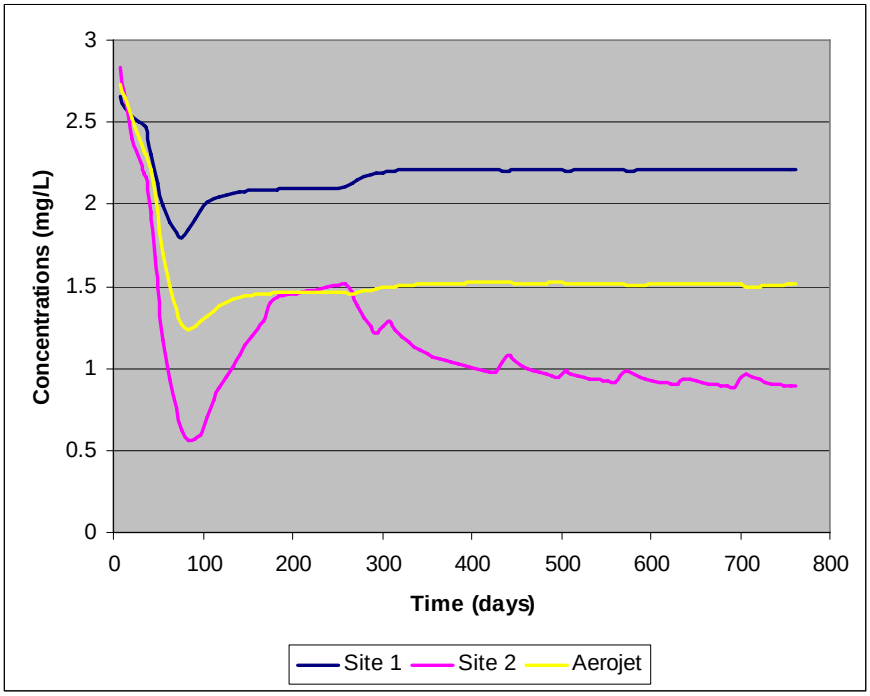


Figure 4.26 Simulated Perchlorate Concentration vs Time at Well NMW7 for Hypothetical Sites 1 and 2 and Aerojet

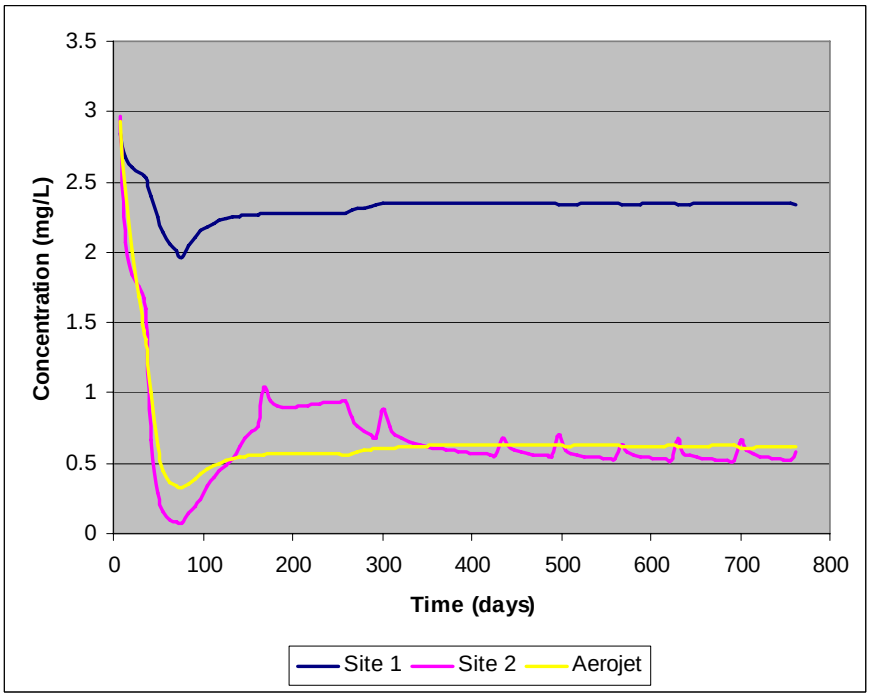


Figure 4.27 Simulated Perchlorate Concentration vs Time at Well 3519 for Hypothetical Sites 1 and 2 and Aerojet

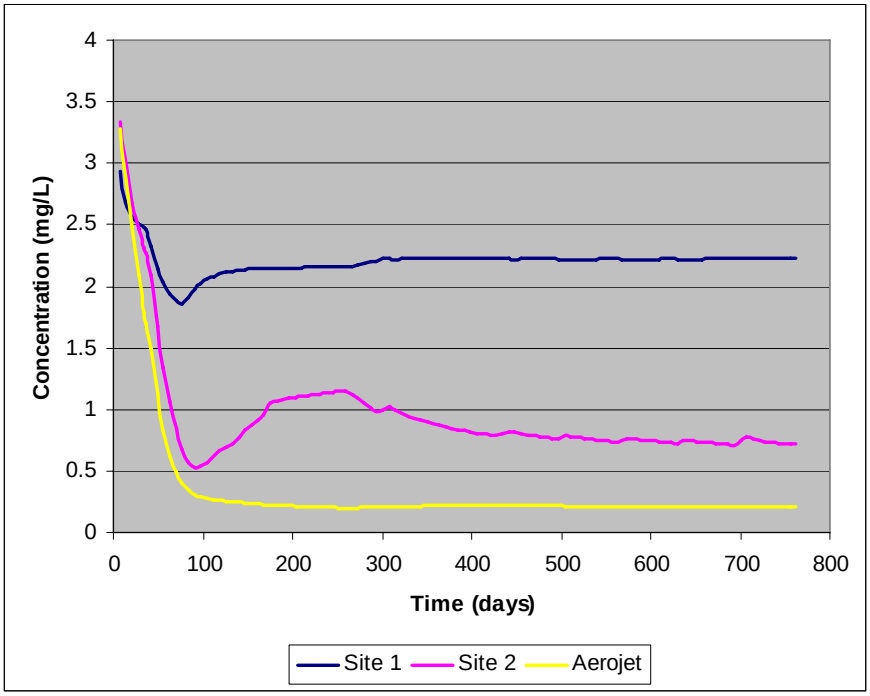


Figure 4.28 Simulated Perchlorate Concentration vs Time at Well NMW10 for Hypothetical Sites 1 and 2 and Aerojet

4.5.2 PERCHLORATE CONTOUR PLOTS

Figures 4.29 through 4.31 show perchlorate contour plots at model layer 5 and at three different times (63, 182, and 364 days, respectively) for the two hypothetical sites, as well as the Aerojet site. Layer 5 of the model corresponds with the lower screen of the HFTWs. Figure 4.29 shows that, at day 63, Site 2 with the high concentrations of electron acceptors and low hydraulic conductivity, has a smaller perchlorate "hole" than the Aerojet site. As time progresses the size of the perchlorate hole increases, though it still remains smaller than the hole at the Aerojet Site at day 182 and day 364.

The simulation results for Site 1, with no competing electron acceptors and high conductivity, show little change from day 63 through day 364. This seems to indicate that steady state is reached quickly with little additional growth of the hole. Despite the size of Site 1's perchlorate hole, the breakthrough curves indicate that the hole is

"shallow", i.e. perchlorate is not being reduced much below the 2.4 mg/L contour line. Based upon the size of the contour hole and the breakthrough curves it appears that the Site 2 and Aerojet perchlorate holes are much "deeper" than Site 1's, i.e. more perchlorate is being reduced.

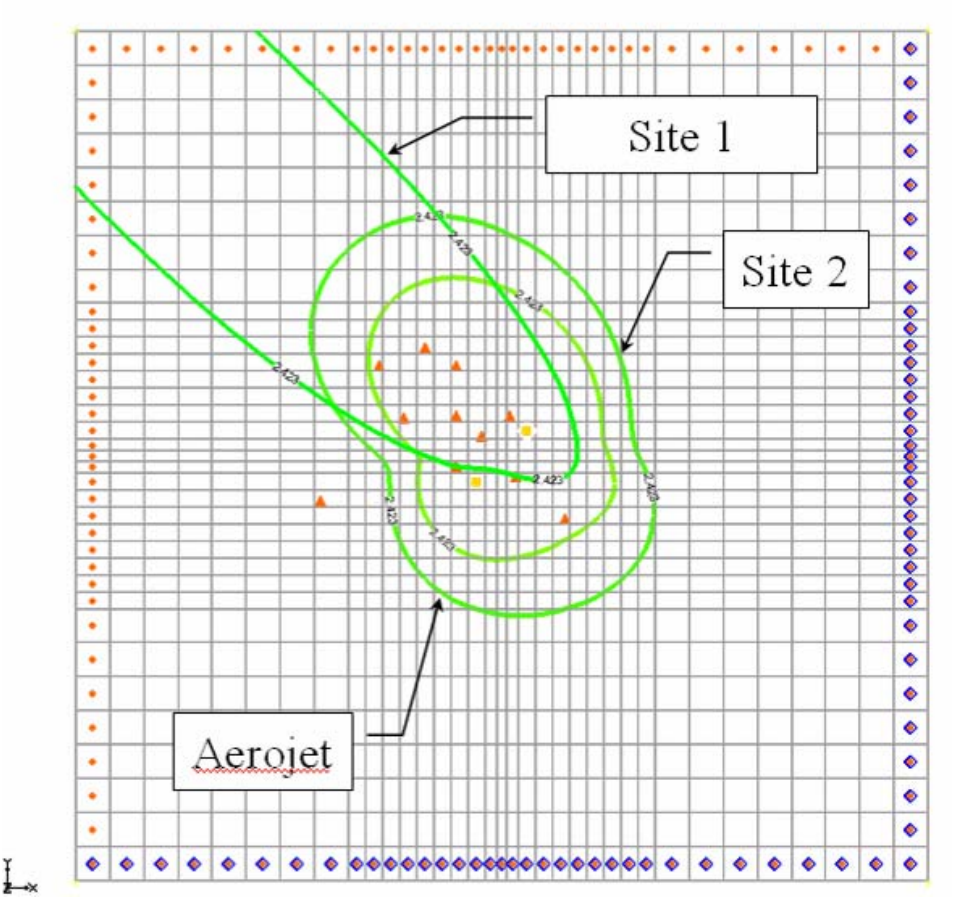


Figure 4.29 Perchlorate "Hole" (defined by 2.4 mg/L contour) at Layer 5 and Day 63

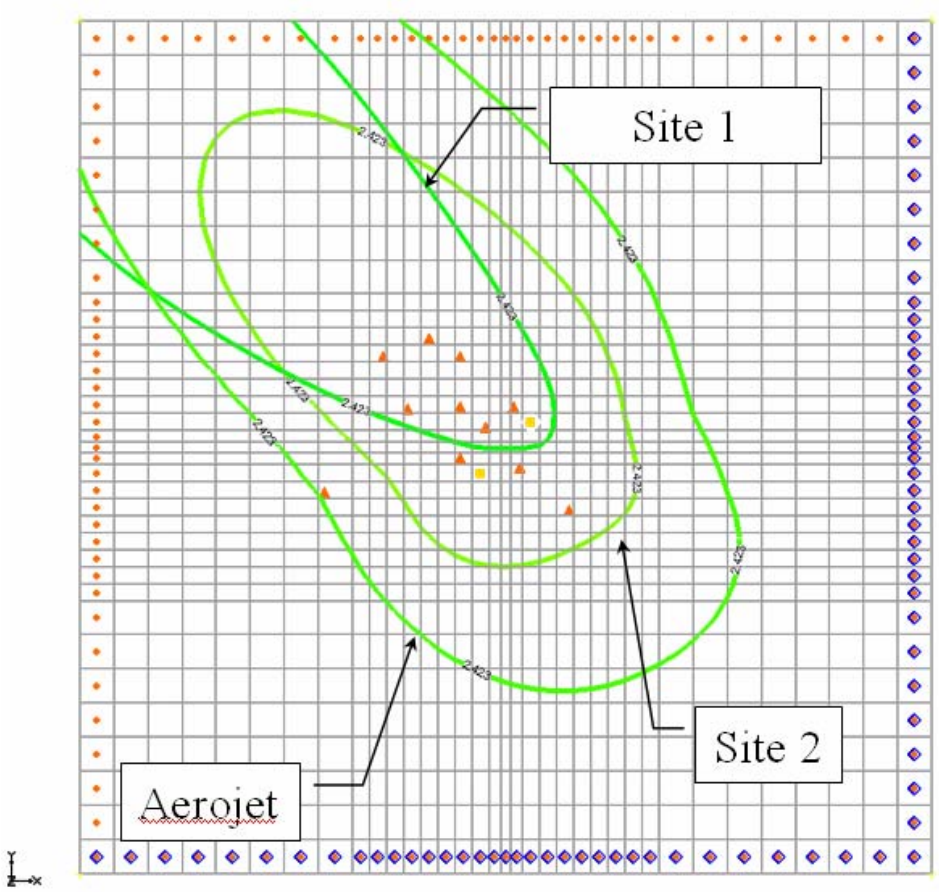


Figure 4.30 Perchlorate "Hole" (defined by 2.4 mg/L contour) at Layer 5 and Day 182

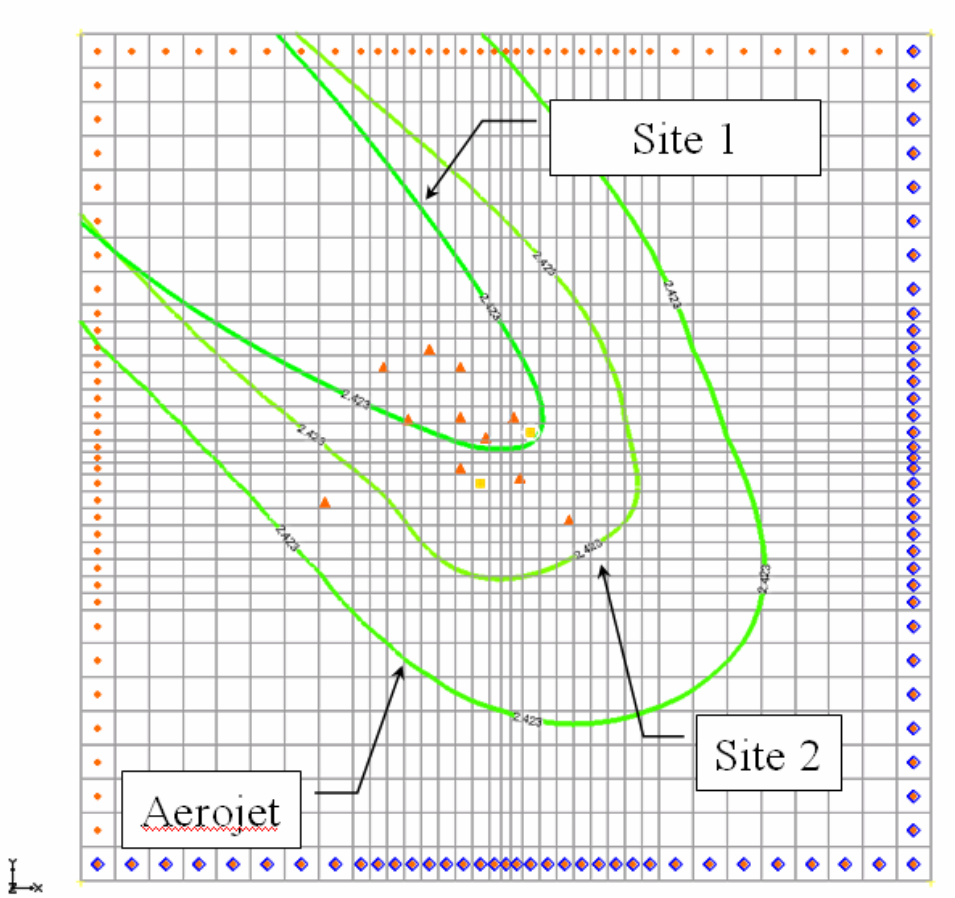


Figure 4.31 Perchlorate "Hole" (defined by 2.4 mg/L contour) at Layer 5 and Day 364

5.0 CONCLUSIONS

5.1 SUMMARY

In this thesis, data obtained from a field evaluation of an innovative technology that applied HFTWs to mix electron donor into perchlorate-contaminated groundwater to stimulate *in situ* biodegradation, were modeled. The first 113 days of field data were used to calibrate the technology model, and then the model was used to predict measured perchlorate concentrations, as well as the concentrations of competing electron acceptors, over the entire 761 days of the evaluation. The parameterized model was then used to simulate how well the technology would perform under various site conditions.

5.2 CONCLUSIONS

- **The technology model appears to simulate the overall behavior of perchlorate and competing electron acceptors at the Aerojet site.** The technology model successfully demonstrated that perchlorate reduction occurs at the site, although the accuracy of the model varies between the shallow and deep aquifers. Using the best-fit parameters obtained by calibrating the model to data measured over the initial period of the field evaluation, oxygen concentration predictions are improved over the predictions obtained using baseline parameter values, while little improvement was seen for model predictions of nitrate and perchlorate concentrations. In general, the model appears to overestimate performance of the HFTW system in the deep aquifer while underestimating its performance in the shallow aquifer. One possible reason for this may be the

accuracy with which the model simulates groundwater flow at the site. The flow model assumes steady-state and is based on fitting layer hydraulic conductivities to pump test results. It does not incorporate surface recharge or seasonal variations, and regional flow is assumed to be horizontal. These assumptions of the flow model may be the cause of the differences between measured and simulated perchlorate concentrations. In particular, the underprediction of perchlorate concentrations in the deep aquifer zones and overprediction in the shallow zones may be due to vertical (downward) flows that the model doesn't account for.

- **Specific parameters within the technology model have a greater effect on model results than others.** Sensitivity analyses indicated that the model was most sensitive to the k_{max} parameter and insensitive to the K_i^{oxy} parameter. With k_{max} having such a significant impact on the model results, it appears additional research is needed to measure k_{max} more accurately. As the technology model proved insensitive to certain parameters (e.g. K_i^{oxy}), the dual-Monod assumption the model is based upon may need to be reevaluated to determine whether or not the technology model may be simplified to a simple Monod or first-order equation.
- **The technology is effective at locations with moderate levels of competing electron acceptors and low hydraulic conductivity.** Results indicated that at locations with a high hydraulic conductivity and no competing electron acceptors, the substrate either becomes too diluted or there's insufficient time to establish an effective bioactive zone within the area of interest. The model appeared to reduce

perchlorate to lower levels at the site with lower hydraulic conductivity and in the presence of competing electron acceptors.

- **A genetic algorithm that uses the RMSE of all the data as the objective function for calibration has the potential to overweight the fit of the model to measured concentration data of one electron acceptor at the expense of fitting data from the other acceptors.** By combining all model errors into one term, the genetic algorithm focused on an overall reduction in errors. Perhaps because of the way the dual-Monod multi-electron acceptor equations are structured, with oxygen's concentration impacting both nitrate and perchlorate reductions, oxygen appeared to be given additional weighting towards error reduction, so the calibrated model was better at fitting the oxygen data than the nitrate and perchlorate data.

5.3 RECOMMENDATIONS

- **Optimize the HFTW system.** Use the calibrated model from this field study to investigate how to engineer an optimized HFTW system. That is, determine the pumping rates, electron donor injection schedule and well configuration that would result in "best" (cheapest, most effective) system performance.
- **Refine the flow model.** As noted above, the flow model makes various assumptions that may result in the differences between measured and simulated perchlorate concentrations. A tracer test may be useful in better defining the flow model.

- **Modify model.** Sensitivity analyses from this study indicated that certain processes in the model, like inhibition from competing electron acceptors, may not significantly affect model results. Conversely, other processes not incorporated in this model (e.g. bioclogging) may significantly affect results. Further study and analysis of the field evaluation results are needed to contribute to model development.
- **Develop a calibration method that allows for better fitting of all the electron acceptor data simultaneously.** As noted in the conclusions, the objective function used in this study had the effect of overweighting the oxygen data at the expense of the nitrate and perchlorate data. The application of weighting factors or the development of a multi-objective optimization may improve the fit of model simulations to all data simultaneously.

- **Investigate whether genetic algorithm efficiency can be improved by limiting the number and range of parameters to be optimized.** As initially configured, the GA evaluated nine parameters over a wide range, using an inordinate amount of computer resources. Focusing the GA on the most important parameters *(e.g.* k_{max}) over a more focused range of values my improve GA performance.

APPENDIX A: DETAILED DESCRIPTION OF THE PARR (2002) HORIZONTAL FLOW TREATMENT WELL (HFTW) TECHNOLOGY MODEL

A.1 INTRODUCTION

The technology model developed by Parr (2002) combined the biological treatment process modeled by the Envirogen dual-Monod multi-electron acceptor model coupled with the Huang and Goltz (1998) numerical HFTW model. The following is a detailed description of technology model as developed by Parr (2002). The technology model referenced previously is a combination of transport equations (A.1-A.4), the biological reaction equations (A.10-A.12) and the biomass growth equation (A.13)

A.2 FLOW AND TRANSPORT MODEL

The numerical flow and transport model used in this study is based on the model developed by Huang and Goltz to simulate aerobic biodegradation of trichlorethene in an HFTW system. It is a three-dimensional model that combines steady-state flow, advective/dispersive transport of dissolved species, equilibrium sorption, and biodegradation. The model assumes microorganisms are stationary, while oxygen, nitrate, perchlorate and the electron donor are affected by advection, dispersion, and in the case of the donor, sorption.

Equations A.1 - A.4 are the three-dimensional advection/dispersion equations used in the numerical model to describe transport of the donor and the three electron acceptors (oxygen, nitrate, and perchlorate).

$$\frac{\partial C^{don}}{\partial t} = D \cdot \nabla^2 C^{don} - v \cdot \nabla C^{don} + r_{don} \quad \text{(A.1)}$$

$$\frac{\partial C^{oxy}}{\partial t} = D \cdot \nabla^2 C^{oxy} - v \cdot \nabla C^{oxy} + r_{oxy} \quad \text{(A.2)}$$

$$\frac{\partial C^{nit}}{\partial t} = D \cdot \nabla^2 C^{nit} - v \cdot \nabla C^{nit} + r_{nit} \quad \text{(A.3)}$$

$$\frac{\partial C^{per}}{\partial t} = D \cdot \nabla^2 C^{per} - v \cdot \nabla C^{per} + r_{per} \quad \text{(A.4)}$$

Dispersion, which is not quantitatively important to this study, was modeled using numerical dispersion and is estimated in the x, y and z directions as

$$D_{x,y,z} = \frac{v_{x,y,z}\Delta\left(d_{x,y,z}\right)}{2} + \frac{\left(v_{x,y,z}\right)^2 \Delta t}{2} \quad \text{(A.5)}$$

The last term on the right hand side of Equations A.1 through A.4 are the sink terms for the biodegradation reactions. As applied to perchlorate remediation, the last term represent biodegradation as modeled using the dual-Monod multi-electron acceptor biological submodel described in the electron donor and electron acceptor sections.

A.3 ELECTRON DONOR

The rate of utilization of the electron donor is described below. The modified dual-Monod model attempts to simulate the effect of competition between multiple electron acceptors on donor and acceptor utilization, and microbial growth.

$$r_{don} = \frac{dC^{don}}{dt} = -X \cdot (r_{don,oxy} + r_{don,nit} + r_{don,per}) \quad \text{(A.6)}$$

Note that r_{don} is the rate of donor consumption (in units of donor mass per volume per time) in contrast to $r_{don,oxy}$, $r_{don,nit}$, and $r_{don,per}$, which are defined below as specific rates of donor utilization (in units of donor mass per biomass per time):

$$r_{don,oxy} = k_{max}^{don/oxy}\left[\frac{C^{don}}{K_S^{don/oxy} + C^{don}}\right]\cdot\left[\frac{C^{oxy}}{K_S^{oxy} + C^{oxy}}\right] \quad \text{(A.7)}$$

$$r_{don,nit} = k_{max}^{don/nit}\left[\frac{C^{don}}{K_S^{don/nit} + C^{don}}\right]\cdot\left[\frac{C^{nit}}{K_S^{nit} + C^{per}}\right]\cdot\left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}}\right] \quad \text{(A.8)}$$

$$r_{don,per} = k_{max}^{don/per}\left[\frac{C^{don}}{K_S^{don/per} + C^{don}}\right]\cdot\left[\frac{C^{per}}{K_S^{per} + C^{per}}\right]\cdot\left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}}\right]\cdot\left[\frac{K_i^{nit}}{K_i^{nit} + C^{nit}}\right] \quad \text{(A.9)}$$

A.4 ELECTRON ACCEPTORS

The rate of utilization of the electron acceptors is modeled below. It can be seen that these rates are directly linked to the rate of utilization of the donor through a factor (F), which is the stoichiometric yield coefficient for the electron donor-electron acceptor

reaction. Assuming $k_{max} = k_{maxdon/per} = k_{maxdon/nit} = k_{maxdon/oxy}$, and $K_s^{don} = K_s^{don/per} = K_s^{don/nit} = K_s^{don/oxy}$ the equations are as follows:

Oxygen

$$r_{oxy} = \frac{dC^{oxy}}{dt} = -X \cdot \left(F_{oxy} \cdot r_{don,oxy}\right)$$

$$r_{oxy} = \frac{dC^{oxy}}{dt} = -X \cdot F_{oxy} \cdot k_{max}\left[\frac{C^{don}}{K_S^{don} + C^{don}}\right] \cdot \left[\frac{C^{oxy}}{K_S^{oxy} + C^{oxy}}\right] \quad \text{(A.10)}$$

Nitrate

$$r_{nit} = \frac{dC^{nit}}{dt} = -X \cdot \left(F_{nit} \cdot r_{don,nit}\right)$$

$$r_{nit} = \frac{dC^{nit}}{dt} = -X \cdot F_{nit} \cdot k_{max}\left[\frac{C^{don}}{K_S^{don} + C^{don}}\right] \cdot \left[\frac{C^{nit}}{K_S^{nit} + C^{nit}}\right] \cdot \left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}}\right] \quad \text{(A.11)}$$

Perchlorate

$$r_{per} = \frac{dC^{per}}{dt} = -X \cdot \left(F_{per} \cdot r_{don,per}\right)$$

$$r_{per} = \frac{dC^{per}}{dt} = -X \cdot F_{per} \cdot k_{max}\left[\frac{C^{don}}{K_S^{don} + C^{don}}\right] \cdot \left[\frac{C^{per}}{K_S^{per} + C^{per}}\right] \cdot \left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}}\right] \cdot \left[\frac{K_i^{nit}}{K_i^{nit} + C^{nit}}\right]$$

(A.12)

A.5 MICROBIAL GROWTH/DECAY

The microbial growth/decay equation utilized in the technology model is as follows:

$$\frac{dX}{dt} = X \cdot \left[Y_{biomass} \cdot (r_{don,oxy} + r_{don,nit} + r_{don,per}) - b\right];\ X > X_{min}$$
$$\frac{dX}{dt} = 0;\ X \le X_{min} \quad \text{(A.13)}$$

Where $r_{don,oxy}$, $r_{don,nit}$ and $r_{don,per}$ are defined in equations A.7-A.9. Equation A.13 also incorporates a "switch" to keep the microbial population from completely dying off in areas where there is no electron donor or acceptor.

A.6 PARAMETER VALUES

Tables A.1 through A.3 represent the various kinetic, environmental and engineering parameters that Parr established (Parr, 2002).

Table A.1 Kinetic Parameters Used in Model Simulations (Parr, 2002)

Parameter	Baseline Value
k_{max}	.21 mg donor/mg biomass/day
K_S^{don}	10.0 mg/L
K_S^{oxy}	10.0 mg/L
K_S^{nit}	15.0 mg/L
K_S^{per}	20.0 mg/L
K_i^{oxy}	10.0 mg/L
K_i^{nit}	15.0 mg/L
$Y_{biomass}$	.25 mg biomass/mg donor
F_{oxy}	0.83 mg oxygen/mg donor
F_{nit}	1.3 mg nitrate/mg donor
F_{per}	1.45 mg perchlorate/mg donor
b	0.01 1/day
X_{min}	.01 mg/L

Table A.2 Environmental Parameters Used in Model Simulations (Parr, 2002)

Parameter	Baseline Value
Pore water velocity	0.279 m/day
Darcy velocity	0.0836 m/day
Horizontal hydraulic conductivity	7.6 m/day
Vertical hydraulic conductivity	0.38 m/day
Hydraulic gradient	0.011 m/m
Porosity	0.3

Table A.3 Engineering Parameters Used in Model Simulations (Parr, 2002)

Parameter	Baseline Value
Time-average electron donor concentration	600 mg/L
Donor injection pulse schedule	3 hrs on 5 hrs off
Well spacing	15 m
Well screen lengths	10 m
Pumping rate	100 m3/day
Well	15 m

A.7 DEFINITION OF TERMS

b biomass decay rate (1/day)

C_{don} concentration of the electron donor (mg/L)

C_{oxy} concentration of the electron donor (an electron acceptor) (mg/L)

C_{nit} concentration of the electron donor (an electron acceptor) (mg/L)

C_{per} concentration of the electron donor (an electron acceptor) (mg/L)

$D_{x,y,z}$ dispersion in the x, y and z directions

$d_{x,y,z}$ cell size in the x, y and z directions

F_{oxy} stoichiometric coefficient for the donor-oxygen reaction (mg oxygen/mg donor)

F_{nit} stoichiometric coefficient for the donor-nitrate reaction (mg oxygen/mg donor)

F_{per} stoichiometric coefficient for the donor-perchlorate reaction (mg oxygen/mg donor)

K_i^{oxy} oxygen inhibition coefficient (mg/L)

K_i^{nit} nitrate inhibition coefficient (mg/L)

k_{max} maximum specific rate of substrate utilization (mg donor/mg biomass/day)

$k_{maxdon/oxy}$ maximum specific rate of substrate utilization in the presence of oxygen when donor concentration is varied and limiting (mg donor/mg biomass/day)

$k_{maxdon/nit}$ maximum specific rate of substrate utilization in the presence of nitrate when donor concentration is varied and limiting (mg donor/mg biomass/day)

$k_{maxdon/per}$ maximum specific rate of substrate utilization in the presence of perchlorate when donor concentration is varied and limiting (mg donor/mg biomass/day)

$K_S^{don/oxy}$ half saturation concentration of the electron donor in the presence of oxygen when donor (xxxxx) concentration is varied and limited (mg donor/L)

$K_S^{don/nit}$ half saturation concentration of the electron donor in the presence of nitrate when donor (xxxxx) concentration is varied and limited (mg donor/L)

$K_S^{don/per}$ half saturation concentration of the electron donor in the presence of perchlorate when donor (xxxxx) concentration is varied and limited (mg donor/L)

K_S^{oxy} half saturation concentration when oxygen (an electron acceptor) concentration is varied and limited (mg/L)

K_S^{nit} half saturation concentration when nitrate (an electron acceptor) concentration is varied and limited (mg/L)

K_S^{per} half saturation concentration when perchlorate (an electron acceptor) concentration is varied and limited (mg/L)

r_{don} rate of electron donor consumption (mg donor/L/day)

$r_{don,oxy}$ specific rate of electron donor consumption using oxygen as an electron acceptor (mg donor/mg biomass/day)

$r_{don,nit}$ specific rate of electron donor consumption using nitrate as an electron acceptor (mg donor/mg biomass/day)

$r_{don,per}$ specific rate of electron donor consumption using perchlorate as an electron acceptor (mg donor/mg biomass/day)

r_{oxy} rate of oxygen consumption (mg oxygen/L/day)

r_{nit}	rate of nitrate consumption (mg nitrate/L/day)
r_{per}	rate of perchlorate consumption (mg perchlorate/L/day)
t	time (days)
$v_{x,y,z}$	groundwater velocity in the x, y and z directions
X	concentration of active biomass (mg/L)
X_{min}	minimum concentration level of active biomass (mg/L)
$Y_{biomass}$	the biomass yield per mass of donor consumed (mg biomass/mg electron donor)

APPENDIX B: MONITORING WELL BREAKTHROUGH GRAPHS

This Appendix includes graphs showing all oxygen, nitrate, and perchlorate concentration data observed at all monitoring wells. In addition, model simulations utilizing the baseline Aerojet parameters and the best-fit parameters determined by calibration with the GA are shown on the graphs. Baseline and best-fit parameters are available in Table 4.2. The simulations using the best-fit parameter values are indicated on the graphs by the lines labeled "Simulated (calibrated)".

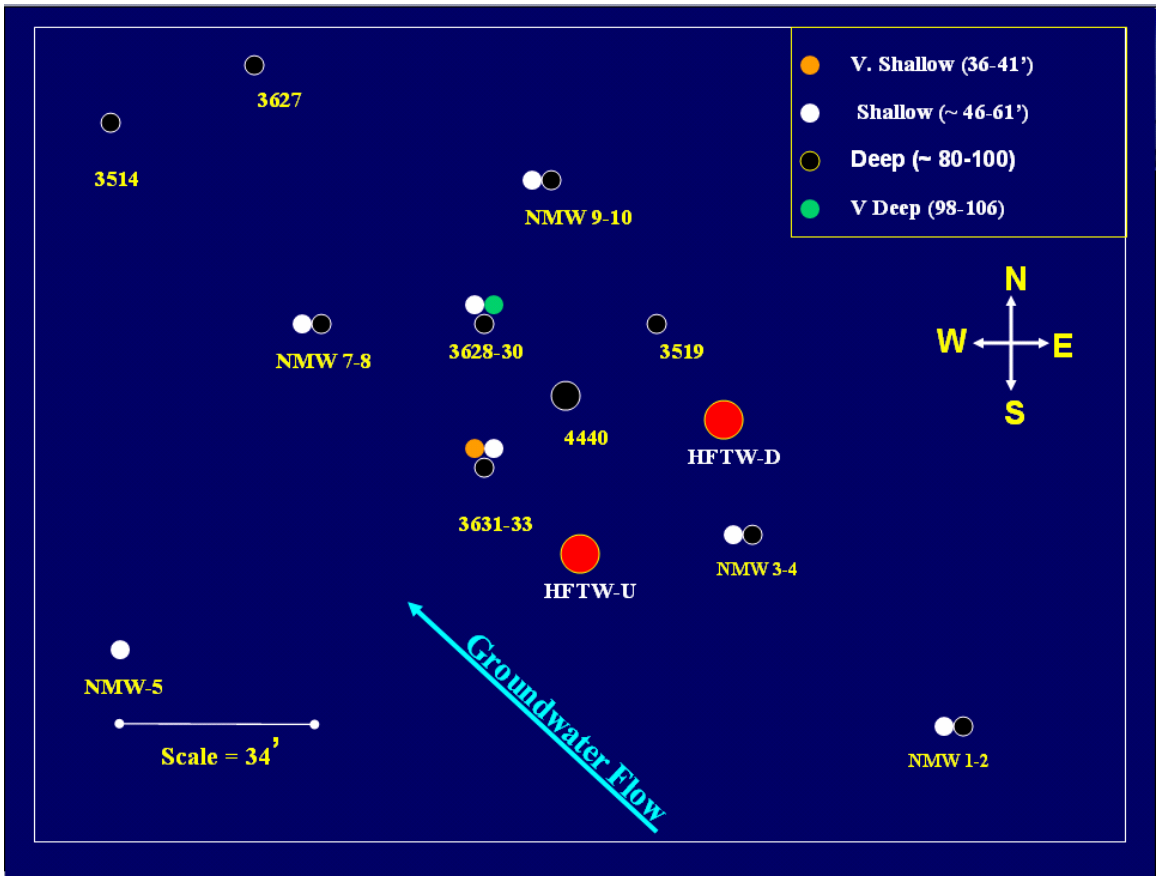


Figure B.1 Aerojet HFTW and Monitoring Well Site Layout

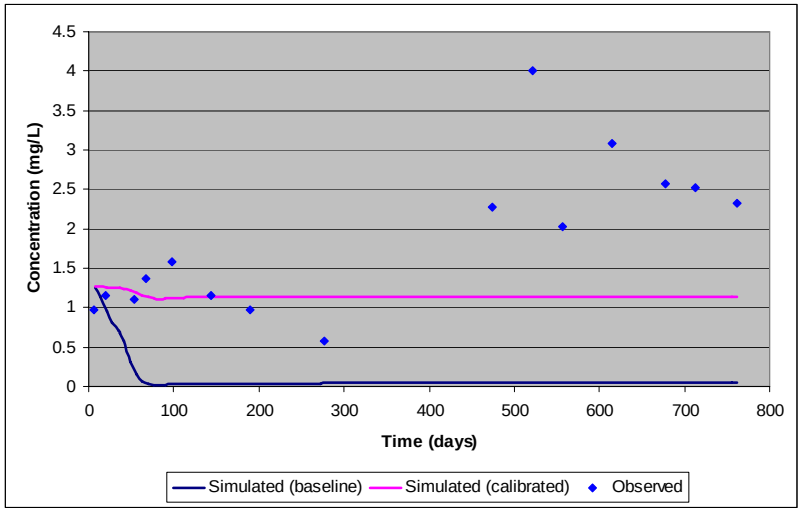


Figure B.2 NMW1 Oxygen Breakthrough

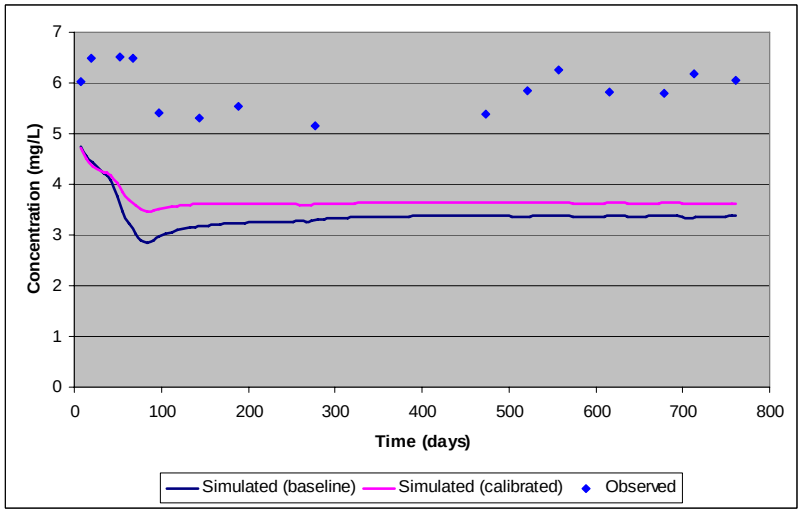


Figure B.3 NMW1 Nitrate Breakthrough

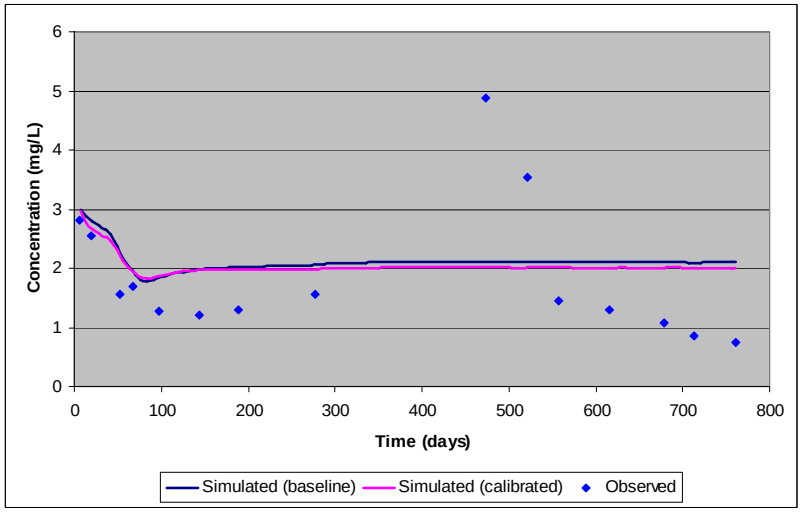


Figure B.4 NMW1 Perchlorate Breakthrough

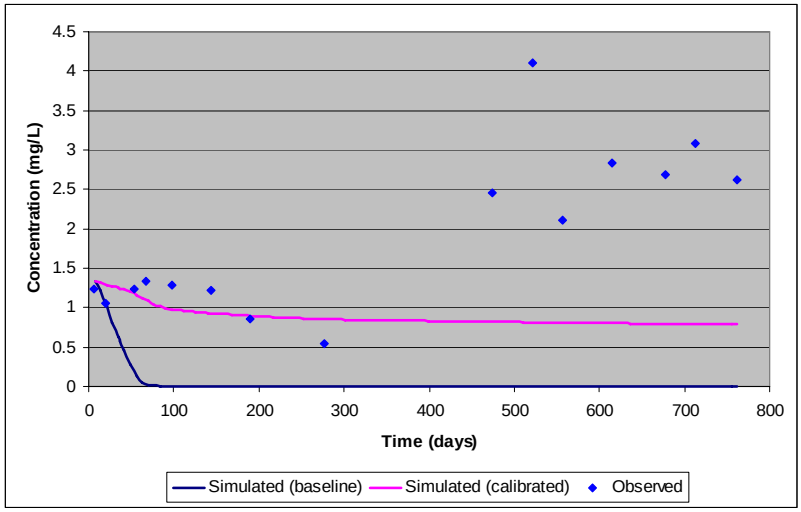


Figure B.5 NMW2 Oxygen Breakthrough

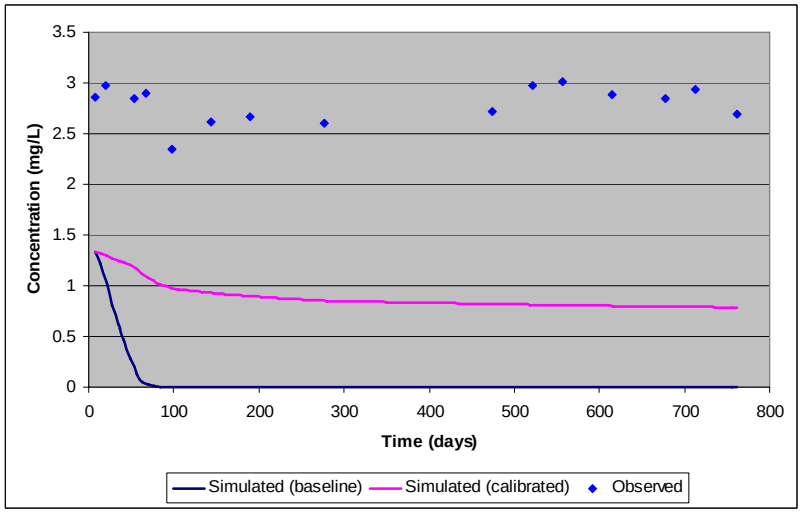


Figure B.6 NMW2 Nitrate Breakthrough

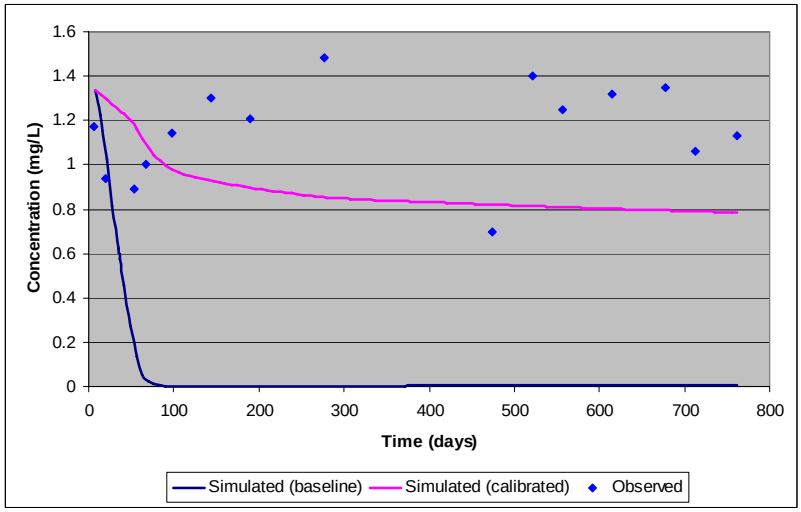


Figure B.7 NMW2 Perchlorate Breakthrough

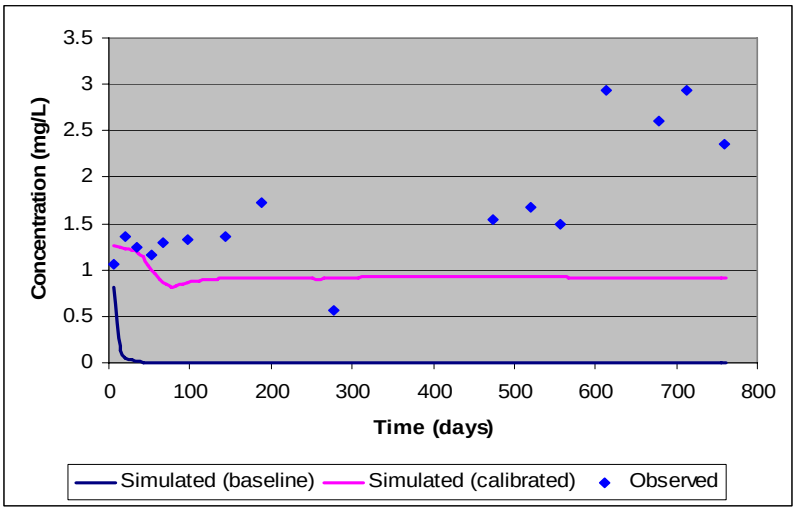


Figure B.8 NMW3 Oxygen Breakthrough

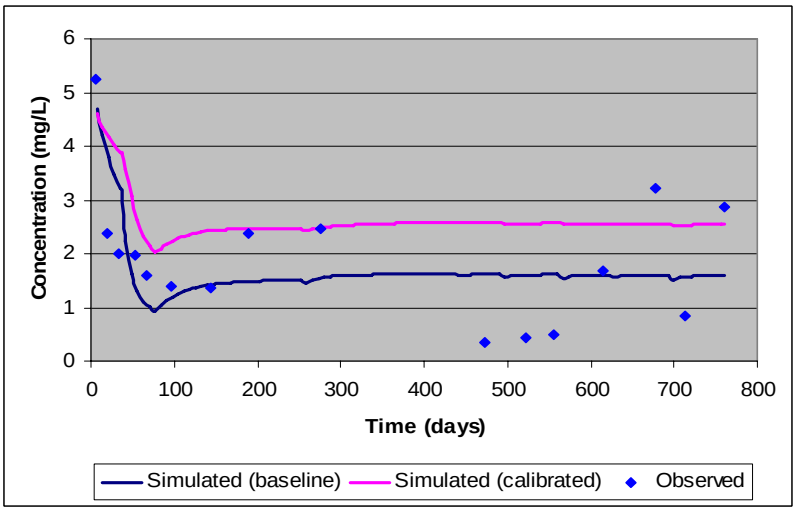


Figure B.9 NMW3 Nitrate Breakthrough

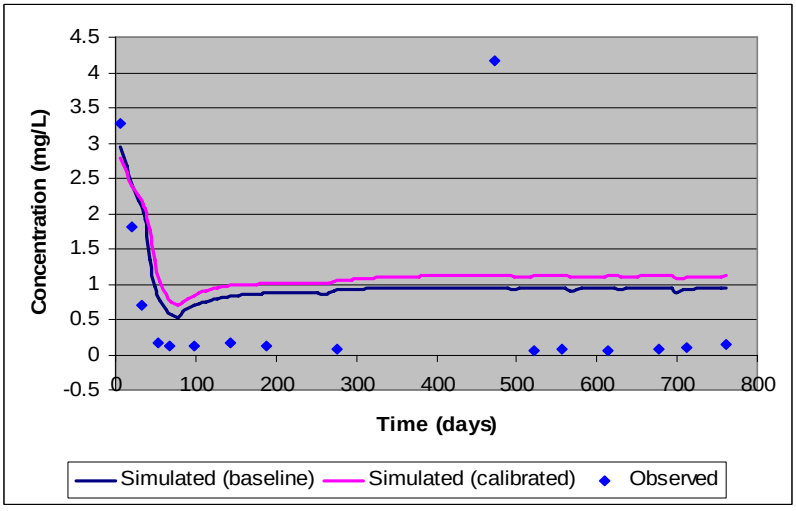


Figure B.10 NMW3 Perchlorate Breakthrough

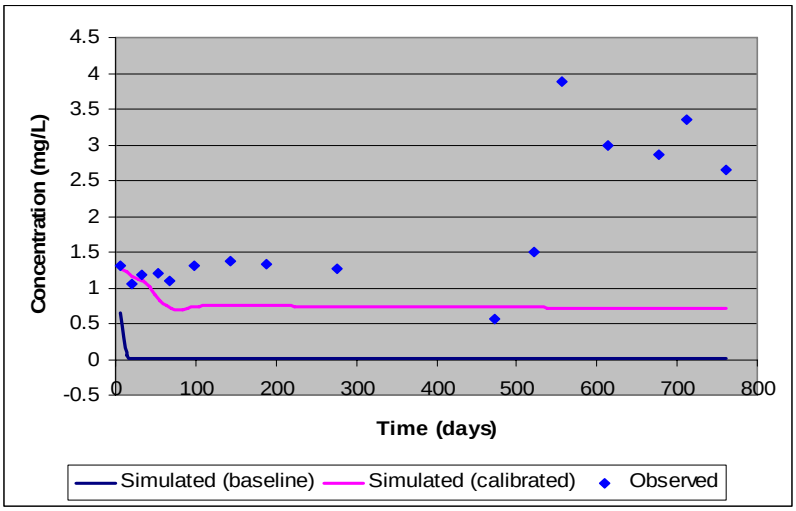


Figure B.11 NMW4 Oxygen Breakthrough

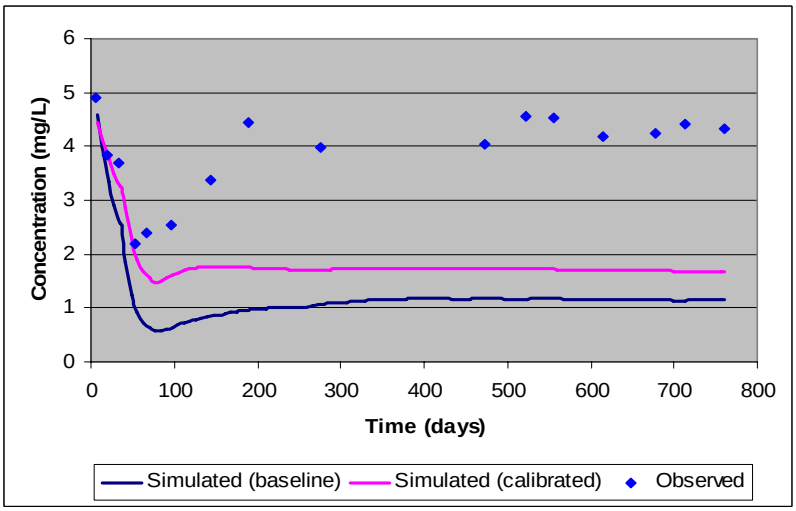


Figure B.12 NMW4 Nitrate Breakthrough

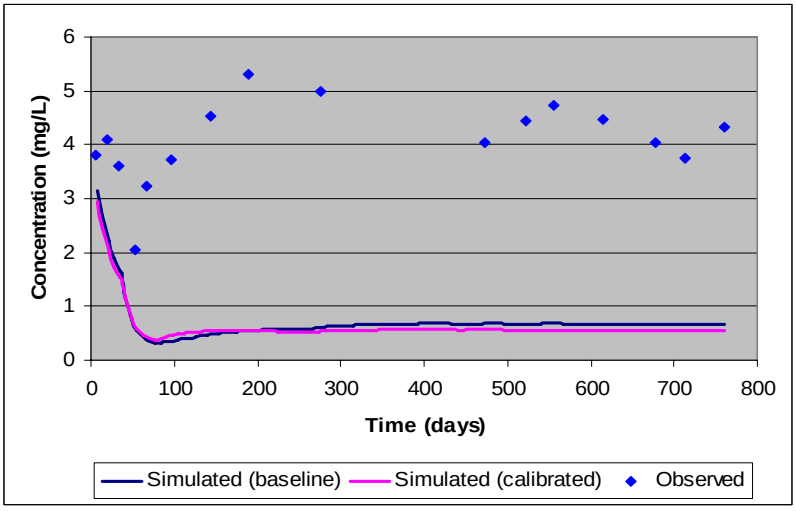


Figure B.13 NMW4 Perchlorate Breakthrough

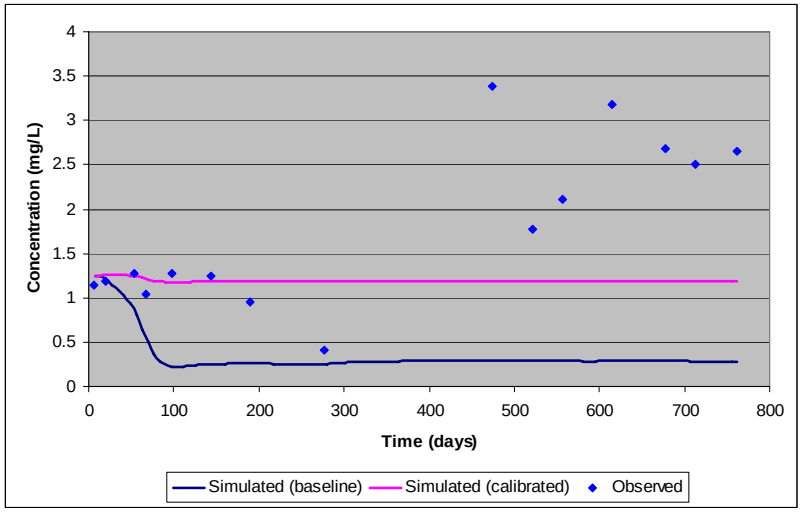


Figure B.14 NMW5 Oxygen Breakthrough

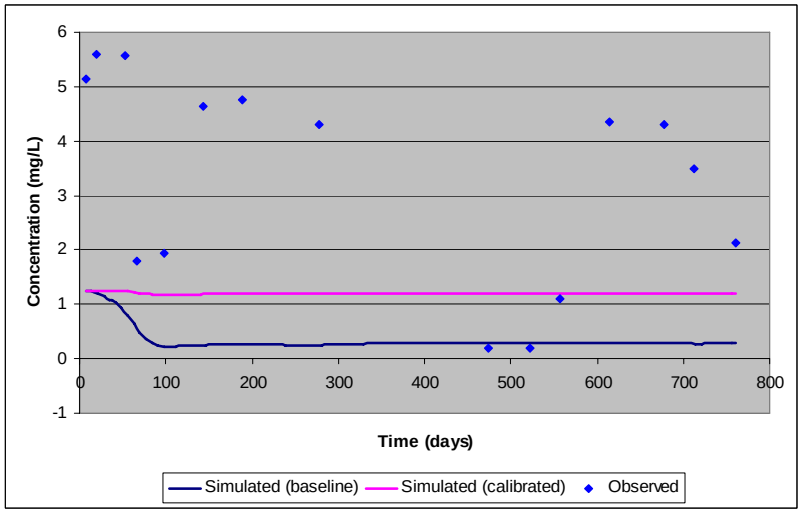


Figure B.15 NMW5 Nitrate Breakthrough

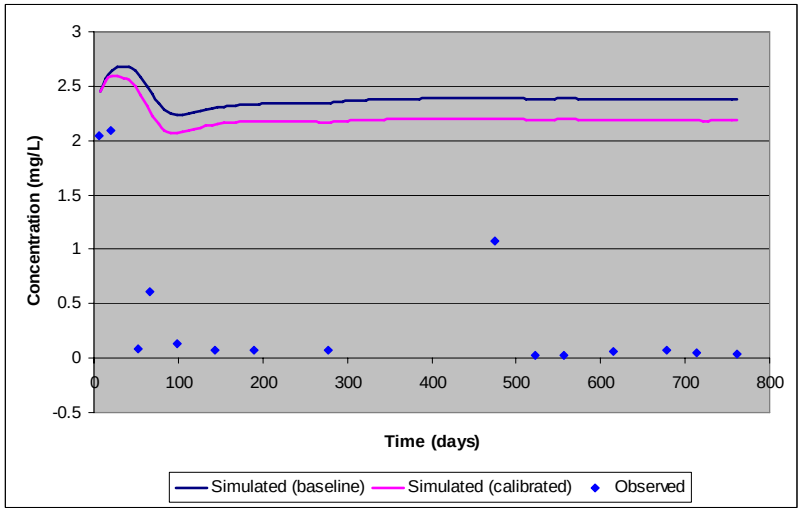


Figure B.16 NMW5 Perchlorate Breakthrough

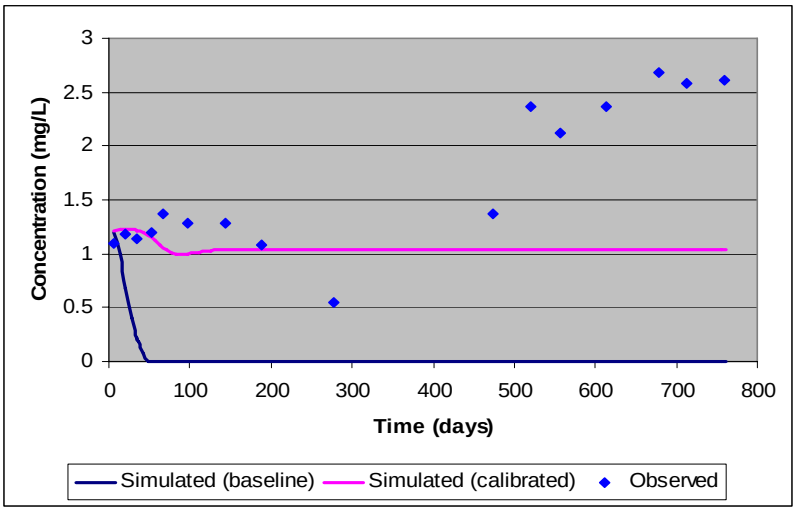


Figure B.17 NMW7 Oxygen Breakthrough

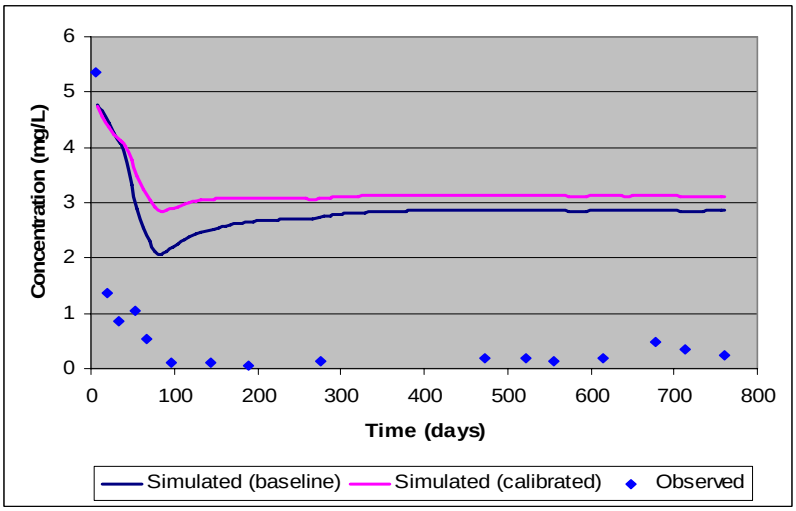


Figure B.18 NMW7 Nitrate Breakthrough

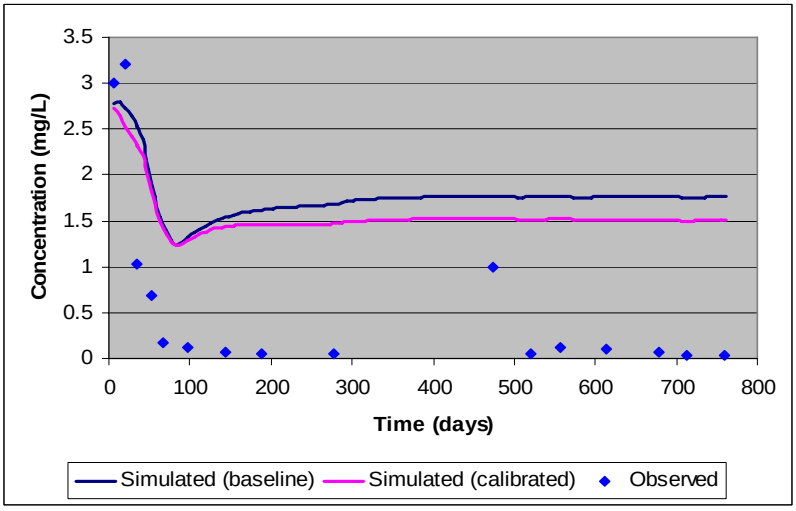


Figure B.19 NMW7 Perchlorate Breakthrough

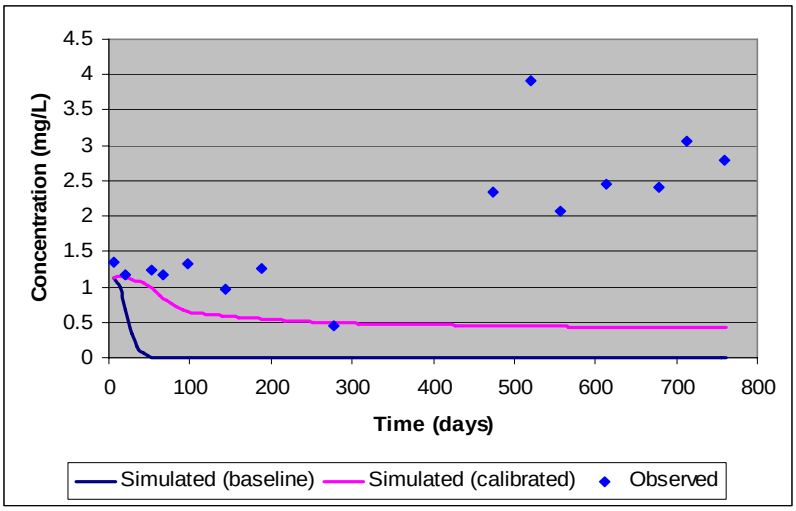


Figure B.20 NMW8 Oxygen Breakthrough

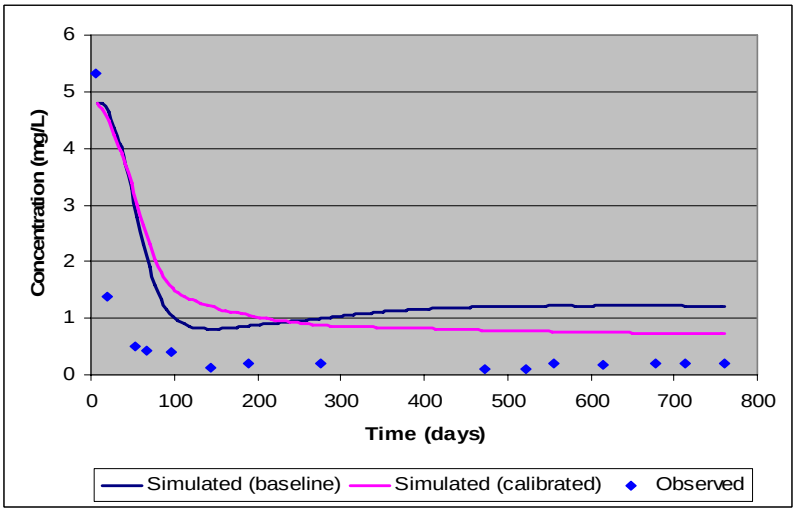


Figure B.21 NMW8 Nitrate Breakthrough

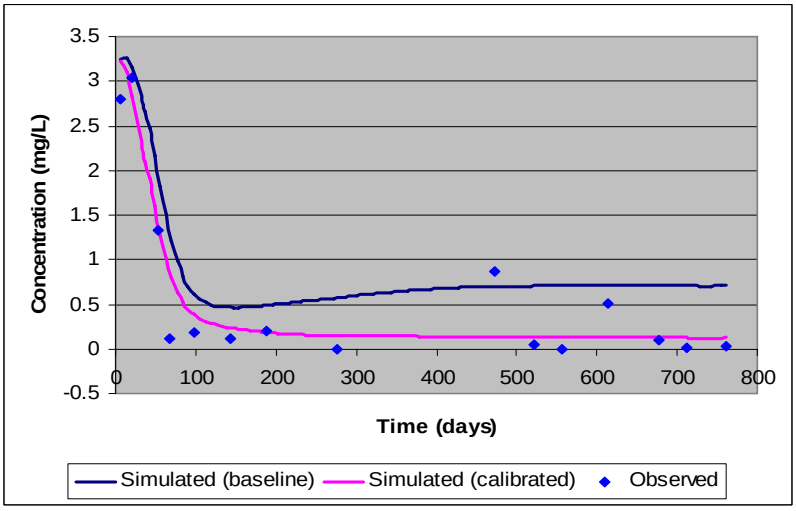


Figure B.22 NMW8 Perchlorate Breakthrough

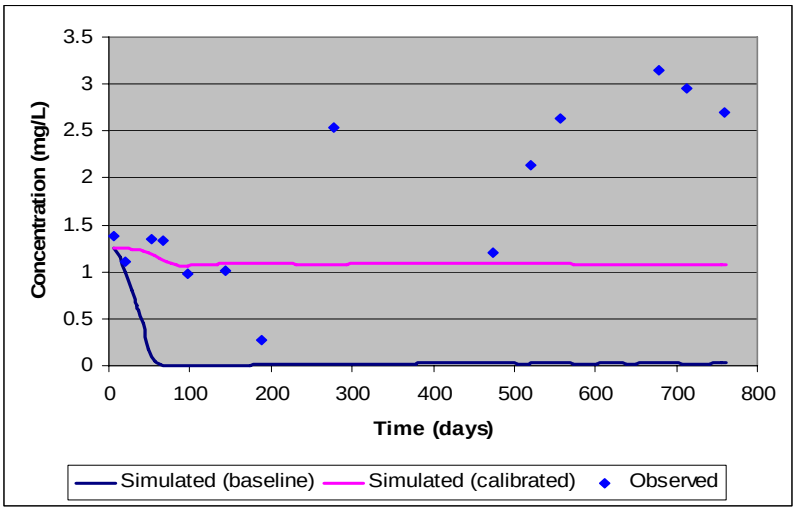


Figure B.23 NMW9 Oxygen Breakthrough

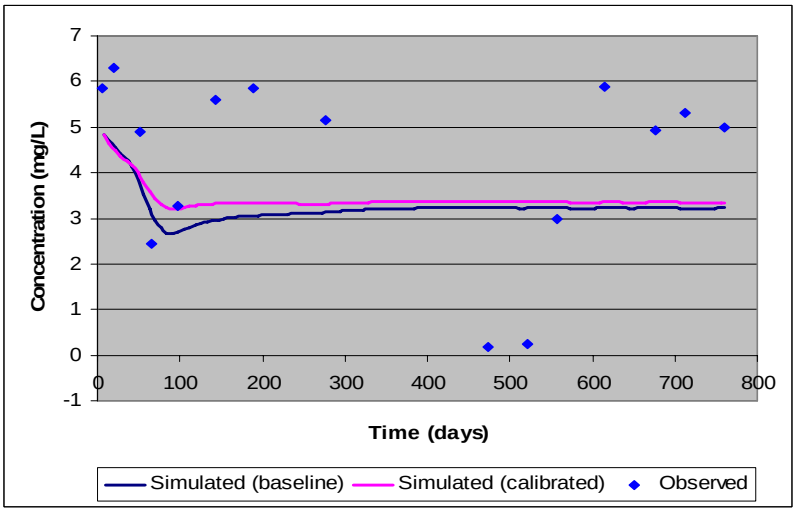


Figure B.24 NMW9 Nitrate Breakthrough

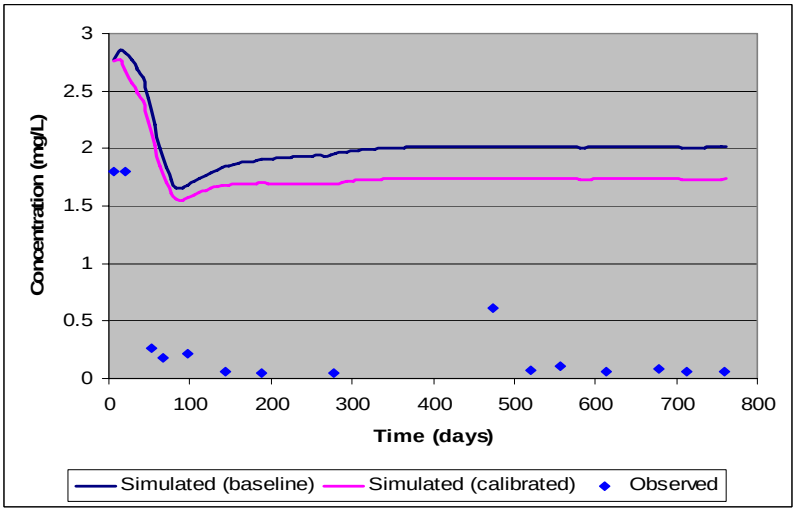


Figure B.25 NMW9 Perchlorate Breakthrough

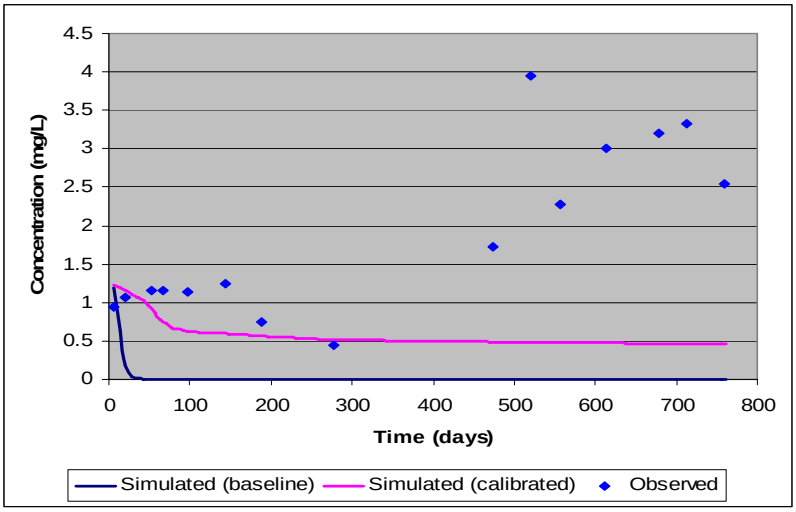


Figure B.26 NMW10 Oxygen Breakthrough

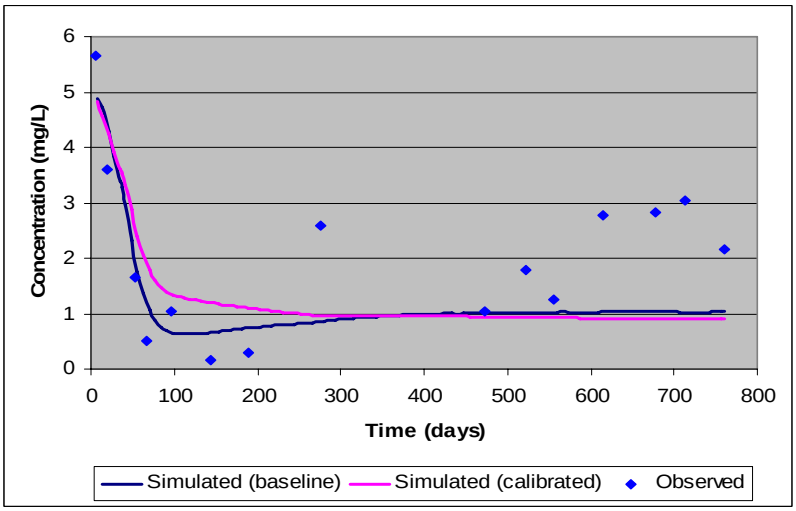


Figure B.27 NMW10 Nitrate Breakthrough

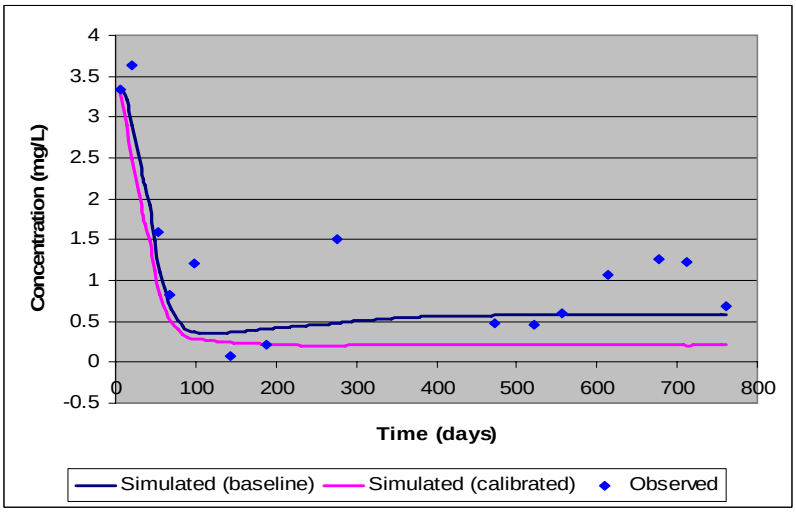


Figure B.28 NMW10 Perchlorate Breakthrough

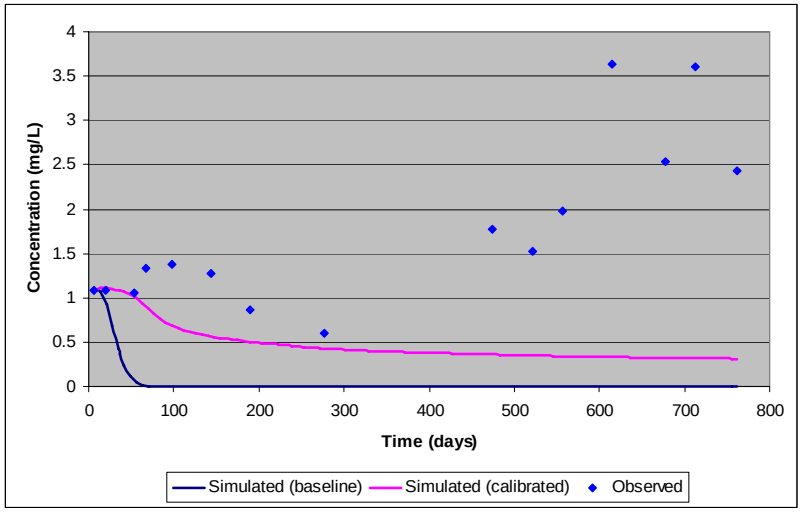


Figure B.29 3514 Oxygen Breakthrough

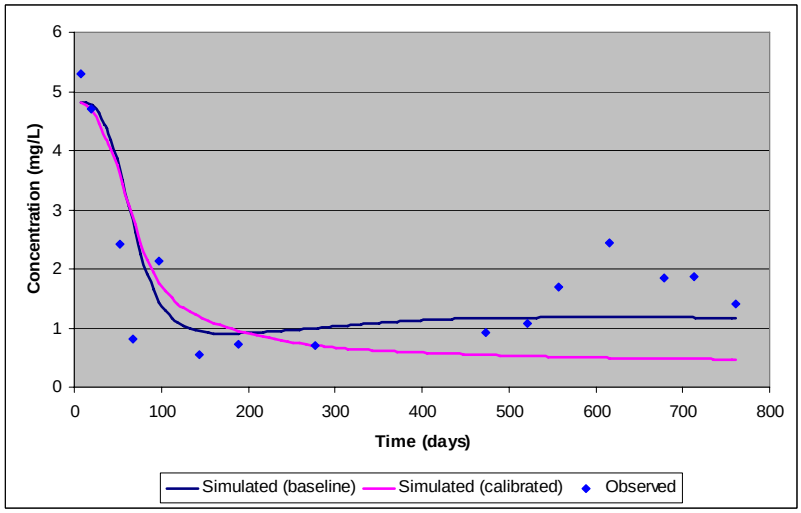


Figure B.30 3514 Nitrate Breakthrough

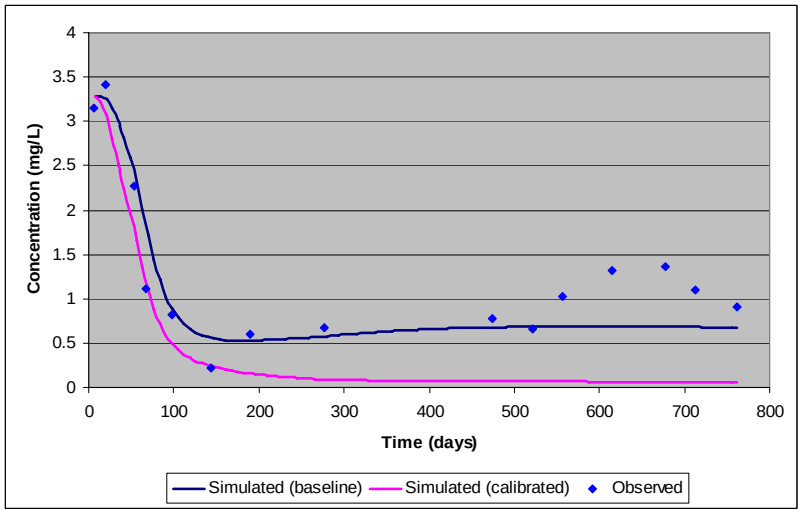


Figure B.31 3514 Perchlorate Breakthrough

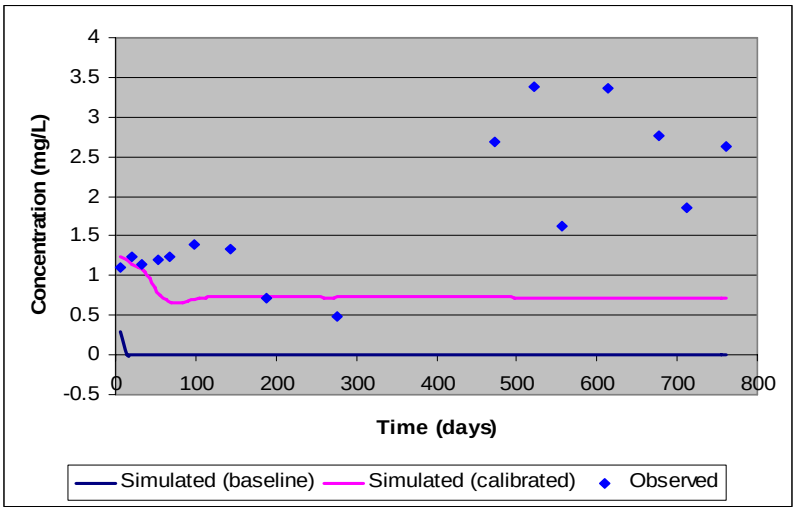


Figure B.32 3519 Oxygen Breakthrough

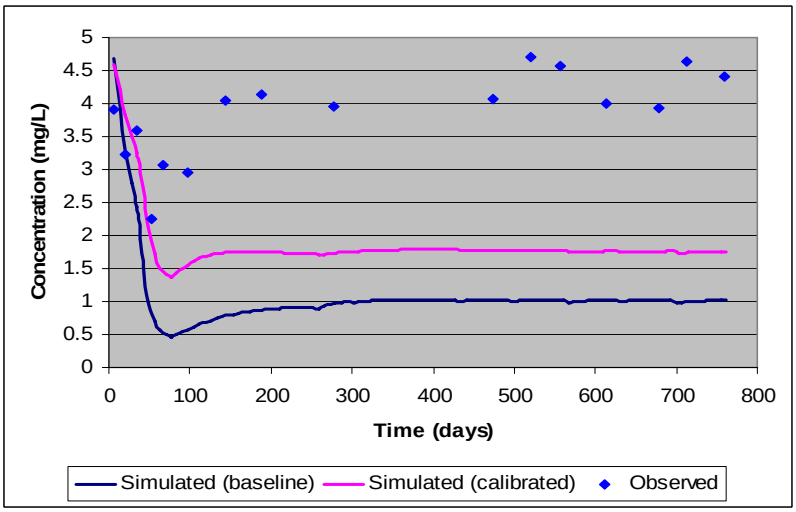


Figure B.33 3519 Nitrate Breakthrough

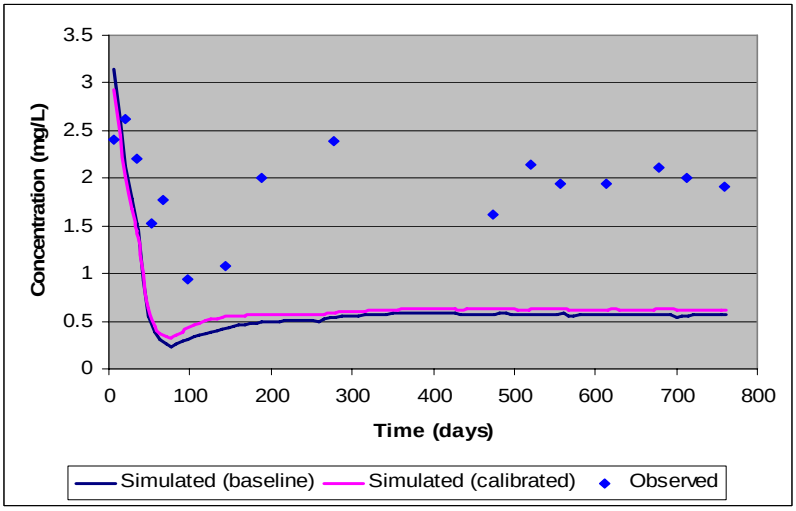


Figure B.34 3519 Perchlorate Breakthrough

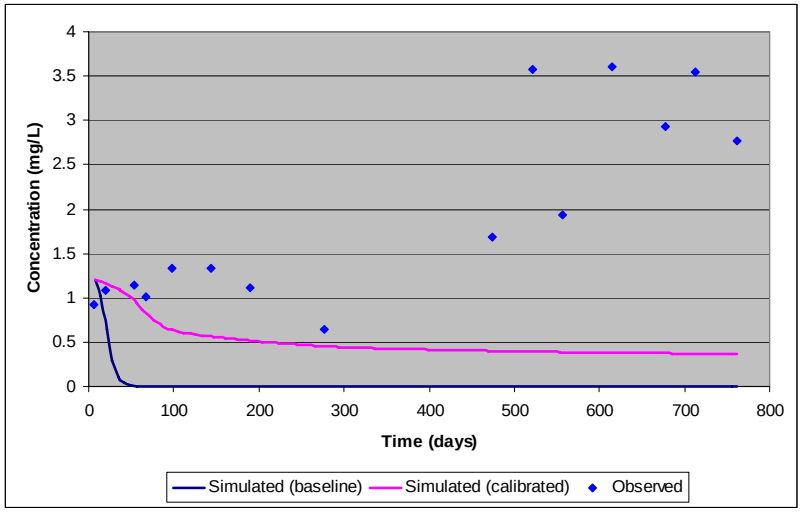


Figure B.35 3627 Oxygen Breakthrough

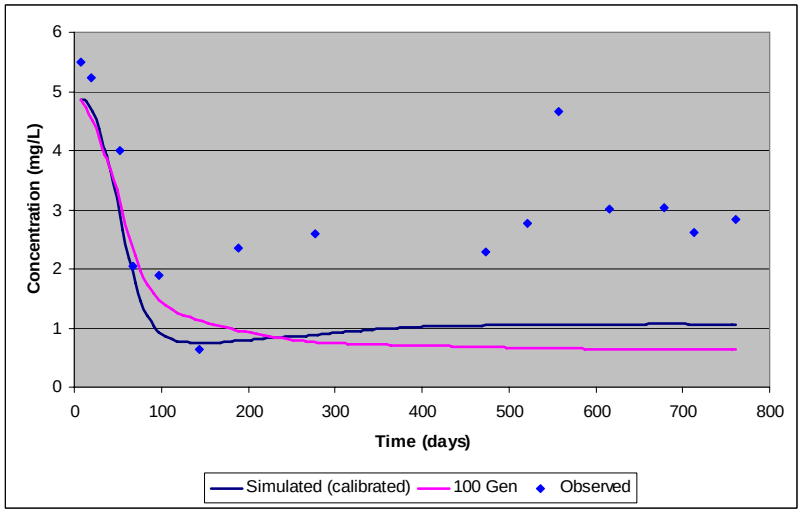


Figure B.36 3627 Nitrate Breakthrough

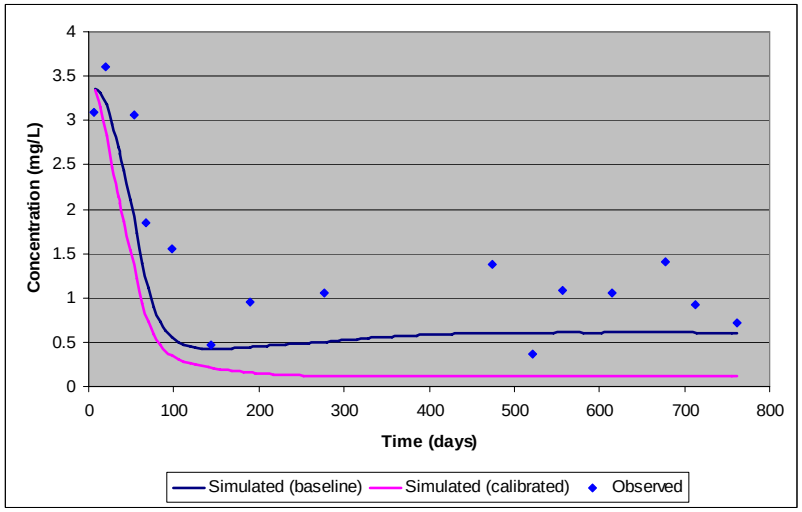


Figure B.37 3627 Perchlorate Breakthrough

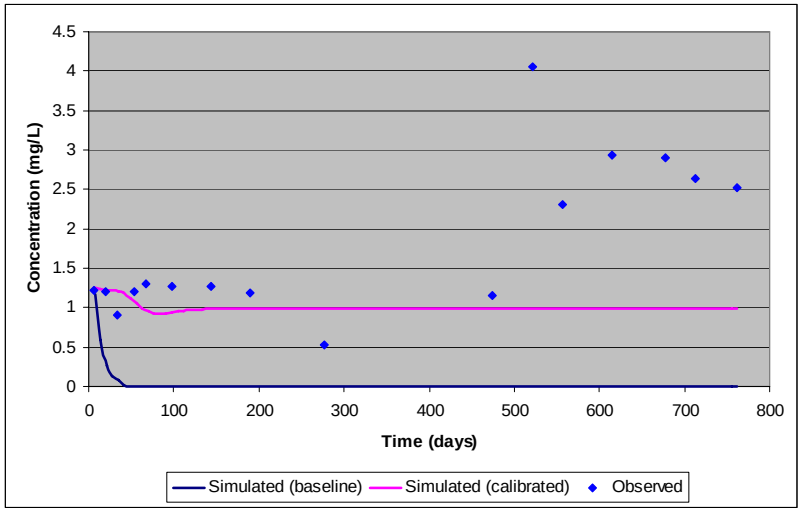


Figure B.38 3628 Oxygen Breakthrough

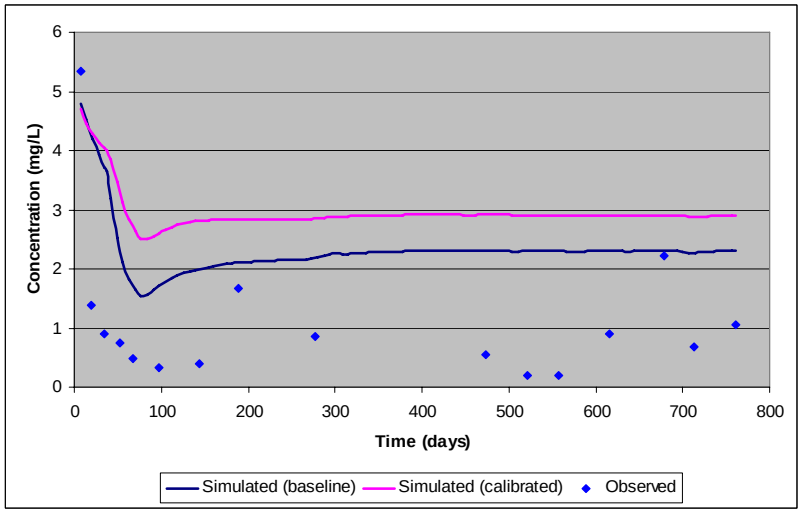
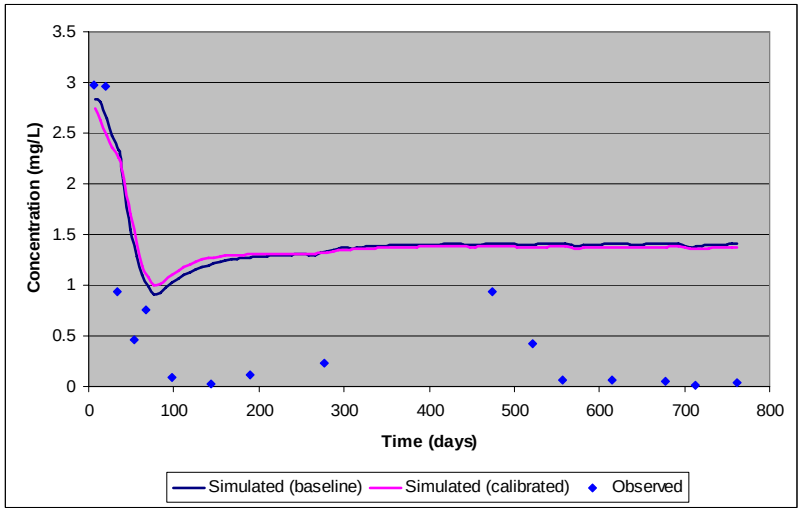


Figure B.39 3628 Nitrate Breakthrough



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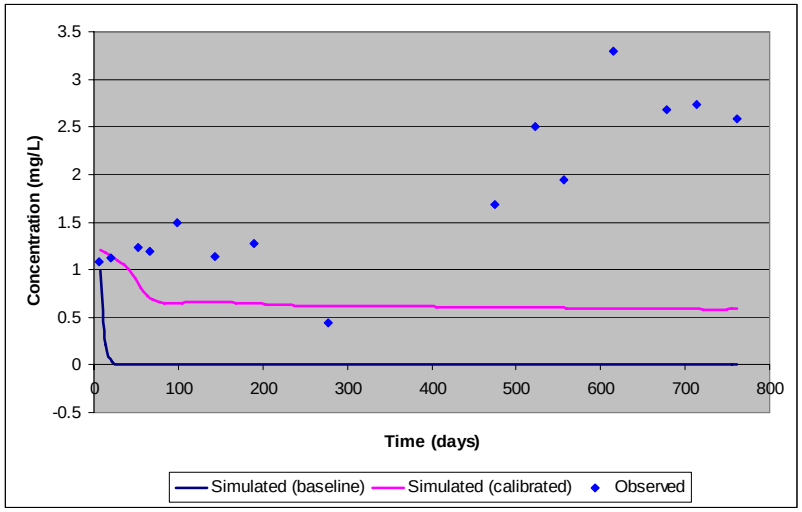

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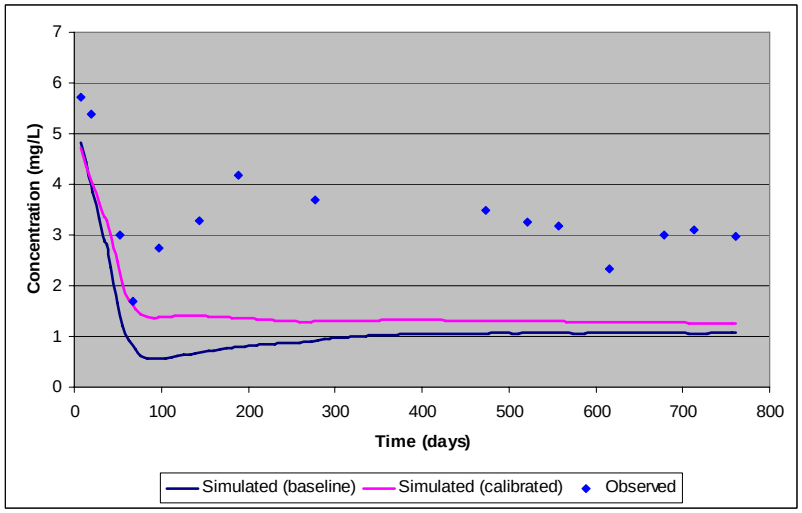

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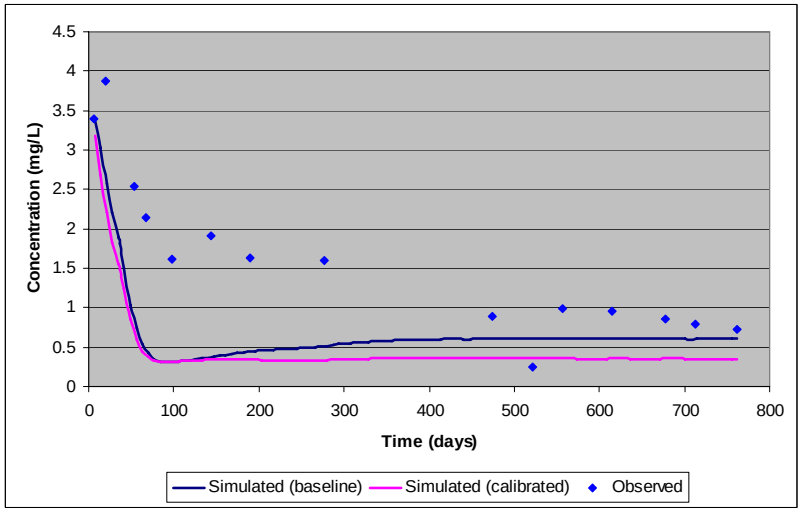

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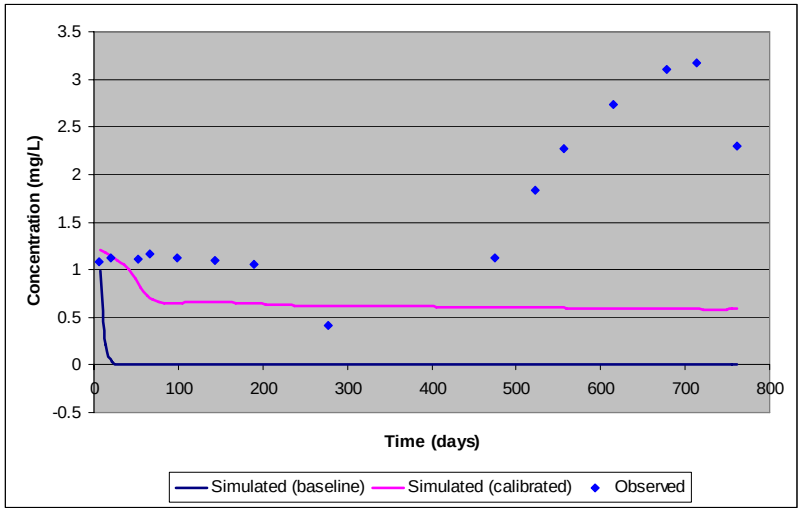
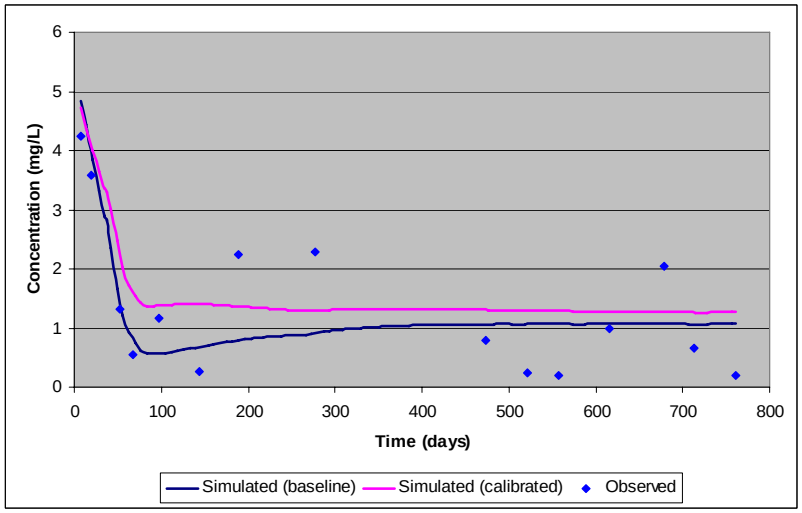


Figure B.44 3630 Oxygen Breakthrough



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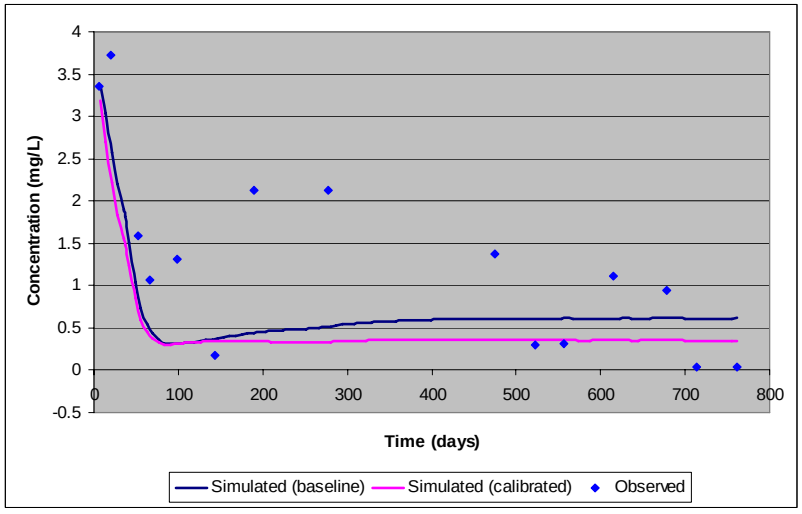

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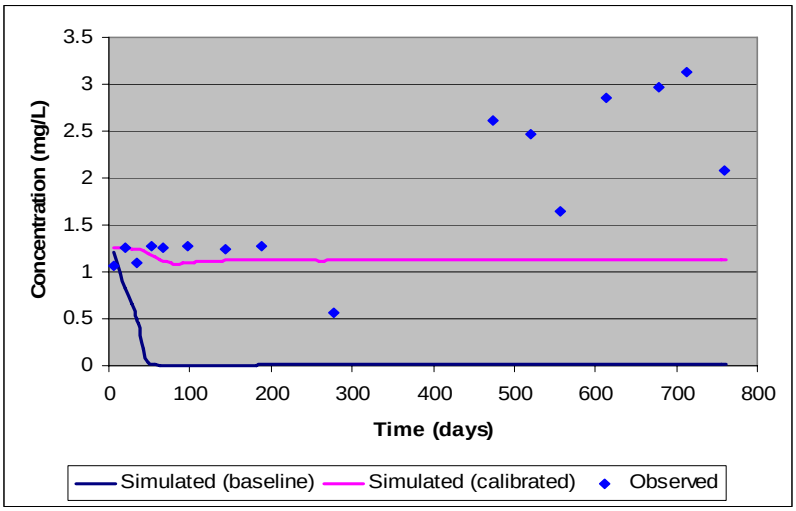
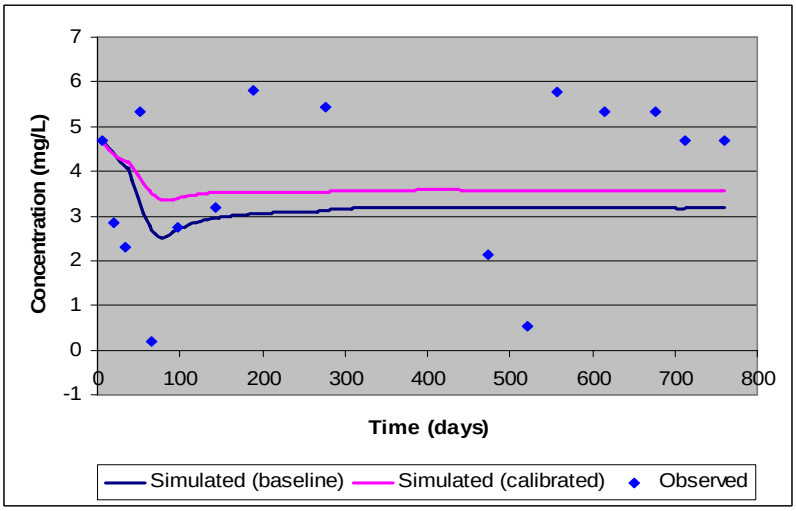


Figure B.47 3631 Oxygen Breakthrough



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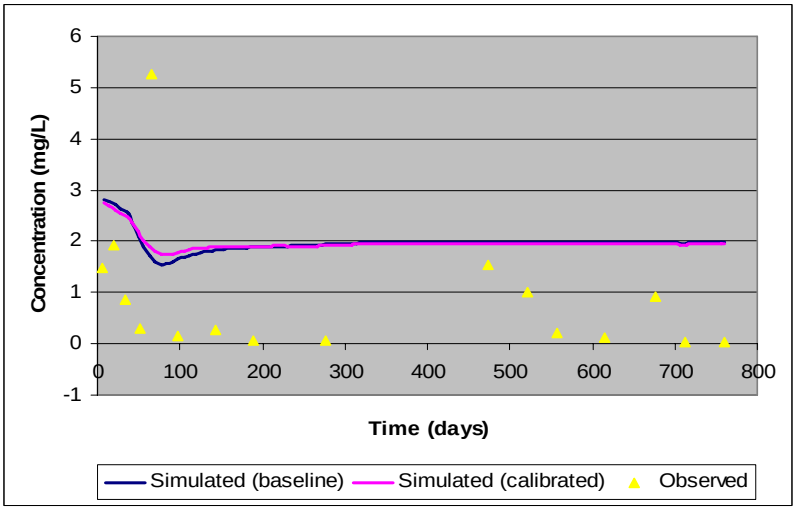

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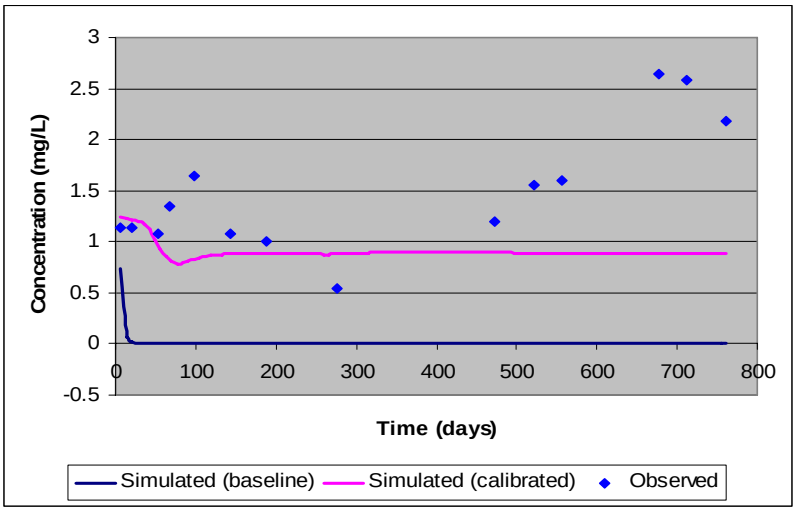

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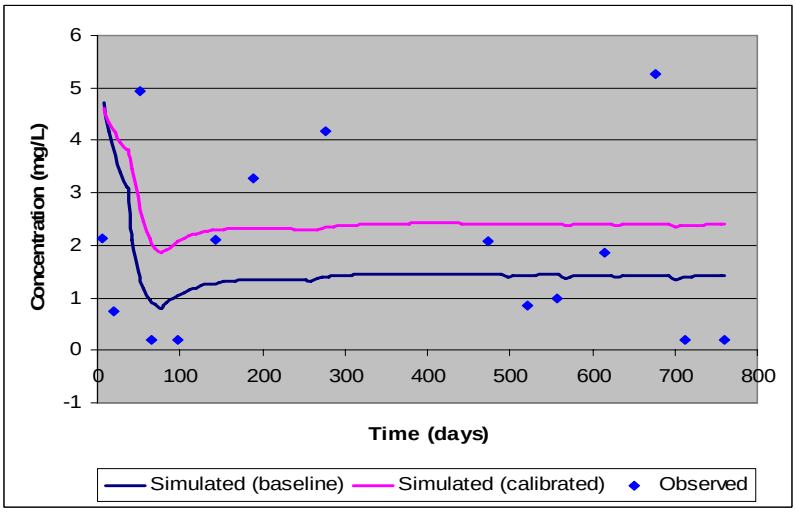

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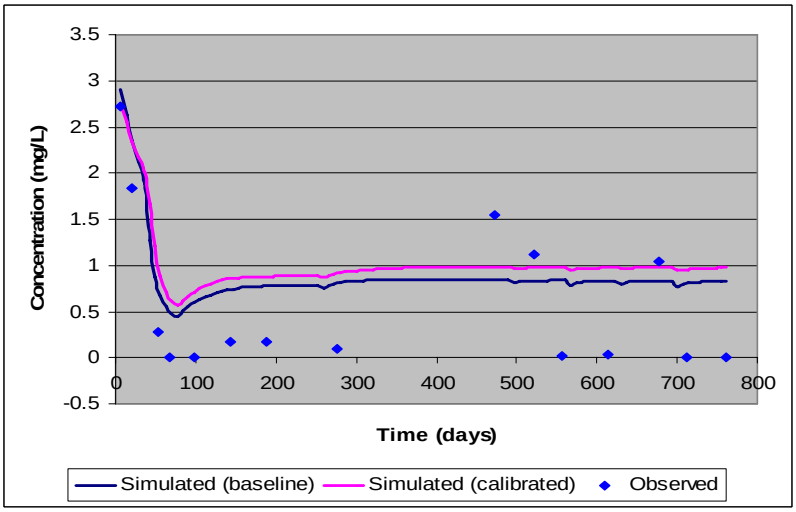
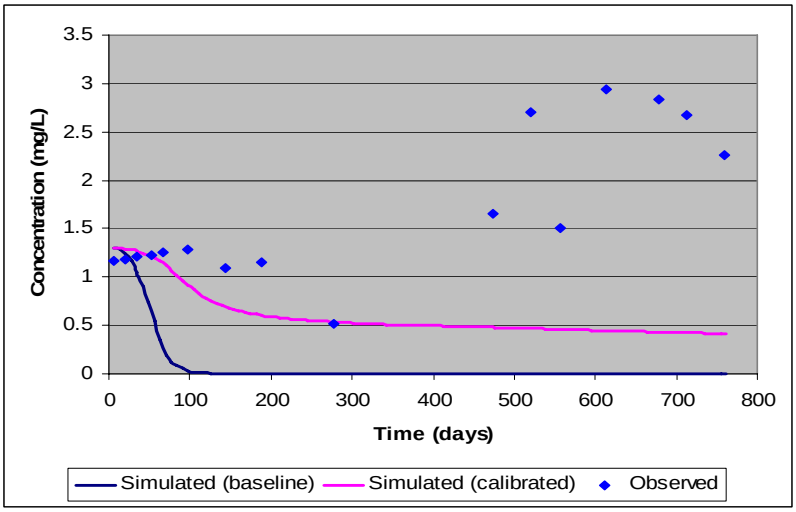


Figure B.52 3632 Perchlorate Breakthrough



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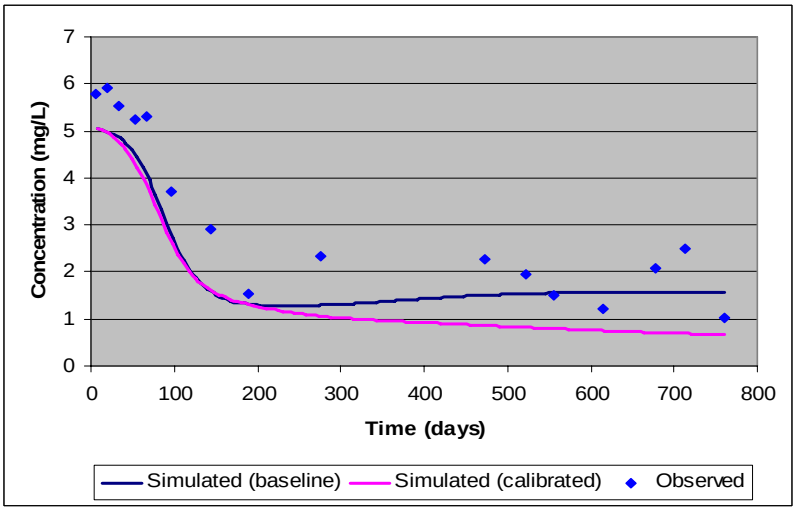

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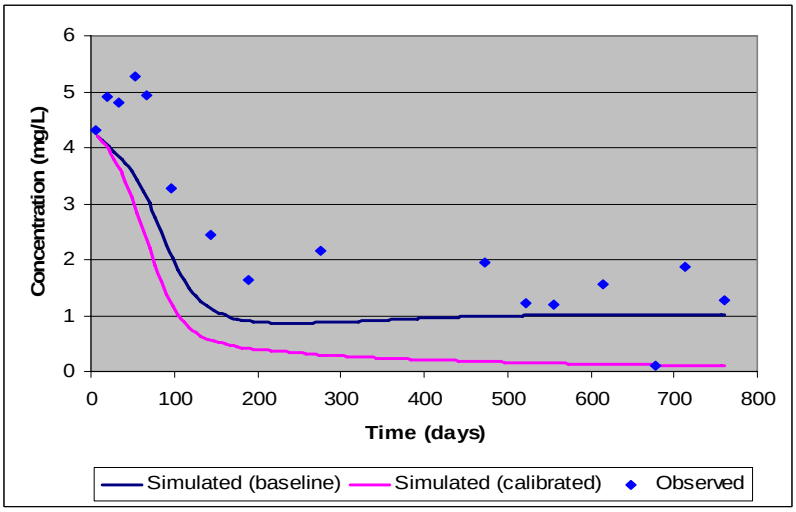

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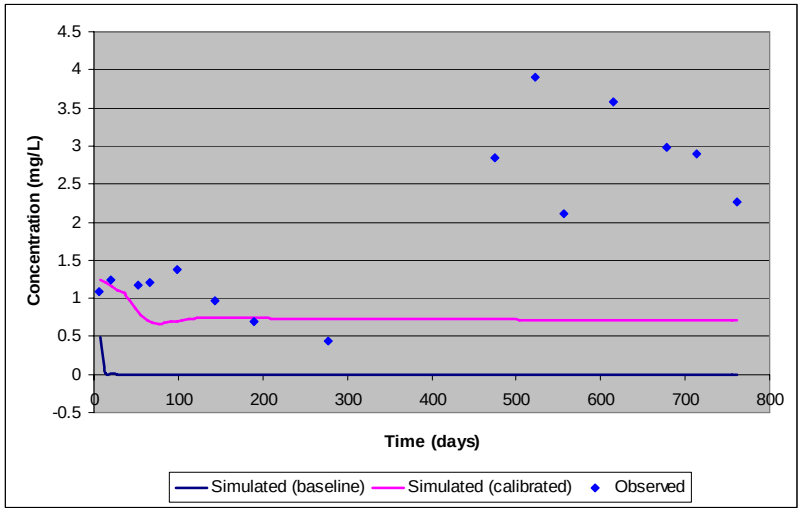

Figure B.56 4440 Oxygen Breakthrough

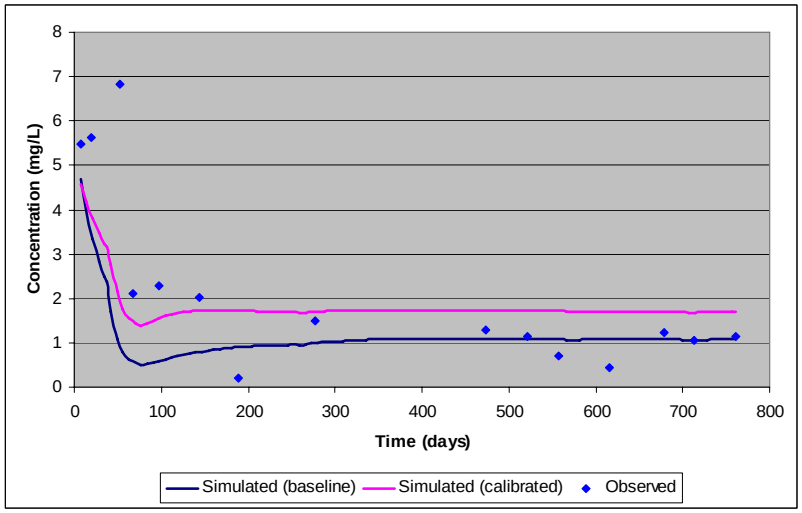

Figure B.57 4440 Nitrate Breakthrough

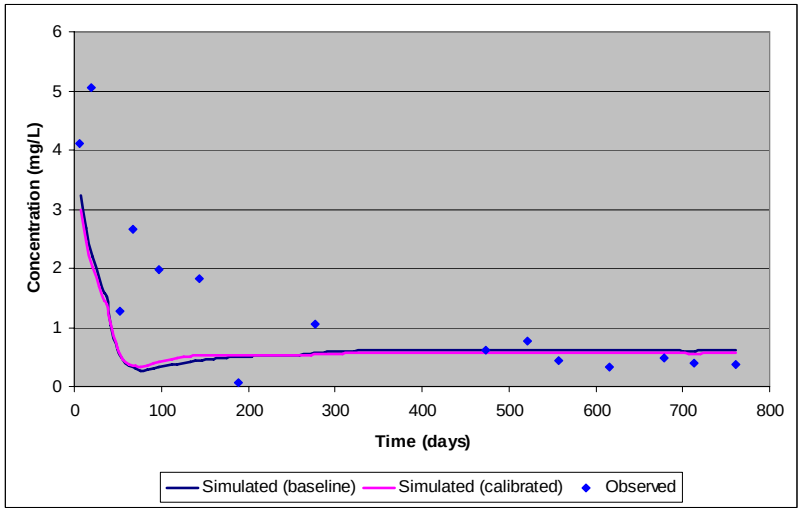

Figure B.58 4440 Perchlorate Breakthrough

BIBLIOGRAPHY

Air Force Center for Environmental Excellence (AFCEE), 2006. "Perchlorate Treatment Technology Fact Sheet: *In situ* Anaerobic Bioremediation." August, 2006.

Arizona Department of Environmental Quality (ADEQ), Arizona Department of Health Services (ADHS). Arizona Department of Water Resources (ADWR), Arizona Department of Agriculture (ADA). Perchlorate in Arizona: Occurrence Study of 2004. December, 2004.

Bäck T. Evolutionary Computing. *Evolutionary Computation 1: Basic Algorithms and Operators*. Institute of Physics Publishing. Bristol and Philidelphia, PA. 2000.

Brandhuber P, Clark S. Perchlorate Occurrence Mapping. Prepared for the American Water Works Association. Denver, CO: HDR Engineering. 2004.

California Department of Health Services (CDHS). Perchlorate in California Drinking Water: Overview and Links. Department of Health Services, Sacramento, California. 2007. http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/perchlindex.htm

Chosa, P.G. Modeling a Field Application of *In situ* Bioremediation of Perchlorate-Contaminated Groundwater Using Horizontal Flow Treatment Wells (HFTWs). MS Thesis, AFIT/GEM/ENV/04M-05, 2004. School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB, OH. March 2004.

Christ, J. A., M.N. Goltz, and Huang J., Development and Application of an Analytical Model to Aid Design and Implementation of *In situ* Remediation Technologies, *Journal of Contaminant Hydrology*, 3 7(3): 295-3 17, 1999.

Clement, T. P. "A modular computer model for simulating reactive multi-species transport in three-dimensional ground water systems." Pacific Northwest National Laboratory, PNNL-SA-11720. Richland WA: PNNL. 1997.

Coates, J.D., Michaelidou, U., O'Connor, S.M., Bruce, R.A., and Achenbach, L.A. The diverse microbiology of (per)chlorate reduction. In E.T. Urbansky, Ed., Perchlorate in the Environment. New York: Kluwer Academic/Plenum Publishers, pp. 257–270. 2000.

Collopy, F. and Armstrong, J. S. "Error Measures For Generalizing About Forecasting Methods:Empirical Comparisons", *International Journal of Forecasting*, 8, 69-80, 1992.

Cox, E.E., Edwards, E., and Neville, S. *In situ* Bioremediation of Perchlorate in Groundwater, *Perchlorate in the Environment*. Ed. Urbansky, E. T.; Kluwer Academic/Plenum Publishers, New York, 2000.

Cunningham, J.A., Hoelen, T.P., Hopkins, G.D., LeBron, C.A., Reinhard, M. Hydraulics of recirculating well pairs for ground water remediation. *Ground Water*. 42 (6), 880–889. 2004.

Eiben A.E. and Smith J.E. *Introduction to Evolutionary Computing*. New York : Springer, 2003.

Envirogen. *In situ* Bioremediation of Perchlorate. SERDP project CY-1136 Final Report. 21 May, 2002.

Environmental Modeling Systems, Inc. (EMS-I). GMS 6.0 Overview. 2007. http://www.ems-i.com/GMS/GMS_Overview/gms_overview.html

Environmental Security Technology Certification Program (ESTCP). *In situ* Bioremediation of Perchlorate Using Horizontal Flow Treatment Wells: ESTCP Technology Demonstration Plan Project CE-0227 Final. United States Department of Defense. December, 2003.

Eshelman L.J. Genetic Algorithms. *Evolutionary Computation 1: Basic Algorithms and Operators*. Institute of Physics Publishing. Bristol and Philidelphia, PA. 2000.

Ground-Water Remediation Technologies Analysis Center (GWRTAC). *Perchlorate Treatment Technologies*, 1st ed. Technology Status Report. 2001.

Harbaugh, A., Banta, E.R., Hill, M.C., & McDonald, M.G., MODFLOW-2000, The U.S. Geological Survey (USGS) Modular Ground-Water Model – User Guide to Modularization Concepts and the Ground-Water Flow Process., USGS, Reston, VA, 2000.

Hassan A. Validation of Numerical Ground Water Models Used to Guide Decision Making. *Ground Water*. 42 (2): 277-290. 2004.

Hatzinger, P.B. and J. Diebold. Interim Project Report: ESTCP Field Pilot Perchlorate Treatment-Horizontal Flow Treatment Wells Shaw Project 683024. Shaw Environmental, Inc. 2005.

Hatzinger, P.B., Whittier M.C., Arkins M.D., Bryan C.W., Guarini W.J. *In-Situ* and Ex-Situ Bioremediation Options for Treating Perchlorate in Groundwater. *Remediation Journal*, 12 (2): 69-86, 2002.

Hatzinger, P.B., Huang, J., Goltz, M.N., Chosa, P.G., Diebold, J., Farhan, Y., Parr, J.C., and S. Neville. Field Evaluation of *In situ* Bioremediation of Perchlorate-

Contaminated Groundwater: Modeling and Preliminary Results. Unpublished research paper. 2005.

Huang J. Personal communication. 2006-2007.

Huang, J. and M.N. Goltz. A Model Of *In situ* Bioremediation Which Includes The Effect Of Rate Limited Sorption And Bioavailability. Proceedings of the 1998 Conference on Hazardous Waste Research, pp 297-295, Snow Bird, UT, 19-21 May, 1998.

Interstate Technology and Regulatory Council (ITRC). Perchlorate: Overview of Issues, Status, and Remedial Options. September, 2005.

Kingscott, J., Weisman, R.J. Cost Evaluation for Selected Remediation Technologies. *Remediation Journal*, 12 (2): 99-116, 2002.

Logan, B. E., A Review of Chlorate- and Perchlorate-Respiring Microorganisms. *Bioremediation Journal*, 2(2): 69-79, 1998

Logan, B. E. Assessing the Outlook for Perchlorate Remediation, *Environmental Science and Technology* 35(23): 482A–87A. 2001.

Massachusetts Department of Environmental Protection (MassDEP). Drinking Water Standard. 2006.
http://mass.gov/dep/water/drinking/percinfo.htm

McCarty, P. L., Goltz, M. N., Hopkias, G.D., Dolan, M. E., Allan, J. P., Kawakami, B.T., and Carrothers, T. J.. Full-scale evaluation of *in-situ* cometabolic degradation of trichloroethylene in groundwater through toluene injection. *Environmental Science and Technology*, 32, 88-100. 1998

National Research Council (NRC). Health Implications of Perchlorate Ingestion. National Research Council of the National Academies. National Academies Press, Washington, D.C. January, 2005. http://www.nap.edu/catalog/11202.html.

Nevada Division of Environmental Protection (NDEP). Defining a Perchlorate Drinking Water Standard. October, 2006.

Parr, J.C. Application of Horizontal Flow Treatment Wells for *In situ* Treatment of Perchlorate Contaminated Groundwater. MS Thesis, AFIT/GEE/ENV/02M-08, 2002. School of Engineering and Management, Air Force Institute of Technology, (AU), Wright-Patterson AFB, OH, March 2002.

Schwartzenbach, R.P., P.M. Gschwend, and D.M. Imboden. Environmental Organic Chemistry. John Wiley and Sons, pp. 488, 539, 540, 1993.

Shaw Environmental and Infrastructure (Shaw). *In situ* Bioremediation of Perchlorate Using Horizontal Flow Treatment Wells. ESTCP Technology Demonstration Plan, Project CU-0224 Final. 2003.

Shaw Environmental and Infrastructure. Aerojet Field Data. Excel Spreadsheet. December, 2006.

Schwartzenbach, R.P., P.M. Gschwend, and D.M. Imboden. *Environmental Organic Chemistry*. John Wiley and Sons. 1993.

Trumpolt, C. W., Crain, M., Cullison, G. D., Flanagan, S. J. P., Siegel, L., & Lathrop, S. Perchlorate: Sources, Uses and Occurrences in the Environment. Remediation Journal, 16(1), 65-89. 2005.

United States Air Force (USAF). *Air Force Guidance on Actions Related to Perchlorate*. June, 2006.

United States Department of Defense (DoD). *Policy on DoD Required Actions Related to Perchlorate*. January, 2006.

United States Environmental Protection Agency. "Announcement of the drinking water contaminant candidate list"; notice. Federal Register. 63:10274-87. 1998.

United States Environmental Protection Agency (EPA). "Drinking Water Contaminant Candidate List and Regulatory Determinations". 2006. http://www.epa.gov/safewater/ccl/index.html

United States Environmental Protection Agency. Known Perchlorate Releases in the US. Excel Spreadsheet. March, 2005. http://www.epa.gov/ogwdw000/ucmr/data/ucmr_list1and2chem.zip

United States Environmental Protection Agency. "Perchlorate and Perchlorate Salts". Integrated Risk Information Management System. 2005. http://www.epa.gov/iris/subst/1007.htm

United States Environmental Protection Agency. Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization Based on Emerging Information. External Review Draft. NCEA-1-0503. Washington, DC: Office of Research and Development; 2002.

United States Environmental Protection Agency. Perchlorate Treatment Technology Update. Federal Facilities Forum Issue Paper. May 2005.

United States Environmental Protection Agency. Request for National Academy of Sciences review of the health impacts of perchlorate. Official memorandum. March, 2003.

United States Environmental Protection Agency. "Terms of Environment: Glossary, Abbreviations and Acronyms". 2006. http://www.epa.gov/OCEPAterms/rterms.html

United States Environmental Protection Agency. "UCM Rounds 1 and 2 and the Six Year Review Data". 2005. http://www.epa.gov/safewater/ucmr/data/r1r26yr_ptables.zip

United States Environmental Protection Agency Office of Solid Waste and Emergency Response (OSWER). "Assessment Guidance for Perchlorate". 2006. http://www.epa.gov/fedfac/pdf/perchlorate_guidance.pdf

United States Government Accounting Office (GAO). 2005. "Perchlorate: A System to Track Sampling and Cleanup Results Is Needed." GAO-05-462. May, 2005. http://www.gao.gov/new.items/d05462.pdf.

Urbansky, E. T., Perchlorate Chemistry: Implications for Analysis and Remediation. *Bioremediation Journal*, 2: 81-95, 1998

Urbansky, E. T., Perchlorate as an Environmental Contaminant. *Environmental Science and Pollution Research*, 9(3): 187-192, 2002.

Xu, J. Y., Y. Song, B. Min, L. Steinberg, and B. E. Logan. "Microbial Degradation of Perchlorate: Principles and Applications," *Environmental Engineering Science* 20(5): 405–22. 2003.

Vita

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Following his commissioning, Maj Secody has had assignments in the Air Force Materiel Command, Pacific Air Forces, and the United States Air Forces in Europe, and four deployments to Saudi Arabia, Oman and Iraq. In September of 2005, he entered the Graduate School of Engineering and Management, Air Force Institute of Technology. Upon graduation, he will be assigned to United States Forces Korea, at Yongsan Army Garrison, Republic of Korea.