FINAL REPORT

Evaluation of Potential for Monitored Natural Attenuation of Perchlorate in Groundwater

ESTCP Project ER-200428

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List of Abbreviations and Acronyms

AFCEE	Air Force Center for Engineering and the Environment
AP	Ammonium Perchlorate
BOD	Biochemical Oxygen Demand
CD	Chlorite Dismutase Enzyme
*c*DCE	*cis*-1,2-Dichloroethenep
cld	Chlorite Dismutase Gene
CVOCs	Chlorinated Volatile Organic Compounds
CSIA	Compound Specific Isotope Analysis
DNA	Deoxyribonucleic Acid
DO	Dissolved Oxygen
DoD	Department of Defense
DPRB	Dissimilatory Perchlorate-Reducing Bacteria
ESTCP	Environmental Security Technology Certification Program
EBAC	Eubacteria
ft bgs	Feet Below Ground Surface
ft msl	Fee Above Mean Sea Level
IDW	Investigation-Derived Waste
ISC	*In Situ* Column
ITF	Interface
ITRC	Interstate Technology and Regulatory Council
K	Hydraulic Conductivity
MDE	Maryland Department of the Environment
MNA	Monitored Natural Attenuation
MBT	Molecular Biology Tool
mRNA	Messenger Ribonucleic Acid
NCSU	North Carolina State University
NPDES	National Pollutant Discharge Elimination System
NPV	Net Present Value
NSWC	Naval Surface Warfare Center
O&M	Operation and Maintenance
ORP	Oxidation-Reduction Potential
PCE	Tetrachloroethene (Tetrachloroethylene)
pcrA	Perchlorate Reductase Gene A

PI	Principal Investigator
PID	Photoionization Detector
PPE	Personal Protective Equipment
P&T	Pump & Treat
PV	Pore Volume
PVC	Polyvinyl Chloride
qPCR	Quantitative Polymerase Chain Reaction Analysis
RAO	Remedial Action Objective
RCRA	Resource Conservation and Recovery Act
RNA	Ribonucleic Acid
sq. ft.	Square Feet
SW	Surface Water
SWMU	Solid Waste Management Unit
TBC	“To Be Considered” Regulatory Standard
TCA	Trichloroethane
TCE	Trichloroethene
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
USGS	United States Geologic Service
VC	Vinyl Chloride
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound

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Executive Summary

Introduction

Solutions-IES conducted an evaluation of the potential for Monitored Natural Attenuation (MNA) of perchlorate as a groundwater remedy at a rocket propellant manufacturing facility in Maryland. The work was funded by the Environmental Security and Technology Certification Program (ESTCP Project ER-0428). The project used a tiered approach described in a Perchlorate MNA Protocol Report (ESTCP, 2008) developed by Solutions-IES for the same project to systematically evaluate the commingled perchlorate and trichloroethene (TCE) plume located at a Solid Waste Management Unit (SWMU) on the east side of the facility.

Demonstration

Tier 1 – Perchlorate Plume Stability and Geometry

Most of the perchlorate contamination within the TCE/Perchlorate SWMU was previously defined using a network of monitoring wells screened in the shallow, intermediate zones of the surficial aquifer and the deep aquifer underlying the site. In the source area, both the shallow and intermediate zones are impacted with perchlorate with reported concentrations as high as 1,240 µg/L. The contaminant plume follows groundwater flow moving from west to east beyond the property boundaries, approximately 2,750 ft from the presumed source. The distal extent appears to be limited at Little Elk Creek as data indicated that perchlorate is below analytical detection beyond (east) of Little Elk Creek. By contrast, limited data suggest that TCE may possibly have migrated beyond the creek. These results suggest that mechanisms that could control perchlorate fate and transport are active prior to groundwater discharging into the creek.

Little Elk Creek is a shallow stream that traverses a zone of undeveloped land covered with shrubs, vines and trees. The width of the naturally occurring buffer on the west side of the creek is approximately 25 feet including the stream bank which is an alluvium deposit composed of sand and gravel. After the pre-demonstration monitoring was performed in 2006, additional monitoring wells were installed to complete the network and further delineate plume geometry. Groundwater results from monitoring well pairs were used to compare shallow zone conditions (less than -20 ft msl) to intermediate zone aquifer conditions (between -20 and -70 ft msl).

Analytical results obtained as a result of the *Tier 1* evaluation confirmed that perchlorate concentrations and mass flux are highest in the intermediate aquifer zone. However, as perchlorate nears Little Elk Creek, the groundwater from the intermediate aquifer zone migrates upward, merging with the shallow aquifer zone, causing an apparent increase in shallow zone concentrations. Analytical results indicated that the overall plume geometry had changed very little since Solutions-IES began monitoring this site in 2006 and the plume is generally stable. The rate that perchlorate concentration changes vs. time in individual monitor wells was calculated to estimate the time required to reach the Maryland Department of Environment's (MDE) standard for perchlorate in drinking water of 2.6 µg /L. Groundwater within the source area is projected to reach the MDE Drinking Water Standard (2.6 µg/L) by 2015, if current trends continue. However, the long travel time through the aquifer will cause perchlorate to remain above drinking water standards in some portions of the plume for decades.

Tier 2- Biogeochemical conditions for Perchlorate Biodegradation
Biogeochemical parameters including dissolved oxygen (DO), oxidation-reduction potential (ORP), total organic carbon (TOC), methane, nitrate, chloride, temperature, and pH were monitored to help determine if groundwater conditions at the site were conducive to the perchlorate biodegradation. In the source and mid-plume areas, DO concentrations and ORP levels were generally oxidative, the pH was generally acidic and there was little TOC to support bioactivity. Methane was not typically produced and the little nitrate and sulfate that was measured showed no change over time. Chlorite dismutase (CD) enzyme assays and qPCR tests for the *pcrA* gene on samples from throughout the plume provided little evidence of perchlorate-reducing bacteria. In contrast, shallow groundwater immediately adjacent to Little Elk Creek did contain some TOC, had a more favorable pH and showed some evidence of methanogenesis. Elevated numbers of perchlorate-reducing bacteria were also identified in this zone. These conditions could better support biodegradation of perchlorate.

Tier 3-Perchlorate Biodegradation
Both laboratory and field tests were performed on site matrices to determine if biodegradation could occur. Laboratory microcosms were set up using saturated soil and groundwater from near a monitoring well pair located close to Little Elk Creek along the plume centerline. The microcosm results showed a reduction in low starting concentrations of perchlorate under ambient conditions to detection limits in about 120 days and a zero-order degradation rate of 0.0025 mg/L/day.

Macrocosm studies were also constructed using saturated soil from borings adjacent to GM-22S/M located near the downgradient plume centerline and contaminated groundwater obtained from GM-22M. Samples were collected from the macrocosm vessels over a 4-month incubation period. Perchlorate was degraded in all five macrocosms at an average 1st-order rate of 2.9 /year.

Three *in situ* columns were installed near the same well pair. Two of the columns remained as live replicates and the other column was inhibited with nitric acid to provide an abiotic control for comparison. The average beginning perchlorate concentration in each column was 148 µg/L. After monitoring groundwater samples from each column for 6.5 months, perchlorate decreased to below the analytical detection limit in both live columns. After normalizing to changes in perchlorate in the abiotic column, the first order degradation rates in the two live columns were 7.6 /yr and 8.5/yr.

Summary

The tiered approached was employed to document the MNA of perchlorate in the plume emanating from the TCE/Perchlorate SWMU on the east side of the facility. In the *Tier 1* evaluation, mass flux analyses showed a slow by statistically significant decline in perchlorate mass during downgradient migration. The absence of perchlorate in groundwater on the opposite side of Little Elk Creek suggested that natural attenuation is occurring prior to groundwater discharging to the creek. The *Tier 2* evaluation of biogeochemical parameters indicated that conditions were not optimal for perchlorate biodegradation in the source and mid-plume areas. However, near the creek, conditions are adequate to support some bioactivity. CD enzyme

assays showed microbial populations capable of perchlorate biodegradation present in the aquifer. Gene copies associated with the specific perchlorate-reducing enzyme were highest in the source area near a previous bioremediation pilot test and near the creek. In *Tier 3*, perchlorate biodegradation was demonstrated in macrocosms and *in situ* columns.

1.0 Introduction

Monitored Natural Attenuation (MNA) is a potential alternative for management of large diffuse perchlorate plumes in a cost-effective manner. Natural attenuation is defined by the USEPA as the "biodegradation, diffusion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility or volume to levels that are protective of human health and the environment"(USEPA, 1999). The term MNA refers to the reliance on natural attenuation processes, within the context of a carefully controlled and monitored site cleanup, to achieve site-specific remedial goals.

Perchlorate is an important contaminant of concern, particularly to the Department of Defense (DoD), as a result of historical use, release and/or disposal of solid rocket fuel and munitions containing ammonium perchlorate. To evaluate whether natural attenuation of perchlorate occurs in the field, multiple lines of evidence should to be established and validated. As part of this Environmental Security Technology Certification Program funded project (ESTCP Project No. ER-0428), two sites were selected for field demonstrations to evaluate the potential for perchlorate MNA as a groundwater remedy: 1) near Building 1419 at the Naval Surface Warfare Center (NSWC), Indian Head, Maryland (Indian Head site), and 2) a TCE/Perchlorate Solid Waste Management Unit (SWMU) at a manufacturing facility in Maryland. The overall goals of this project were:

1. Document the extent of perchlorate natural attenuation in the field;
2. Demonstrate to regulatory agencies through field study that perchlorate MNA is effective for controlling adverse impacts to the environment; and
3. Provide DoD managers with the tools needed to evaluate whether MNA may be appropriate for management of perchlorate–impacted groundwater on their site(s).

MNA of perchlorate in groundwater was evaluated using a tiered approach described in the technical Protocol report developed by Solutions-IES, Inc. in 2008 (ESTCP, 2008). The tiers include: 1) plume stability and geometry; 2) biogeochemical parameter and biological indicator evaluation; and 3) biodegradation indicators. This technical report documents the evaluation of MNA of perchlorate contamination in groundwater at the manufacturing site. Documentation of perchlorate MNA at the Indian Head, Maryland site was presented in a separate report.

1.1 Background

Releases of perchlorate have resulted in extensive contamination of surface and groundwater supplies. Perchlorate is a highly mobile, soluble anion that sorbs poorly to most aquifer material, and can persist for decades under aerobic conditions even though a wide variety of microorganisms can degrade perchlorate to chloride and oxygen (Coates et al., 1999; Coates and Pollock, 2003; Coates and Jackson, 2009). Perchlorate-reducing organisms are widespread in the environment (Coates et al., 1999; Logan, 2001; Coates and Jackson, 2009) and can use a variety of different organic substrates (e.g., acetate, propionate, lactate, etc.) as electron donors for perchlorate reduction (Herman and Frankenberger, 1998; Coates et al., 1999). Perchlorate biodegradation can occur under strict anaerobic conditions as well as facultative anaerobic conditions. In addition, some facultative anaerobic microorganisms are capable of both aerobic respiration under low oxygen tension and anaerobic respiration when oxygen is not present. This metabolic versatility suggests that perchlorate-reducing bacteria may be active in a variety of environments, increasing the potential for natural attenuation of perchlorate.

Oxygen is an inhibitor of perchlorate reduction, but the absence of oxygen alone is not enough to induce the perchlorate-reducing enzymes to function. Facultative anaerobic perchlorate metabolism is inhibited by dissolved oxygen (DO) concentrations in excess of 2 mg/L (Rikken et al., 1996; Chaudhuri et al., 2002). Nitrate can also negatively affect the activity of perchlorate reductase enzymes. However, in mixed environmental cultures, when biodegradable organic substrates are present, the available DO and nitrate will be preferentially consumed, increasing the likelihood of perchlorate biodegradation in the natural environment (Coates and Jackson, 2009). Trace amounts of molybdenum are also required due to its functional role in the biochemistry of the perchlorate reductase enzyme (Chaudhuri et al., 2002). The biodegradation pathway of perchlorate is illustrated below (**Figure 1-1**).

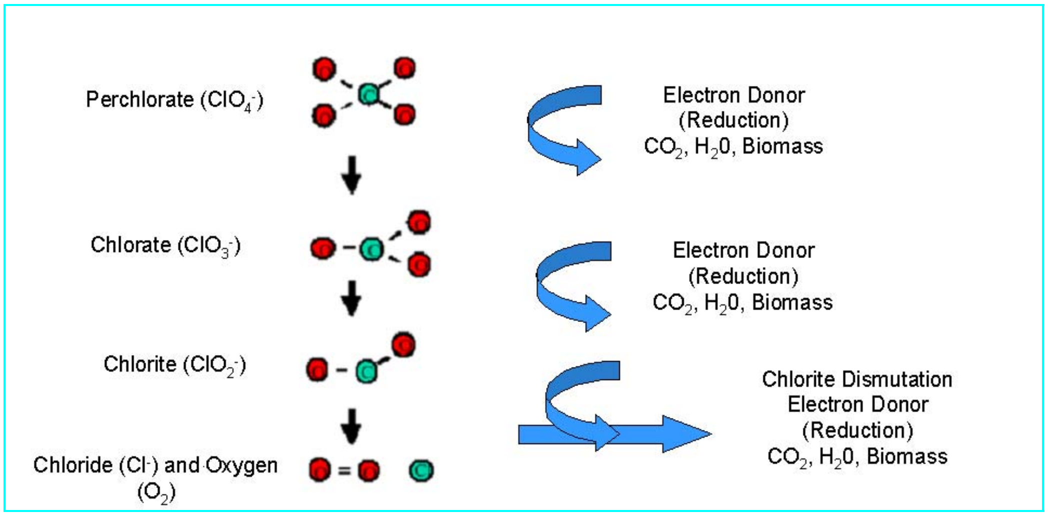

Figure 1-1. Perchlorate Biodegradation Pathway

Work by Coates et al. (1999), Chaudhuri et al. (2002), and Bender et al. (2002) indicates that the *Dechloromonas* and *Azospira* groups represent the primary chlorate and dissimilatory perchlorate-reducing bacteria (DPRB) in the environment, but more that 30 different strains of perchlorate-reducing microbes have been identified. The rate-limiting step in the three-step degradation process is the conversion of perchlorate to chlorate by a perchlorate reductase enzyme (Coates and Jackson, 2009). Subsequent conversion of chlorate to chlorite is also catalyzed by a perchlorate reductase enzyme. Chlorite removal by the chlorite dismutase (CD) enzyme is the final step in perchlorate reduction.

1.2 Objectives of the Demonstration

The objectives of the technical demonstration were to:

- Develop and evaluate multiple lines of evidence for MNA of perchlorate at a field site.
- Evaluate the use of various biological indicators of perchlorate biodegradation.
- Compare biodegradation rates measured in microcosm studies with biodegradation rates in the field.
- Evaluate the suitability and cost-effectiveness of MNA of perchlorate in groundwater at a field site.
- Transfer the knowledge gained about perchlorate MNA to the regulatory community.

Prior to beginning work at the site, a site-screening process was conducted to identify sites with moderate to good potential for MNA of perchlorate. This included an initial survey of knowledgeable representatives at approximately 120 potential DoD or DoD-related sites. By comparing the responses received to the selection criteria in the Technology Demonstration Plan, these were pared down to seven potential sites for further study. Samples of aquifer material and groundwater were then collected from each of these sites and microcosm studies were performed to measure perchlorate biodegradation in a laboratory setting. The details of the site-selection process and results of microcosm testing are described in a previous report titled “Field and Laboratory Evaluation of the Potential for Monitored Natural Attenuation of Perchlorate in Groundwater, Final Technical Report” (i.e., Treatability Report; ESTCP, 2007). Based on the microcosm studies, site logistics, and cost considerations, the Maryland manufacturing site was selected as one of two sites to evaluate the potential for MNA of perchlorate in groundwater.

1.3 Regulatory Drivers

Release of perchlorate to the environment can impact ground and surface water with the potential for human consumption through direct (drinking water) and indirect (crop uptake from irrigation water) pathways. Sampling performed by the USEPA in 2004 revealed that over 11 million people in the United States had greater than 4 µg/L of perchlorate in their drinking water (Stroo et al., 2009). It appears that the primary exposure to perchlorate in the United States is through consumption of food (USFDA, 2007). This is a significant concern because high levels of perchlorate interfere with iodide uptake by the thyroid (NRC, 2005).

As of 2010, a federal cleanup standard for perchlorate in groundwater or soil had not been promulgated (USEPA, 2005; ITRC, 2005). However, in January 2006, the USEPA issued “Assessment Guidance for Perchlorate” identifying 24.5 µg/L as the recommended “to be considered” (TBC) concentration and preliminary remediation goal for perchlorate (USEPA, 2006). Since then several states have generated advisory levels that range in concentration from 1 µg/L to 18 µg/L (Hatzinger, 2005). Massachusetts promulgated the first state drinking water standard in 2006 at 2 µg/L (MADEP, 2006) and California has established a drinking water standard of 6 µg/L (CDHS, 2007). In 2008, Maryland adopted 2.6 µg/L as its drinking water standard (MDE, 2008)

1.4 Stakeholder/End-User Issues

An overall goal of this project was to produce a protocol that could be used by scientists, engineers and managers to guide implementation of perchlorate MNA as a remedial strategy. The technical demonstration at the Maryland industrial site (and the Indian Head, MD site, as well) allowed Solutions-IES to evaluate different lines of evidence during the site selection process and produce a protocol for implementing MNA. Where MNA can be shown to be protective of human health and the environmental, end-users often find it to have lower short-term costs. However, the process is not fast and longer project life cycles may sometimes result in greater life-cycle costs compared to other alternatives. MNA should not be viewed as a “no action” approach to groundwater treatment.

Stakeholders and end-users such as base managers and environmental consultants may not have considered MNA for perchlorate because there was no guidance for implementing the technology. The Protocol Report developed from our work and used to evaluate the demonstration sites (ESTCP, 2008) will help users select the correct tools for performance monitoring and overall evaluation of perchlorate MNA as a remedial alternative for their site. By properly applying the steps described in the Protocol Report, local regulators and the general public can gain confidence that perchlorate MNA is protective of the public welfare, human health and the environment.

2.0 Technology Description

2.1 Monitored Natural Attenuation (MNA) Development

In the 1980s and 1990s, field monitoring data indicated that many groundwater plumes were not migrating as far as predicted, and in some cases were stable or receding. Detailed laboratory and field research demonstrated that the combined action of naturally occurring physical, chemical, and biological processes was limiting downgradient migration and adverse impacts, without any active human intervention. As a result of this work, Monitored Natural Attenuation (MNA) became a widely accepted practice for effective management of groundwater contamination. MNA is the use of these natural processes, along with careful documentation and monitoring, to manage contaminated sites.

An integral component of any MNA remedy for groundwater is a clear understanding of the hydrogeologic conditions present in the site area. A general conceptual site model must be formulated and then calibrated against site data. Physical conditions within the aquifer, groundwater flow characteristics (e.g., flow velocity, dilution and dispersion), and contaminant concentration data must be obtained and evaluated. It is also important to understand the primary chemical and biological processes controlling contaminant mobility and degradation.

The USEPA and others have developed protocols and guidance documents for implementing MNA for specific contaminants. Published methods for evaluating MNA of petroleum hydrocarbons (Wiedemeier et al, 1995; USEPA, 1999) and chlorinated solvents (USEPA, 1998) have been in use for many years. These documents describe systematic steps for delineating contaminant plumes, describing trends in contaminant fate and transport, monitoring site geochemistry, evaluating site biology and even scoring a site for its potential to support natural attenuation (USEPA, 1998). Wiedemeier et al. (1998) developed a tiered approach to systematize the approach to MNA at any given site. The three tiers are as follows:

- Tier 1 - Plume Stability and Geometry Assessment
- Tier 2 - Biogeochemical Parameter and Biological Indicators
- Tier 3 - Biodegradation Indicators

Prior to current work, MNA of perchlorate had not been systematically tested in the field. One objective of this demonstration was to identify useful indicators of perchlorate attenuation that would be applicable to field sites. The information gained during this project was also used to document the use of the technical Protocol Report prepared for this project for implementing this technology at perchlorate contaminated sites (ESTCP, 2008).

2.2 Advantages and Limitations of the Technology

2.2.1 Cleanup Objectives

The objective of all remediation approaches should be to return groundwater to its beneficial uses within a timeframe that is reasonable given the particular circumstances of the site. MNA is an appropriate remediation method when its use is protective of human health and the environment and it is capable of achieving site-specific remediation objectives within a timeframe that is reasonable compared to other alternatives. Over the short-term, the contaminant plume should be stable or shrinking. Over the long-term, the mass and/or concentration of contaminants should decrease.

2.2.2 Advantages of Perchlorate MNA

Natural attenuation is a combination of physical, chemical and biological processes. Because perchlorate is an inorganic salt, it is very soluble and particularly mobile in groundwater. It is subject to greater dilution than many organic contaminants. High solubility is both an advantage and disadvantage. Flushing and dilution can reduce concentrations rapidly, but solubility can result in extended plumes with low concentrations that are difficult to capture and expensive to treat.

As paraphrased from Wiedemeier et al. (1998), primary advantages of using MNA as a technology for remediating perchlorate in groundwater are:

- Lower volume of remediation-derived wastes;
- Reduced potential for cross-media transfer of contaminants;
- Reduced risk of human exposure to contaminants, contaminated media and other hazards;
- Destruction of contaminants *in situ* via natural processes;
- Less disturbance to site operations and ecological receptors;
- No artificial impact to groundwater geochemistry and biology;
- Applicability to all or a portion of a site depending on site characteristics and goals;
- Ability to be used in combination with other technologies; and
- Lower capital costs and low, if any, maintenance costs.

2.2.3 Limitations of MNA

The primary limitations of MNA include:

- Potential longer life cycles to reach remediation goals compared to active remediation measures at the site;
- More detailed site characterization is needed to demonstrate attenuation which may mean more complex and costly up-front investigation;
- Institutional controls may be required to ensure long-term protectiveness;
- Long-term performance monitoring will generally be more expensive and for a longer time period;
- Potential exists for continued contaminant migration, and/or cross-media transfer of contaminants;
- Changing site conditions over time may require a re-evaluation of MNA; and
- Public acceptance may be more difficult and costly to obtain.

3.0 Demonstration Design and Evaluation

3.1 Performance Objectives for the Demonstration

The overall objective of this project was to evaluate the potential for MNA of perchlorate in groundwater. Once perchlorate attenuation is demonstrated, regulators and site owners can evaluate use of MNA along with other remediation strategies. If natural attenuation processes are not sufficient to prevent significant adverse impacts, other remediation strategies may need to be implemented before application of MNA.

Qualitative and quantitative performance objectives were developed in the Technology Demonstration Plan (Solutions-IES, 2006). As shown in **Table 3-1**, the performance objectives were achieved. Sections of the report where each objective is discussed are noted in the table.

3.2 Site-Selection Process

To identify sites for participation in the perchlorate MNA project, three levels of site screening were conducted. Screening Level 1 was performed in the office and involved gathering historical information from approximately 120 perchlorate-impacted sites across the United States. Past remediation activities, if any, were considered. Screening Level 2 included reviewing the gathered information and selecting seven sites for initial and comparative field characterization. The seven sites selected for further screening included:

1. Little Mountain Test Annex Sludge Drying Beds, Hill AFB, Utah
2. ATK Thiokol, Inc., Utah
3. Beale Air Force Base, California
4. John C. Stennis Space Center, Mississippi
5. Redstone Arsenal, Alabama
6. Manufacturing Facility in Maryland
7. Naval Surface Warfare Center, Indian Head, Maryland

Level 3 screening included collection and analysis of soil and groundwater samples from the seven field sites selected during the Level 2 screening step. The site matrices collected were analyzed in the laboratory for parameters potentially useful for determining the suitability of the site for MNA of perchlorate. Field measurements included pH, dissolved oxygen (DO) and oxidation-reduction potential (ORP). Laboratory analyses included perchlorate concentration, total organic carbon (TOC) concentration, CD enzyme analysis, and 6-month biological oxygen demand (BOD_6). Detailed information about the screening process and the results of the analyses performed at all seven sites is provided in the Treatability Report (ESTCP, 2007). Additional site-matrix sediments and groundwater were collected from perchlorate-impacted areas of each site to use in laboratory microcosm studies. The pre-demonstration findings associated with the selection of the manufacturing facility in Maryland are described in the following sections.

Table 3-1. Performance Objectives

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance (Objective Met?)	Reference Section
Qualitative	1. Reduce risk	Reduce concentrations and mass flux of perchlorate during downgradient migration.	Yes	Sections 6.1.4 & 6.1.3.2
	2. Capital costs	**Capital costs are significantly lower than active remedial alternatives.**	Yes	Section 8.3.1
	3. Maintenance	Maintenance costs are low and are typical of those associated with a monitoring well network.	Yes	Sections 8.2 & 8.3.1
	4. Uncomplicated implementation	Implementation is similar to that of a typical monitoring program.	Yes	Section 7.0
	5. Regulatory acceptance	MNA approach is generally accepted by regulatory community, with conditions.	Yes	Sections 1.3 & 9.2
	6. Monitoring approach	Monitoring approach is consistent with current industry practice. Results are easy to understand and interpret.	Yes	Section 6.0
Quantitative	1. Reduce perchlorate concentrations	Decreases in the average perchlorate concentration are statistically significant and can be attributed to natural attenuation.	Yes	Section 6.1
	2. Reduce mass flux of perchlorate	Decreases in the total mass flux during the downgradient migration of perchlorate are consistent, reproducible, statistically significant and can be attributed to natural attenuation.	Yes	Section 6.14
	3. Multiple lines of evidence	Two or more lines of evidence support perchlorate attenuation.	Yes	Sections 6.1, 6.2 & 6.3
	4. Stable isotope ratios	Observe statistically significant change in isotopic ratio of perchlorate during downgradient migration.	Not tested	
	5. Enzyme activity	RNA levels of perchlorate degraders are elevated at some locations in the plume relative to background locations.	Yes	Section 3.5.3 & 6.2.10
	6. Meet regulatory standards	Perchlorate concentrations are below regulatory levels at compliance point.	No	Sections 6.1

3.2.1 Site History and Description

Solutions-IES initially contacted Mr. William Lucas, P.E., Plant Engineer, at the facility about the potential for including the TCE/Perchlorate SWMU as a demonstration site for the Perchlorate MNA project. Mr. Lucas provided additional information regarding groundwater investigations across the site prepared by other consultants, and anecdotal information. Subsequent to Mr. Lucas' retirement, Mr. Rich Zambito, P.E., provided continuing support for the demonstration.

The following reports prepared by ARCADIS G&M, Inc. (Arcadis), were used as the primary source of historical information about the site.

> Kladias, M.P. and J.P. Sgambat, ARCADIS Geraghty & Miller, Inc., *Perchlorate Investigation Sampling Plan,* April 15, 1999 (Kladias and Sgambat, 1999).
>
> ARCADIS G&M, Inc., *Interim Site-Wide Investigation Technical Report and Work Plan,* May 2003 (Arcadis, 2003).
>
> Kendall, G.S., M.P. Kladias and J.P. Sgambat, ARCADIS G&M, Inc., *Conceptual Site Model of Groundwater Flow and Transport at the (Confidential) Facility,* September, 2004 (Kendall et al., 2004).

The facility covers approximately 600 acres (**Figure 3-1).** The facility is bounded on the south by US Route 40, commercial properties, and residential areas. The facility extends to the east to Maryland Highway MD 279 (Elkton Rd). The north and northeast property line is formed by Little Elk Creek which traverses the entire facility from the northwest portion all the way to Elkton Road. To the north and west, the site is surrounded by agricultural areas. The facility has been used for industrial purposes, such as fireworks manufacturing, munitions production, pesticide production, and research and manufacturing of solid propellant rockets since the 1930s. Previous site owners reportedly used TCE at the site until 1974. Ammonium perchlorate continues to be used to manufacture and test rocket engines at the facility. The surrounding areas also have a diverse history of industrial activities.

There are two working areas at the facility: the southern Plant Area, located at the end of the entrance to the facility off Thiokol Rd., and the Manufacturing Area located in the north-northwest portion of the site. The Plant Area is also known as "A-Area" and the Manufacturing Area is also known as "C-Area". The "C-Area" is located in the northwest portion of the facility and is not shown on the site drawings.

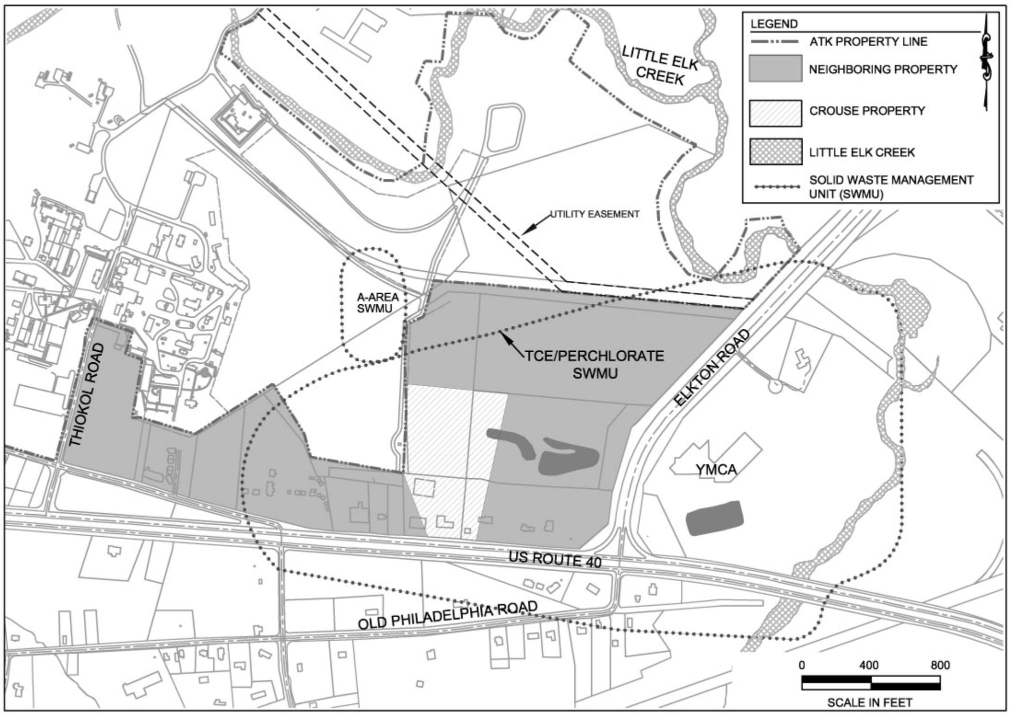

Figure 3-1. Site Layout Map

Volatile organic compounds (VOCs) were first discovered in groundwater from two production wells in the A-Area in 1984. TCE concentrations were found in groundwater on the south side of US Route 40 and most of the properties with private wells south of the site were connected to the municipal water supply system in the late 1980s.

Two SWMUs are identified in the A Area. The A-Area SWMU shown on **Figure 3-1** was a former burn field (closed in 1958) used to dispose of waste solid fuel rocket propellant. The TCE/Perchlorate SWMU consists of a groundwater plume that extends beyond the property boundaries to the east towards Little Elk Creek. The entire TCE/perchlorate plume is considered the SWMU rather than a particular location where former waste handling was known or presumed to occur. Previous investigations showed that the commingled TCE and perchlorate plume extends off site to the east under Elkton Road to Little Elk Creek beyond the neighboring YMCA property, and to the south side of U.S. Route 40. The horizontal extent of the TCE and perchlorate in groundwater originating in A-Area and extending across the TCE/Perchlorate SWMU is shown in **Figure 3-2**.

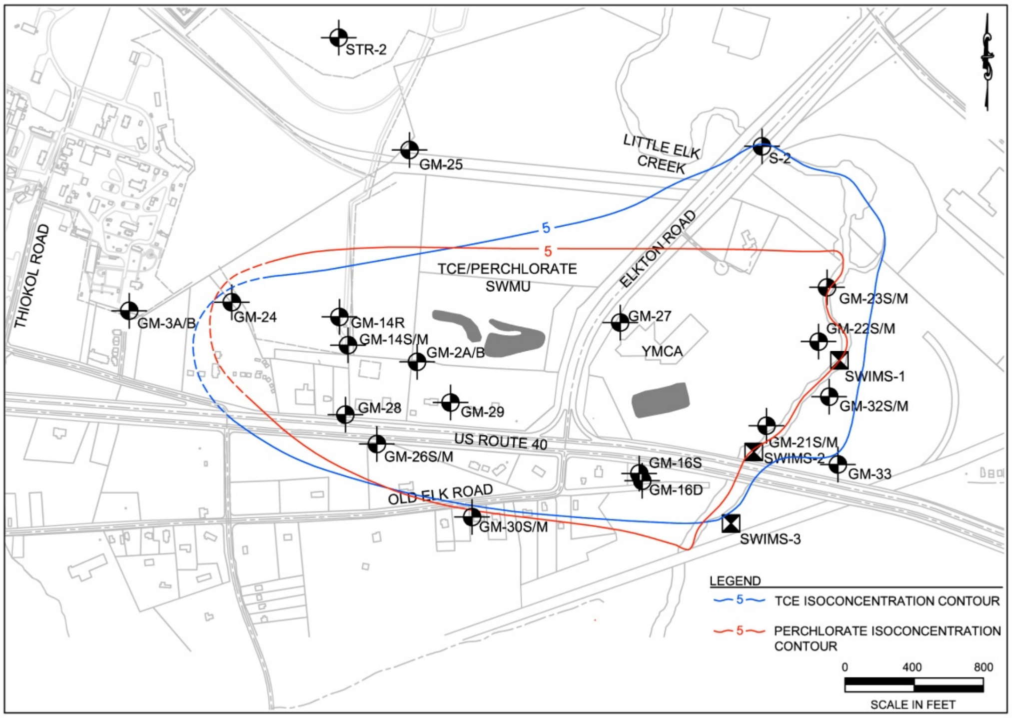

Figure 3-2. Horizontal Extent of the Commingled TCE and Perchlorate Plume

3.2.2 Previous Remediation Studies

3.2.2.1 A-82 Pump & Treat System

As an interim remedial measure, an extraction well and shallow-tray air stripper system was installed in the vicinity of monitor well GM-14 in 1997. Recovery well GM-14R **(Figure 3-2)** was installed into the intermediate aquifer to capture and withdraw contaminated groundwater from the vicinity of the source. The air-stripper system has a treatment capacity of 45 gpm. However, according to the owner, typical flow rates have been between 7 and 15 gpm due to the limited capacity of the extraction well. Treated water is discharged through a pipe carrying the water approximately 1,800 ft north to the closest point along Little Elk Creek. Discharge is allowed by a National Pollution Discharge Elimination System (NPDES) permit.

The pump and treat (P&T) system has operated since 1998, effectively accounting for the removal of almost 800 lbs of VOCs from the aquifer. Perchlorate recovered by the system was only reported in the influent waste stream occasionally during the years of monitoring. For example, 31 lbs of perchlorate were recovered in 2003 and 12 lbs in 2007, but since perchlorate is not treated by air stripping it is assumed that it was discharged directly to Little Elk Creek.

3.2.2.2 *In Situ* Bioremediation Pilot Test

In 2004, Arcadis performed a pilot test to demonstrate the effectiveness of injection of a molasses solution into the aquifer to promote *in situ* bioremediation of chlorinated VOCs (CVOCs) and perchlorate. The bioremediation pilot test was conducted in the vicinity of monitor well GM-14M where TCE and perchlorate levels were initially 1,000 µg/L and 1,240 µg/L, respectively. The test was monitored for about 1 year during which time TCE concentrations at GM-14M fluctuated, but never dropped appreciably. By contrast, the concentration of perchlorate dropped from the baseline level to non-detect after approximately seven months. Once the added carbon was depleted, mass flux of perchlorate from shallow upgradient portions of the plume caused a rebound in perchlorate levels.

3.2.3 Pre-Demonstration Testing

3.2.3.1 Groundwater and Soil Sampling

The wells of interest during the site-screening process included GM-3B, GM-14M, GM-2B, GM-22S and GM-22M. As shown on **Figure 3-2**, these wells generally form a line starting close to the plant and moving east (i.e., downgradient) toward the eastern leg of Little Elk Creek. During the site-selection process, samples were collected from these existing monitoring wells using a peristaltic pump and polyethylene tubing. Field parameters were collected during low-flow sampling at each monitoring well. A soil sample (SB-1) from a depth of approximately 3 to 5 feet bgs was also collected by hand augering adjacent to GM-22S (**Figure 3-3**). This sample was from below the water table and represented conditions in the shallow aquifer. **Table 3-2** summarizes CVOC and perchlorate concentrations measured during the groundwater and soil sampling activities at each monitoring well. **Table 3-2** also summarizes the results of additional field and laboratory tests that were run on the samples.

Figure 3-3. Location of GM-22S and GM-22M near the Wooded Riparian Buffer on the West Side of Little Elk Creek

Table 3-2. Groundwater Characterization in Selected Monitoring Wells (January 19, 2005)

Relative Location		**Upgradient**	**Source**	**Downgradient**	**Downgradient**	**Midgradient**	**Soil near GM-22S**
	units	**GM-3B**	**GM-14M**	**GM-22M**	**GM-22S**	**GM-2B**	**SB-1 (Sed)**
Perchlorate	µg/L	<4	1,200	190	240	1,300	NT
Dichloromethane	µg/L	BQL	100	930	620	530	NT
1,1-Dichloroethene	µg/L	BQL	3	BQL	55	BQL	NT
trans-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Dichloroethane	µg/L	BQL	8	34	24	24	NT
cis-1,2-Dichloroethene	µg/L	BQL	48	74	41	53	NT
Chloroform	µg/L	BQL	2	7	5	5	NT
1,1,1-Trichloroethane	µg/L	BQL	86	1,000	640	620	NT
Carbon tetrachloride	µg/L	BQL	BQL	BQL	BQL	7	NT
Trichloroethene	µg/L	1	1,300	6,30	3,400	2,400	NT
Tetrachloroethene	µg/L	BQL	3	4	3	10	NT
Vinyl Chloride	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Chloroethane	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Chloroemethane	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Total CVOCs	**µg/L**	**1**	**1,500**	**8,400**	**4,800**	**3,600**	**NT**
Ethane	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Ethene	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Methane	µg/L	BQL	BQL	BQL	BQL	BQL	NT
Total Organic Carbon	mg/L	<1.0	1.1	<1.0	<1.0	<1.0	<1,000
Chloride	mg/L	24	45	65	101	24	NT
Nitrate	mg/L	11	9.9	2.4	2.8	10	NT
Sulfate	mg/L	1	8.9	3.2	5.2	1	NT
Phosphate	mg/L	<1.0	<1.0	<1.0	<1.0	<1.0	NT

Table 3-2. Groundwater Characterization in Selected Monitoring Wells (January 19, 2005)

Relative Location		**Upgradient**	**Source**	**Downgradient**	**Downgradient**	**Midgradient**	**Soil near GM-22S**
	units	**GM-3B**	**GM-14M**	**GM-22M**	**GM-22S**	**GM-2B**	**SB-1 (Sed)**
pH	SU	5.5	4.5	5.0	4.8	6.0	NT
Dissolved Oxygen	mg/L	1.5	2	1.5	1	4	NT
Chlorite Dismutase	pos/neg	NT	NT	NT	NT	NT	++
Oxidation-Reduction Potential	mV	130	220	210	200	170	NT

BQL = below quantitation limit
NT = not tested
++ = positive detection
Concentrations rounded to 2 significant figures

3.2.3.2 Laboratory Microcosm Studies

Microcosm studies were conducted as part of the site-screening process using soil and groundwater collected from the vicinity of GM-22S. Solutions-IES created 250-mL microcosm bottles (**Figure 3-4**) to test three conditions: 1) natural attenuation of perchlorate starting at relatively low concentrations (i.e., ~300 µg/L); 2) natural attenuation of perchlorate starting at relatively high concentrations (i.e., ~5,000 µg/L); and, for comparison, 3) attenuation in the presence of added simple and complex electron donors (i.e., lactate and EOS®[1] solutions, respectively). The treatments testing natural attenuation received no amendments unless perchlorate had to be added to achieve the desired starting concentration. Poison/killed controls were used to account for abiotic losses.

Figure 3-4. Microcosm Bottles Used in the Laboratory Studies

The microcosms were incubated at room temperature and monitored for approximately one year. Samples were tested for the changes in perchlorate, TCE, *cis*-1,2-dichloroethene (*c*DCE), vinyl chloride (VC), ethene, methane, DO, nitrate, sulfate, and chloride concentrations with time. As reported in the Treatability Report (ESTCP, 2007), none of the ambient condition microcosms showed evidence of TCE dechlorination. In the EOS® and lactate-amended microcosms, there was a sharp drop in TCE with concurrent increase in *c*DCE and methane. However, there was no further conversion to VC or ethene.

In the high concentration microcosms, nitrate decreased to below detection, while sulfate, chloride, and DO remained constant over time. The average perchlorate concentration declined

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[1] EOS® is a registered trademark of EOS Remediation, Inc., Raleigh, NC. The product, EOS® 598B42, was provided by the manufacturer for use in this study.

from 5,400 µg/L to 1,400 µg/L or >70% reduction over the one year incubation period (**Figure 3-5a**). In one of the high perchlorate microcosm replicates, perchlorate was reduced to below the detection limit. In the low and high perchlorate killed microcosms, perchlorate, chloride, sulfate, and DO remained constant showing no biodegradation. In low concentration microcosms, there was a lag period of approximately 100 days while oxygen and nitrate were depleted, followed by relatively rapid perchlorate biodegradation from an average of 290 µg/L to below the analytical detection limits at 60 days (**Figure 3-5b**).

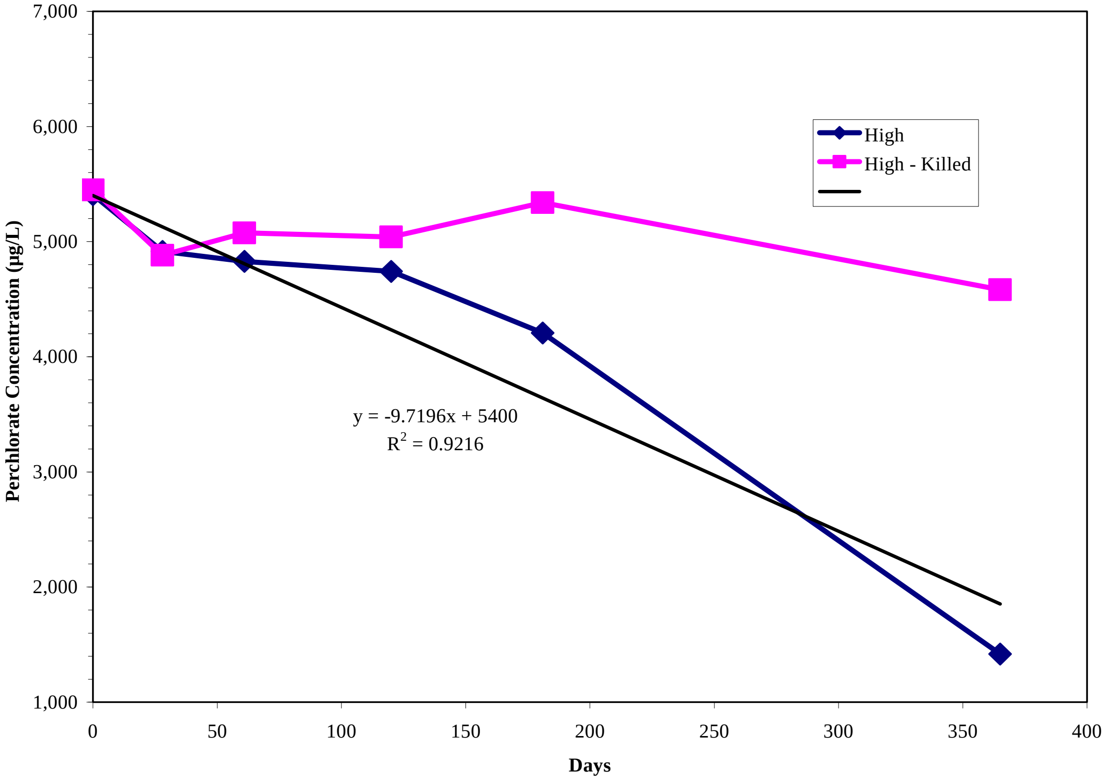

Figure 3-5a. Ambient Degradation of High Starting Concentrations of Perchlorate in Microcosms (ESTCP 2007)

In the EOS® and carbon-amended microcosms, DO, nitrate, and sulfate were consumed concurrently, indicating a rapid conversion to conditions more favorable for perchlorate biodegradation. Not unexpectedly, perchlorate was degraded to below the analytical detection limit within 28 days (**Figure 3-5b**).

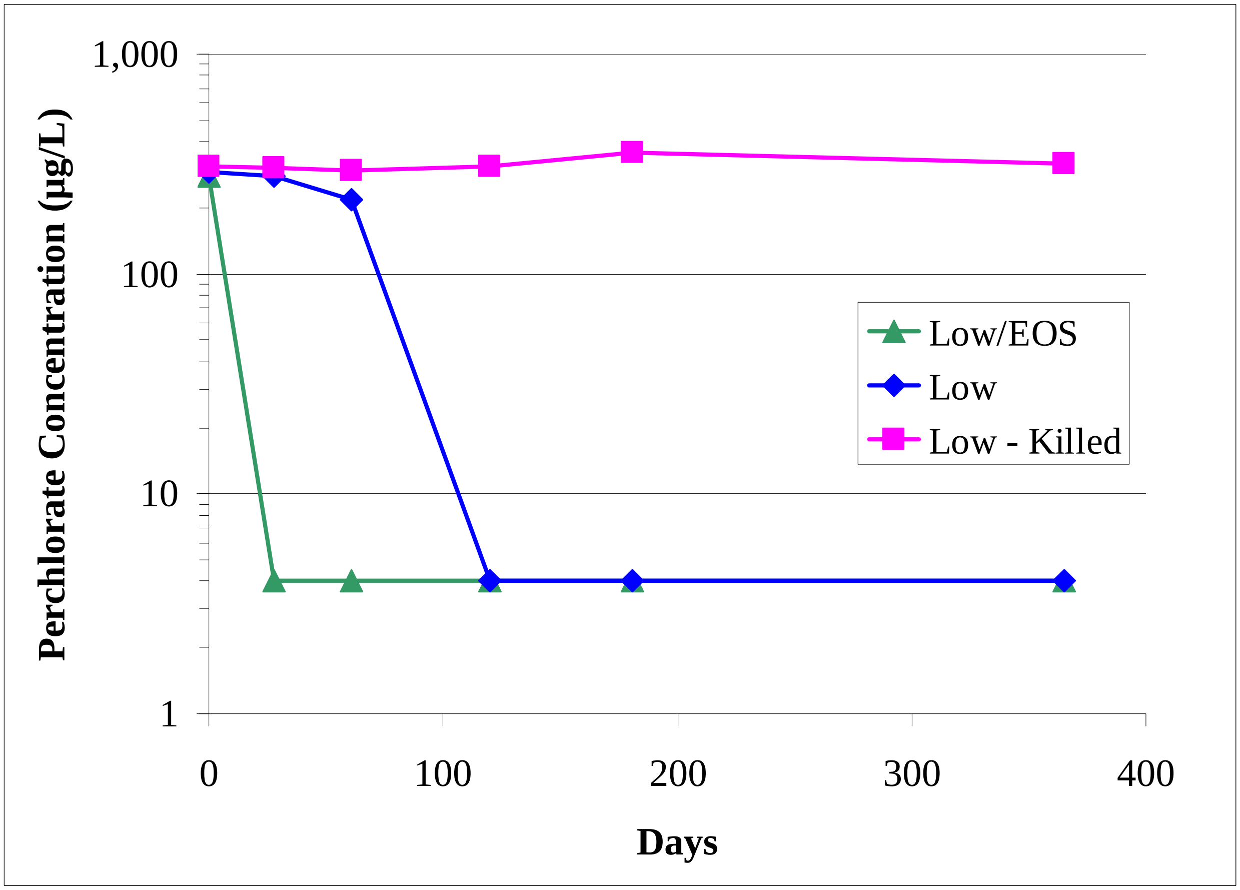

Figure 3-5b. Degradation of Low Starting Concentrations of Perchlorate in Microcosms with and without Added Substrate (ESTCP 2007)

Trend lines were applied to the perchlorate data. At high starting concentrations, the best fit curve was shown to be zero-order resulting in an ambient perchlorate degradation rate of approximately 9.72 µg/L/day ($R^2 = 0.92$). In microcosms with low starting perchlorate, a lag lasting ~61 days was observed followed by a measureable decrease in perchlorate concentration. The zero-order rate between Day 61 and Day 120 was 3.64 µg/L/day and the first-order degradation rate for the same period was 0.068/day. For comparison, the degradation rates for perchlorate in the treatments amended with EOS® were calculated from Day 0 to Day 28. The zero-order rate was 274 µg/L/day and the first-order decay rate was 4.24/day.

The decrease in perchlorate concentration over one year under ambient conditions and the accelerated degradation in the presence of substrate demonstrated that microorganisms capable of perchlorate reduction are present in soil and groundwater near the presumed plume discharge area in the vicinity of Little Elk Creek. In addition, perchlorate and electron acceptor concentrations remained constant over time in the killed control microcosms, further indicating the observed reduction in perchlorate and nitrate in ambient microcosms was due to biological activity.

3.2.4 Selection Criteria Summary for the Maryland Manufacturing Facility

Subsequent to the sampling activities and laboratory studies, a scoring system was devised to assist in the decision regarding which of the seven sites of interest would be suitable for the technical demonstration of the MNA of perchlorate. In similar fashion to the preliminary screening analysis for evaluating the MNA of CVOCs (Wiedemeier et al., 1998), each parameter was assigned a value and scored based on the likelihood that the result would be conducive to natural attenuation.

The geochemical data from the facility that were factored into its selection were obtained from GM-22S where conditions for perchlorate biodegradation appeared to be most favorable. The field monitoring results suggested the presence of measurable DO and ORP suggesting more oxidative conditions (ESTCP, 2007) and the groundwater pH generally was below the optimal neutral range. Nonetheless, there were some indications that this area of the site could support biodegradation. The carbon-amended microcosm treatments strongly supported the presence of perchlorate reducing microorganisms in the aquifer. The CD assay on saturated soil from near GM-22S showed some positive indication of microorganisms that can produce CD enzyme.

In the low perchlorate ambient microcosms, perchlorate was depleted in all the three replicates also suggesting potential for natural perchlorate biodegradation to occur. A steady decrease was also observed in the high perchlorate microcosms. It appears that the aquifer material collected near Little Elk Creek contained sufficient organic material to support degradation of both nitrate and perchlorate. The degradation rates were zero-order with high staring concentrations and first-order with low starting concentrations. If there is sufficient contact time, some portion of the perchlorate may be degraded naturally before it discharges to the stream.

Additional criteria were also factored into the evaluation including site logistics such as accessibility, weather, presence of unexploded ordnance and terrain. The depth to groundwater and type of drilling required, which relates to cost, as well as the interest of the base managers in supporting the project, were also considered. The scores were totaled and despite the variability of some important field conditions, the observed decrease of perchlorate in the plume from the source toward Little Elk Creek suggested that there is a potential for natural attenuation of perchlorate at this site. Based on having the second highest score compared to the other six sites[2], the plume from the TCE/Perchlorate SWMU at the Maryland manufacturing site was selected and approved by ESTCP as one of two demonstration sites.

3.3 Demonstration Approach

Widespread acceptance of MNA requires multiple lines of evidence to demonstrate its value as a remedial alternative. Analytical methods are available to monitor the concentration of perchlorate in the environment with high sensitivity and selectivity, geochemical tests can indicate whether ambient conditions are conducive to perchlorate biodegradation, and molecular biological tools (MBTs) are available to monitor the activity and sustainability of perchlorate-reducing bacterial populations. When properly applied, MNA of perchlorate and can be protective of human health and the environment.

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[2] Internal project Site Selection Memorandum to ESTCP, September 20, 2005.

The MNA Protocol (ESTCP, 2008) created during the early stages of the project was used to guide the planning and selection of tasks to address the challenges at the site. The objective was to use the three-tiered approach described in the Protocol to evaluate how this approach would work for perchlorate on a real project site. As noted in Section 2.1 above, the tiers include: 1) plume stability and geometry assessment; 2) biogeochemical parameters and biological indicator evaluation; and 3) biodegradation indicators. The methods, processes and tools used in the demonstration are discussed in the following sections.

The demonstration activities included both field and laboratory components. Groundwater sampling activities were performed once as a baseline and four additional times over the course of the performance monitoring period to evaluate aquifer conditions, and how those conditions might affect the potential for natural biodegradation of perchlorate. The well network was expanded during the course of the work. Therefore, not all wells were available or sampled during each event. The groundwater sampling events were conducted over a 2-year period (~24 months) on the dates shown in the **Table 3-3**.

Table 3-3. Performance Monitoring Schedule

Sampling Date	Days	Months
05/18/2006 (Baseline)	0	0
02/06/2007	263	~9
05/15/2007	362	~12
10/03/2007	501	~17
4/29/2008	711	~24

3.4 Field Methods

Field activities were adapted to evaluate the fate and transport of perchlorate through different surface conditions encountered as groundwater moves from the area near GM-14R toward Little Elk Creek. Field methods implemented during the demonstration included the installation of borings, monitor wells, instantaneous and continuous water level determinations, measurement of field parameters and hydraulic conductivity, and installation and testing of specialized *in situ* columns to measure perchlorate biodegradation rates.

3.4.1 Monitoring Well Installation

A large monitor well network existed at the site as a result of prior assessments. In general, the unconfined aquifer has been divided into shallow and intermediate zones which are separated by a semi-confining layer. The shallow aquifer zone, the intermediate aquifer zone, and the deep bedrock unit are generally defined at elevations above -20 feet below mean sea level (ft msl), between -20 ft msl and -70 ft msl, and below -70 ft msl, respectively. To further delineate the plume geometry, fill in gaps in areal coverage, and provide additional sources of data from which to evaluate MNA and perchlorate mass flux, Solutions-IES installed several new monitor wells. Four additional monitoring well pairs were constructed in December 2006: three monitoring well pairs east of Elkton Road on the property owned by the YMCA (designated SMW-9S and 9M, SMW-11S and 11M, SMW-13S and 13M), and one well pair west of Elkton Road (SMW-8S and SMW-8M). The boring logs associated with the new wells are included in **Appendix A**. One well in each well pair was terminated within the shallow zone and one well in the intermediate zone. Each of the monitoring wells was constructed of 2-inch diameter PVC well materials with a 10-foot long screen. The shallow monitoring wells were generally terminated so that the screened interval was approximately 20 to 30 ft bgs, and each intermediate monitoring well was terminated so that the screened interval was approximately 50 to 60 ft bgs. **Table B-1** in **Appendix B** provides construction details for both pre-existing and new monitor wells. Each of the new well locations was surveyed in relative to existing monitoring well locations. The overall well network is illustrated on **Figure 3-6**.

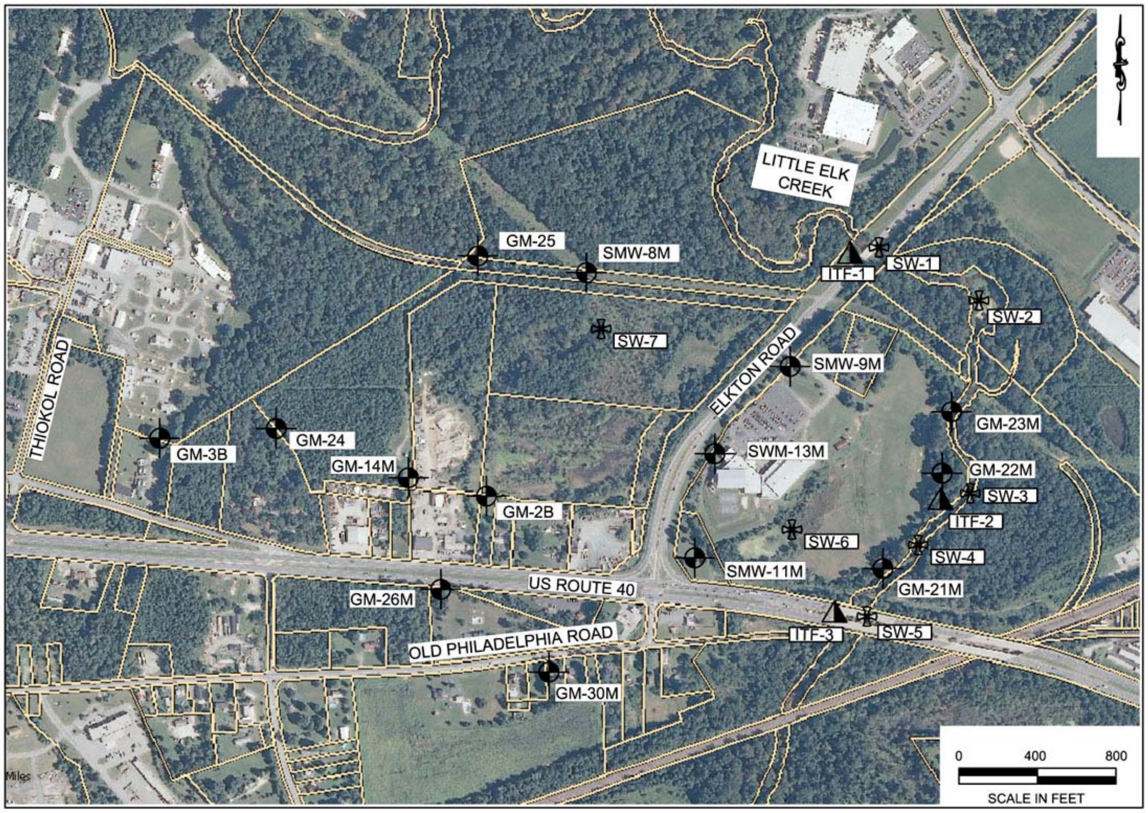

Figure 3-6. Monitoring Well Network Used to Evaluate the TCE/Perchlorate Plume

3.4.2 Groundwater Sampling

Water levels were measured in the wells prior to the collection of groundwater samples. Each well was sampled using low-flow purging and sampling procedures. Monitoring wells with a depth to water of 25 ft bgs or less were sampled with a peristaltic pump and monitoring wells with a depth to water greater than 25 ft bgs were sampled with a bladder pump.

When the monitoring wells were sampled using a low-flow methodology, an adequate purge was achieved when the pH, specific conductance, and temperature of the groundwater stabilized as defined in the Technology Demonstration Plan. The parameters measured in some wells were altered when necessary in order to collect the volume of sample required for perchlorate analysis.

After an adequate purge was achieved, field measurements were obtained using field meters and groundwater samples were collected for analysis. The field parameters that were typically measured included DO, ORP, pH, temperature, specific conductance and turbidity. Some of these parameters were not collected if the sample volume was too low.

When groundwater samples were collected using a peristaltic pump, the sample for DO analysis was collected as water flowed out of the sampling tubing by inserting a field test self-filling DO ampoule (CHEMetrics, Inc, Calverton, VA) into the end of the tube. The ampoule tip was broken off inside the tube below the flowing water surface, pulling water into the ampoule while being careful to exclude any air. The DO concentration was determined by a visual comparison to color standards. Other DO measurements were obtained using a downhole probe and YSI 556 water quality meter.

3.4.3 Surface Water and Groundwater Interface Sampling

Seven surface water samples were also collected at the locations identified on **Figure 3-6** as SW-1, SW-2, SW-3, SW-4, SW-5, SW-6 and SW-7. SW-6 was collected from a pond located adjacent to the YMCA building and SW-7 was collected from standing water in wetland area in the north–central portion of the TCE/perchlorate SWMU just south of the power line easement. A surface water sample was only collected from SW-7 during one sampling event to evaluate the presence of perchlorate and TCE in the freshwater forested/shrub wetland area along the northern edge of the TCE/perchlorate groundwater plume. The other five were collected from points along Little Elk Creek. Creek samples were collected from downstream locations to upstream to reduce potential for cross-contamination that could be caused by disturbing stream sediments during the sampling procedures. Samples for VOC analysis were collected by dipping a clean jar into the stream, collecting water, and gently pouring the sample into pre-preserved VOA vials. Samples for other analyses were collected directly into laboratory-supplied containers. All samples were immediately labeled and placed on ice in coolers before submittal, under chain-of-custody control, to the appropriate laboratory.

Three groundwater-surface water interface samples were also collected near the surface water sampling locations upstream, midstream and downstream of the existing plume. These locations are identified as ITF-1, ITF-2 and ITF-3 on **Figure 3-6**. A hand auger was used to bore a hole into the ground along the edge of the creek bank until groundwater was encountered approximately 2.5 ft bgs. A stainless steel drive point was then pushed into the ground and tubing was inserted into the point. Groundwater discharging within the drive point screen was collected for analysis using peristaltic pump/tubing set-up. Groundwater was purged from the sample point prior to sample collection (**Figure 3-7**). The samples were processed in similar fashion to those collected from standard monitor wells. The surface water and interface groundwater samples were analyzed for field parameters as well as perchlorate, chlorate, chlorite, TOC, chloride, bromide, nitrate, nitrite, sulfate, phosphate, alkalinity, methane, ethane, ethene and chlorinated VOCs. Not all parameters were analyzed at each event. The sample collection and analysis plan is shown in **Table 3-3**.

Figure 3-7. Groundwater Collection from Interface Sample Location along Bank of Little Elk Creek

3.4.4 Soil Sampling

An important consideration when evaluating the potential for MNA of perchlorate to occur is the presence of bioavailable organic carbon in the aquifer. To help evaluate this condition, during monitor well installation in December 2006, split-spoon soil samples were collected at four or five depths along each borehole of SMW-8M, SMW-9M, SMW-11M and SMW-13M. The soil samples were placed in laboratory-supplied glassware, packaged on ice and submitted to the laboratory under chain-of-custody control for TOC analysis.

3.5 Laboratory Methods

Samples were collected from the monitoring wells, surface water and groundwater/surface water interface locations during monitoring events over a 24-month period. The analytical methods used for each analysis is shown in **Table 3-4.**

Table 3-4. Sample Collection and Analysis Details

Number of Sample Bottles per Sample Location	Containers	Target Constituent/ Method	Field/ Laboratory
Groundwater			
1	250-ml plastic bottle	Specific conductivity, temperature, pH, oxidation-reduction potential/ Field Meters	Field
0	From tubing	Dissolved oxygen/ CHEMetrics™ Field Test Kit	Field
1	0.45 µm filtered sample	Dissolved manganese and iron/ CHEMetrics™ Field Test Kit	Field
2	40-mL VOA vial (no preservative)	Methane/gas chromatography	NCSU CCEE Lab* Raleigh, NC
1	250 ml plastic bottle minimum of 120 ml sample while retaining headspace (no preservative) coupled 1.0µm and 0.45µm filtering setup	Perchlorate/ EPA Method 314 (ion chromatography)	NCSU CCEE Lab Raleigh, NC
1	A minimum of 120 ml (no preservative) coupled 1.0µm and 0.45µm filtering setup confirmation samples (10%)	Perchlorate/Method 332 (Ion chromatography/ tandem mass spectroscopy)	West Coast Analytical Service (formerly Bodycote) Santa Fe Springs, Ca
1	250-mL plastic bottle (preservative)	Chloride, Nitrate, Sulfate, Chlorate, Chlorite, Bromide, and Phosphate (ion chromatography)	NCSU CCEE Lab Raleigh, NC
1	250-mL amber bottle preserved with HCL)	Total organic carbon (groundwater)/Method 9060	Environmental Science Corp. Mount Juliet, TN
1	1-L amber bottle (no preservative)	Chlorite Dismutase/DNA	Microbial Insights, Inc. Rockford, TN
Multiple	enzyme filter traps with a minimum flow through of groundwater (500 mL to 1 L)	Molecular Biology Tools: Perchlorate Reductase/DNA	Microbial Insights, Inc. Rockford, TN
Soil			
1	4-oz jar	Total organic carbon (soil)/EPA Method 415 (Loss on ignition)	Environmental Science Corp., Mount Juliet, TN

3.5.1 Sampling for Standard Analysis

Samples were collected in laboratory-prepared sample containers appropriate for the analytical method being used. The sample containers were immediately sealed, labeled, and placed on ice in an insulated cooler for subsequent delivery to the analytical laboratory. Chain-of-custody forms accompanied samples sent to the laboratory. Groundwater/sediment pore water samples collected from monitoring wells during performance monitoring were generally analyzed for perchlorate, TOC, chloride, nitrate, sulfate, and methane as well as dissolved iron and manganese. A subset of the samples was also analyzed for chlorite, chlorate, bromide, and phosphate during some sampling events. As shown in **Table 3-4**, most of the analyses were performed using standard field or laboratory methodologies. However, several relatively new approaches were used for collecting and processing samples for perchlorate and microbial testing. These special methods are described in the following sections.

3.5.2 Groundwater Collection for Perchlorate Analysis

The method for collecting aqueous perchlorate samples was described and illustrated in the MNA Protocol (ESTCP, 2008). After the water is withdrawn from the monitoring well or collected from the surface water location, solids within the sample were allowed to settle in a closed plastic container. After the sediment had settled, a 60-ml syringe was used to withdraw the sample from the top to avoid solids. Then, the syringe was used to push approximately 30 mL of groundwater through sequentially stacked 1.0 µm and 0.45 µm filters into a 40-mL unpreserved VOA vial (**Figure 3-8**). The remaining headspace in the vial maintains an aerobic environment to eliminate further bioactivity on the sample; the sample was then placed on ice for shipment. The combination of filtration, an aerobic headspace and cooling has been shown to effectively preserve the samples and provide a representative sample for laboratory analysis. All samples were analyzed for perchlorate at the North Carolina State University Civil, Construction and Environmental Engineering (NCSU-CCEE) Laboratory by ion chromatography similar to EPA Method 314. Approximately 10% of groundwater samples were sent to a subcontract laboratory for confirmatory analysis of perchlorate by EPA Method 332.

Figure 3-8. Field Preservation of Aqueous Perchlorate Sample by Filtration through a Filter Stack

3.5.3 Biological Testing – qPCR Analysis

Molecular biology tools (MBTs) provide a sensitive, rapid approach to quantify specific microorganisms and enzyme functions involved with bioremediation. These methods can be applied selectively to detect and/or enumerate the proportion of active perchlorate reducing bacteria in a total population of bacteria. The quantitative polymerase chain reaction (qPCR) method identifies organisms involved with perchlorate reduction by targeting the specific genes found in these organisms: the perchlorate reductase gene (*pcrA*) that codes for the enzyme that mediates the initial breakdown of perchlorate to chlorate and chlorite, and the chlorite dismutase gene (*cld*) that codes for the single enzyme that mediates breakdown of chlorite, the final step in reduction of perchlorate to chloride and oxygen.

The PCR methods can be applied to different genetic material, i.e., RNA-based and DNA-based PCR assays. The RNA-based assay is used to determine the expression of a particular functional gene based upon the abundance of messenger RNA (mRNA). The perchlorate reducing microorganisms use the mRNA to assemble the CD enzyme, and its abundance in the groundwater sample is a direct indication of enzyme activity and, therefore, the active biodegradation of perchlorate. While RNA is the best indicator of activity, it degrades rapidly and can be lost during field and lab procedures, and therefore, results may be less reliable.

At the time of this project, the DNA-based PCR assays were considered more stable and less subject to sample collection and matrix variability[3]. For this reason, only the DNA-based PCR assays were used during demonstration at the site. The methods enabled the selective enumeration of the bacteria capable of dissimilatory perchlorate reduction by targeting a perchlorate reductase gene (*pcrA*) found in the DNA of these organisms. This method provides a direct measurement of the number of active bacteria capable of producing perchlorate reductase.

For DNA based CD analysis, approximately 1 liter of groundwater was collected from selected monitoring wells in bottles provided by Microbial Insights, Inc., placed on ice and forwarded to Microbial Insights, Inc. For perchlorate reductase analysis, Bio-Flo filters provided by Microbial Insights were connected in-line with the peristaltic pump tubing during groundwater sampling. The groundwater was allowed to flow through the enzyme filter trap until 0.5 to 1 L of groundwater had passed through the filter. In some cases the filters became plugged before the required volume of water had passed through the filter. In these cases, an additional filter was used. The exposed filters were capped and the volume of water passing through each was recorded. The filters were shipped under chain-of-custody to Dr. Kate Scow at the University of California - Davis for a DNA based analysis of the perchlorate reductase gene (*pcrA*) using qPCR techniques.

3.6 *In Situ* Biodegradation Testing

3.6.1 *In Situ* Columns

In situ columns can be used to evaluate contaminant degradation *in situ*. Using this procedure, Borden et al. (1997b) showed that decay rates measured using *in situ* columns provided a better match with plume-scale degradation rates than conventional laboratory microcosms. The

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[3] Personal communication, Microbial Insights, August 2008

application of *in situ* columns for use with perchlorate sites is discussed in the MNA Protocol (ESTCP, 2008)

A cluster of three *in situ* columns was installed adjacent to the GM-22S/M well pair, an area of the plume where the perchlorate was reported in groundwater and the CD enzyme assay performed during the site selection treatability process showed a positive response. Each column consisted of a 3.1-foot (1.0-m) long stainless steel chamber allowing sediment and groundwater to be isolated from the surrounding aquifer (**Figure 3-9**). The columns were designated ISC-A, ISC-B, and ISC-C. Each column was constructed in a borehole drilled to a depth of approximately 2 feet below the water table (estimated total depth of 10 ft bgs). After cleaning out the borehole, a 6-inch (15-cm) diameter PVC casing was installed in the borehole and the stainless steel *in situ* column (Solinst, Inc., **Figure 3-10**) was pushed into place through the PVC casing to a depth of 2 to 5 feet below the water table (estimated 10 to 13 ft bgs). After the columns were installed, suction was applied to the feed-line to ensure that the chamber completely filled with aquifer material.

Approximately 3-feet of sand were added in the annular space and the remaining annular space of this casing was sealed with hydrated bentonite pellets to just below land surface. The casing was closed with a locking cap, and completed with an aboveground PVC casing set in a small concrete pad at land surface. This construction helped isolate groundwater from surface infiltration.

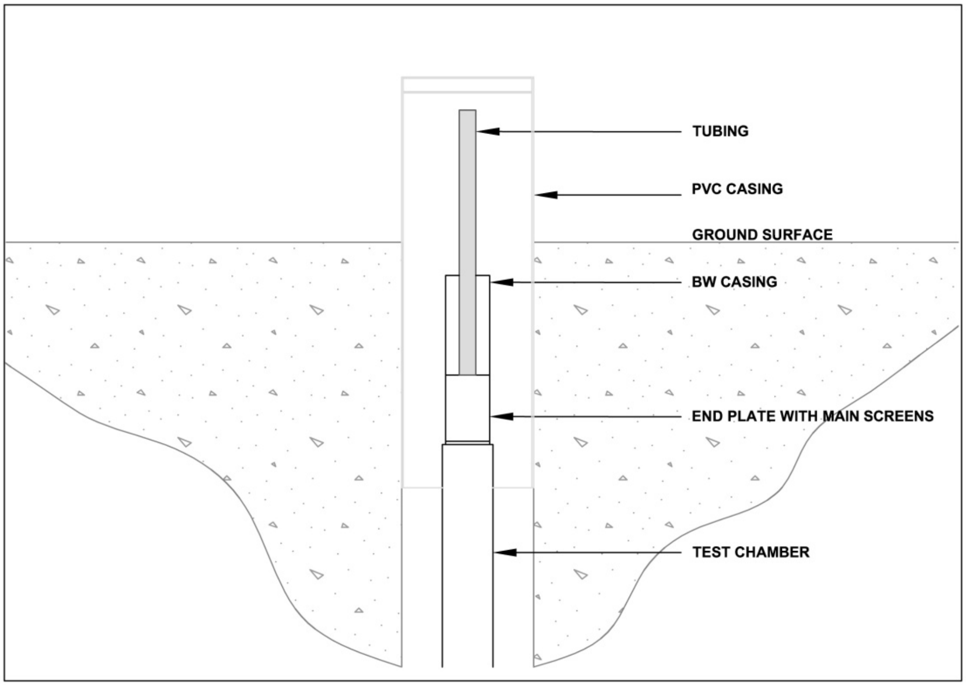

Figure 3-9. General Design of *In Situ* Columns

Figure 3-10. Stainless Steel Solinst® *In Situ* Column Showing Sampling Port Attachment

Total volume of each *in situ* column was approximately 4.2 L. At each sampling event a peristaltic pump (with flow rate adjusted to withdraw less than 250 mL/minute from the 1/8-inch diameter tubing from the columns) was used to purge approximately 10 to 20 mL of water from the sampling tubing before collecting samples from the next 60 mL of groundwater from within the ISC. After laboratory samples were collected, another 10 to 20 mL were obtained for analysis of field parameters including only pH and DO. Additional field parameters including ORP, temperature and specific conductivity were measured during the last field event. Groundwater samples were processed for perchlorate and anion analysis as described in Section 3.5.2 and **Table 3-4**. No biological testing was done on *in situ* column samples. A discussion of the results of the *in situ* column biodegradation study is provided in Section 6.3.2.

3.6.2 Macrocosms

Macrocosms are scaled-up versions of the microcosms used in the treatability testing. They employ a larger volume of representative site matrix material affording greater volumes of material to sample over time. To construct macrocosms, the drilling contractor installed several soil borings to the depth of approximately 2 feet below the water table in the vicinity of the GM-22S/M well pair. The initial drill cuttings were reserved for use in backfilling the borehole. Each borehole was then advanced to approximately 5 feet below the water table (estimated 13 ft bgs). The top 6 inches of cuttings returned from this interval were removed and soil from the remainder of the interval of interest was processed for macrocosm construction. Approximately 85 pounds of moist soil were collected and randomly placed into five different plastic tubs until approximately 17 to 18 pounds of soil had been placed in each tub. Each borehole was then backfilled with the native material that had been reserved.

The soil matrix material of interest was mixed manually in the plastic tubs until homogenous; large rocks (>0.5 inch diameter) were removed using decontaminated tongs or spoons. Using stainless steel scoops, the material was then transferred into separate, sterile 5-gallon glass carboys containing groundwater from GM-22M. The groundwater was collected under an argon blanket in the casing (above the water column) to minimize aeration of the groundwater. A sample of the groundwater that was used in preparing the macrocosms was collected separately and held for field and laboratory analysis as described in Section 3.5.2 and **Table 3-4**.

Approximately 3 lbs of soil were added incrementally to each gallon of groundwater in the carboys. After each addition, the carboy was rolled to release entrapped air bubbles from the soil. After 17 to 18 lbs of soil were added, each carboy was filled with groundwater from GM-22M and sealed. After allowing the material to settle, any residual the air was released and replaced with groundwater. The carboy was then purged with argon, sealed so that no air was present, labeled and transported to the engineering laboratory at NCSU for further setup, incubation and analysis.

In the laboratory, samples were collected through a needle placed into the sample matrix water while maintaining an anoxic headspace by purging the headspace with nitrogen via a needle placed through the carboy stopper (**Figure 3-9**). The macrocosms were not amended and were incubated in the dark at room temperature. A discussion of the macrocosm study results is provided in Section 6.3.1.

Figure 3-11. Macrocosm in 5-Gallon Carboy

3.7 Residuals Handling

Several types of investigation-derived waste (IDW) were generated on this site, including:

- Personnel protective equipment (PPE).
- Disposable equipment, such as plastic ground and equipment covers, aluminum foil, tubing, bailers, discarded or unused sample containers, boxes, etc.
- Soil cuttings/drilling muds/cores from well installation.
- Groundwater obtained through well development or well purging.
- Cleaning fluids such as detergents, spent solvents and wash water.
- Packing and shipping materials.

Groundwater derived from well purging was collected in 5-gallon buckets and taken to the A-82 air stripper system located at the facility for disposal. Based on generator knowledge, IDW was classified as non-hazardous. At the time of generation, soil cuttings/cores were drummed, labeled, sampled and staged on site in the utility easement west of Elkton Rd. After received the analytical profile, the drums were removed from the site by KJ Grace, LLC of Elkton, MD for disposal.

4.0 Site Hydrogeology

4.1 Regional Hydrogeology

The town of Elkton lies within the Western Shore Uplands Region of the Atlantic Coastal Plain Physiographic Province of Eastern Maryland. The Region is bounded by rivers to the east and west and the fall zone to the north. The town of Elkton lies at the mouth of the Elk River at the northern end of the Elk Neck Peninsula. The ridge of the peninsula acts as a drainage divide between the Elk River and the Chesapeake Bay. Average groundwater recharge in the Big Elk Creek Basin is about 12 inches per year. The 7-day / 10-year low flow is 198 gallons per day per acre or 0.2 cfs per sq. mi. (Sloto, 2002). The topography of the area is characterized by a flat to rolling upland surface underlain by mostly unconsolidated sediments of Cretaceous age known as the Potomac Group sediments. According to Higgins (1990), the sediments are exposed at the surface just west of the town of Elkton but are overlain by Quaternary fluvial deposits of sands and gravels near the site. The Potomac sediments are generally less than 100 feet thick near Elkton and thicken to the south and southeast to as much as 1,300 ft thick near the southeast corner of Cecil County.

The Potomac Group, which includes the Patuxent, Arundel, and Patapsco formations, consists of a thick sequence of non-marine sands, silts, clays and gravelly sands. The sediments were deposited in alluvial fans or elongated fluvial channels resulting in numerous irregular layers and lenses with little extensive continuity. The gravel and sands are chiefly composed of quartz and quartzite. Abundant clays in shades of red, purple, yellow and gray suggest that during depositional times, mud flats may have existed which were subject to intermittent flooding. Saprolite formed by the weathering of the underlying crystalline rocks lies beneath the Potomac sediments in varying thicknesses. The bedrock surface is undulating and dips in a general southeasterly direction.

4.2 Local Subsurface Conditions

The description of the geology and hydrogeology beneath the facility was derived, in part, from the Site Conceptual Model prepared by Kendall et al. (2004) and the Site-Wide Corrective Measures Study (Arcadis, 2007) which focused on the relevant geology and hydrogeology from the Plant Area east toward Elkton Road and Little Elk Creek beyond the YMCA property.

4.2.1 Subsurface Conditions in the Site Area

Borings on and near the site reveal that bedrock underlying the site is micaceous, feldspar gneiss. The depth to bedrock ranges from about 90 to 150 ft bgs between the plant area and Little Elk Creek to the east. The thickness of the overlying saprolite ranges from 5 to 64 ft. The saprolite is micaceous, silty, and friable, becoming more cohesive and resistant to drilling with depth. Cross-sections illustrating the aquifer zones beneath A-Area of the demonstration site are provided in **Appendix C**.

The sediments of the Potomac Group overlie the bedrock/saprolite. A layer of predominantly fine sandy silt (varying in thickness from 18 to 35 feet) was encountered at the base of the Potomac in boreholes throughout the site. The Potomac sediments above the basal silt are much more variable in composition. Interstratified sands, silts and clays make up the majority of sediments, with occasional peat or gravel beds included. Lateral discontinuity within the Potomac Group renders correlation of most beds uncertain, even over short distances.

Quaternary alluvium overlies the Potomac Group in some areas of the site and is composed of heterogeneous mixtures of clay, silt, sand and gravel. Limited data indicate an alluvial thickness of 0 to 40 feet; these beds are extremely variable in their horizontal and vertical extent.

4.2.2 Hydraulic Conductivity of the Surficial Aquifer

During the 2003 Interim Site-Wide Investigation, a pumping test was performed on GM-14R located within the TCE/perchlorate SWMU. Based on the results of this test, the hydraulic conductivity was estimated to range from 8.97 to 31.3 ft/day with an average of 15.8 ft/day. With a reported gradient of 0.006 and effective porosity of 0.20, the average groundwater velocity was estimated to be approximately 58 feet per year (Arcadis, 2003).

Solutions-IES conducted specific capacity testing in seven monitoring wells in May 2007 using the method of Wilson et al. (1997). The average hydraulic conductivity (K) in four shallow monitoring wells was 6.3 ft/day. The average K in three intermediate monitoring wells was 10.1 ft/day (**Table 4-1**). These values are in general agreement with average hydraulic conductivity of 15.8 ft/day calculated by Arcadis. Based on an average hydraulic gradient of approximately 0.0033 and an assumed soil porosity of 20 percent, the estimated groundwater flow velocity ranges from 38 ft/yr to 61 ft/yr. This is consistent with the estimate of 58 ft/yr calculated by Arcadis.

Table 4-1. Hydraulic Conductivity Measurements
(May 14, 2007)

	Hydraulic Conductivity*	
Well ID	**cm/sec**	**ft/day**
SMW-8S	1.54E-03	4.37
SMW-9S	5.46E-05	0.15
SMW-11S	4.20E-04	1.19
GM-22S	6.89E-03	19.5
Average	**2.23E-03**	**6.30**
SMW-8M	3.73E-03	10.6
SMW-13M	3.34E-03	9.47
GM-22M	3.65E-03	10.4
Average	**3.57E-03**	**10.1**

*Hydraulic conductivity calculated from Specific Capacity tests

4.3 Groundwater Flow at the Site

The groundwater flow regimes in the vicinity of the facility can be generally defined as: a shallow unconfined water table aquifer (shallow zone), an intermediate Potomac Group aquifer (intermediate zone), and a deep saprolite aquifer. A low permeability unit separates the shallow and intermediate zones of the Potomac Group sediments. The low permeability unit is present beneath most of the site but thins eastward and is not present in borings near Little Elk Creek. Quaternary aged fluvial deposits overlie the Potomac Group sediments in some portions of the site including an area located just east of the facility and along Little Elk Creek. Groundwater flow in the shallow unconfined water-table aquifer is generally influenced by topography and surface-water flow.

Groundwater measurements collected during the demonstration indicate that the depth to groundwater in the TCE/Perchlorate SWMU ranges from just below ground surface adjacent to Little Elk Creek to approximately 10 ft bgs along Elkton Road. Groundwater levels west of Elkton Rd. within the intermittent wetland area were generally shallower than those recorded along Elkton Rd. The groundwater elevation data are tabulated in **Table D-1** in **Appendix D**.

The hydraulic gradients in the shallow and intermediate aquifer zones were calculated by comparing groundwater elevation in wells in the presumed TCE/perchlorate plume source area with the elevations immediately across Elkton Rd. at well pair SMW-13S/M and further downgradient, just before the riparian buffer on the west side of the creek at GM-22S/M. The results are summarized in **Table 4-2**. The hydraulic gradient across the site in both the shallow and the intermediate aquifer zone is 0.0033 ft/ft. In either case there is little change between the gradient across the manufacturing property to Elkton Road and the gradient from Elkton Road to Little Elk Creek.

Table 4-2. Horizontal Hydraulic Gradient in Shallow and Intermediate Aquifers

A	B	C	D	E	F
Upgradient Well ID	Groundwater Elevation (ft msl)	Downgradient Well ID	Groundwater Elevation (ft msl)	Distance Between Wells (A-C) (ft)	Hydraulic Gradient (B-D)/E
GM-14S	14.75	GM-22S	5.43	2,720	.0034
GM-14S	14.75	SMW-13S	10.52	1,930	.0022
SMW-13S	10.52	GM-22S	5.43	1,170	.0044
GM-2B	14.19	GM-22M	6.52	2,320	.0033
GM-2B	14.19	SMW-13M	11.00	1,180	.0027
SMW-13M	11.00	GM-22M	6.52	1,170	.0038

Groundwater elevations recorded April 29, 2008
ft msl = feet above mean sea level
Distance between wells measured in straight line off CAD drawing from well in column A to well in column C

Vertical hydraulic gradients between the shallow and intermediate aquifer zones were calculated by comparing groundwater elevations in nested well pairs across the site. The results are summarized in **Table 4-3**. Within the source area and upgradient portions of the aquifer, vertical hydraulic gradients are small and variable. For example, the wells closest to the source area (GM-14S/GM-14M) show a small upward hydraulic gradient, while GM-26S/GM-26M located a short distance south show a small downward hydraulic gradient. Farther downgradient, there is a consistent upward gradient as groundwater flows upward from the intermediate zone into the shallow zone, and then discharges into Little Elk Creek. Vertical flow velocities were computed assuming a porosity of 20 percent and a vertical hydraulic conductivity of 0.8 ft/d, which was 10% of overall average horizontal K as shown in **Table 4-1**.

Table 4-3. Vertical Hydraulic Gradient between Shallow and Intermediate Aquifer Zones

Shallow Zone		Intermediate Zone		Distance Between Well Screen Mid-points (A-C) (ft)	Vertical Hydraulic Gradient (B-C)/E	Vertical Velocity (ft/day)
Well ID	GW Elevation (ft MSL)	Well ID	GW Elevation (ft MSL)			
A	**B**	**C**	**D**	**E**	**F**	**G**
GM-14S	14.75	GM-14M	15.34	52.6	+0.01	+0.05
GM-26S	13.93	GM-26M	12.88	38.2	-0.03	-0.11
SMW-8S	14.39	SMW-8M	14.42	44.12	+0.0007	+0.003
SMW-9S	10.19	SMW-9M	10.07	43.67	-0.003	-0.01
SMW-11S	11.11	SMW-11M	11.06	26.94	-0.002	-0.007
SMW-13S	10.52	SMW-13M	11.0	44.67	+0.01	+0.04
GM-21S	5.74	GM-21M	7.87	33.12	+0.06	+0.26
GM-22S	5.04	GM-22M	6.52	19.29	+0.08	+0.31
GM-23S	5.43	GM-23M	6.48	14.52	+0.07	+0.29

+ indicates an upward hydraulic gradient
- indicates a downward hydraulic gradient
Groundwater elevations recorded April 29, 2008.

4.4 Generalized Hydrogeologic Model

The site hydrogeology consists of three primary units: a transient perched water zone, an unconfined aquifer composed of Potomac Group sediments, and saprolite overlying crystalline bedrock. A freshwater forested/shrub wetland covers approximately 54 acres between the source area and the YMCA. The approximate boundaries of the wetland are shown on **Figure 4-1**.

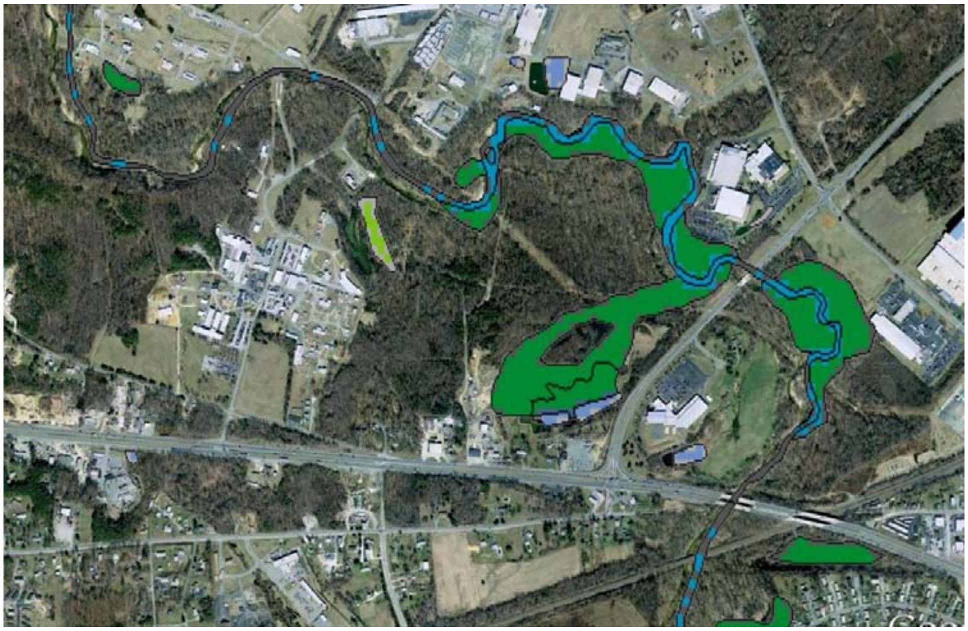

Figure 4-1. Approximate Extent of Wetland (Source: US Fish and Wildlife Service, National Wetlands Inventory, downloaded August 2010)

Figure 4-2 shows hydric soils in the vicinity of the site including Hatboro silt loam (Ht), Codorus silt loam (Ch), Comus silt loam(Cp) and water (W). Ht is classified as frequently flooded and Ch and Cp as occasionally flooded. The playing fields between the YMCA and Little Elk Creek are not currently classified as wetlands. However, hydric soils are present throughout this area indicating this area was a wetland prior to land development. This is supported by visual observations of ponded water throughout this area during much of the winter and spring.

Figure 4-2. Hydric Soils (Source: Web Soil Survey, downloaded August 2010)

The unconfined aquifer has been divided into shallow and intermediate zones which are separated by a semi-confining layer. The shallow aquifer zone, the intermediate aquifer zone, and the deep bedrock unit are generally defined at depths less than -20 ft msl, between -20 ft msl and -70 ft msl, and greater than -70 ft msl, respectively. The water table surface generally slopes from the plant area towards Little Elk Creek. The dominant direction of groundwater flow within the shallow and intermediate zones is towards Little Elk Creek which bounds the site to the north and east (**Figures 4-3 and 4-4**). Closer to the facility, the groundwater flow within the shallow and intermediate zones is influenced by the active pump-and-treat system located in Area A, near pumping well GM-14R, and surface water.

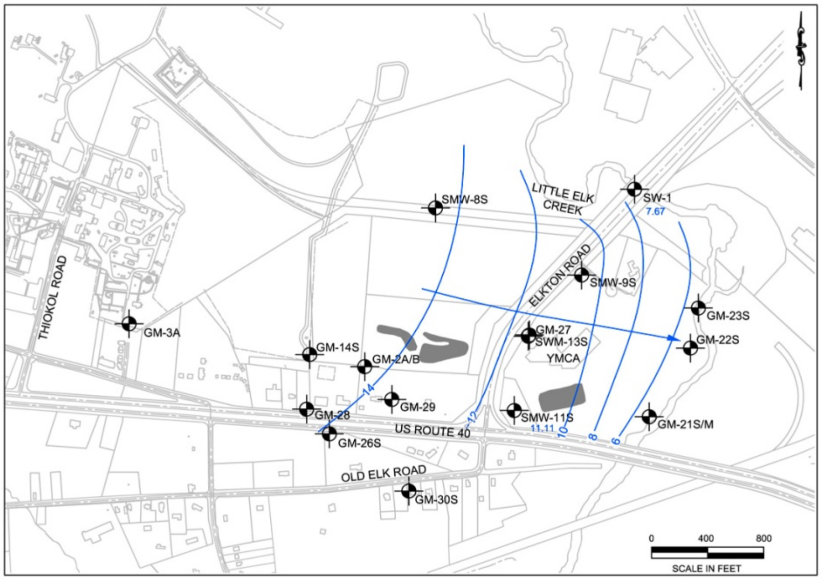

Figure 4-3. Groundwater Potentiometric Surface Map in the Shallow Aquifer in April 2008

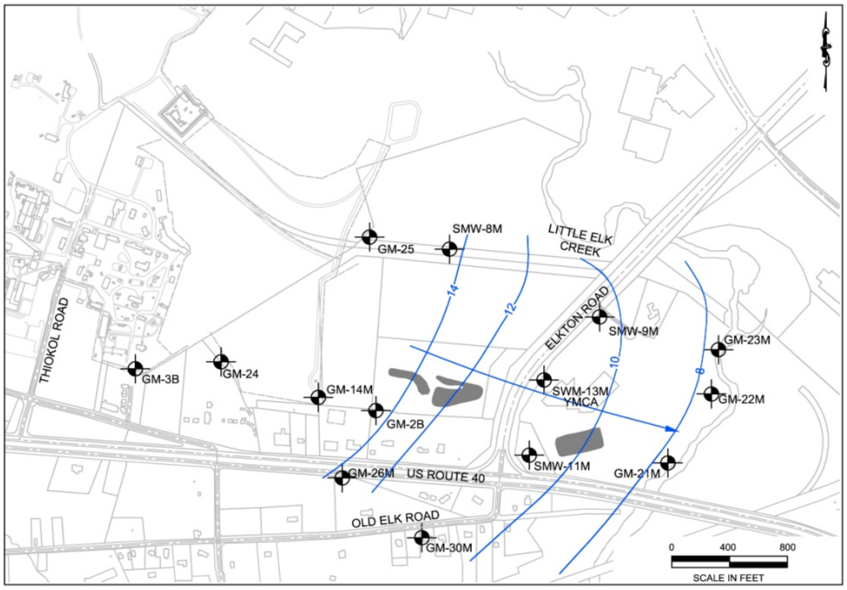

Figure 4-4. Groundwater Potentiometric Surface Map in the Intermediate Aquifer in April 2008

5.0 Conceptual Model of Perchlorate Transport and Fate

This section presents a general conceptual model for the transport and natural attenuation of perchlorate as it migrates through the shallow and intermediate aquifers within the TCE/Perchlorate SWMU. The presumed source area for the perchlorate plume is a former burn field (closed in 1958) used to dispose of waste solid fuel rocket propellant (A-Area shown on **Figure 3-1**) and other unspecified historical waste handling practices in the same general vicinity. Perchlorate is present in wells immediately downgradient of this area in both the shallow (GM-14S) and intermediate zones (GM-14M), but has not been detected in the deep bedrock zone (GM-14D). Perchlorate is believed to have entered the intermediate aquifer after migrating through the shallow aquifer with infiltrating groundwater. However, perchlorate concentrations are now significantly lower in the shallow zone than the intermediate zone. This is presumably due to more rapid flushing of the shallow zone.

Perchlorate has been detected in the intermediate zone groundwater all the way from the presumed source area to Little Elk Creek. The plume appears to be approximately 3,400 feet long from west to east and 2,000 feet wide from north to south at its presumed widest point near Little Elk Creek. As groundwater migrates from the presumed source area towards Little Elk Creek, perchlorate concentrations in the intermediate aquifer zone gradually decline, due to both dilution and anoxic biodegradation in isolated organic rich layers.

Near Little Elk Creek, perchlorate concentrations decline in the intermediate zone and increase in the shallow zone due to upward flow of perchlorate laden groundwater. Little Elk Creek is bounded on both sides by wooded riparian buffer with a vegetative understory all the way to the edge of the creek (**Figures 5-1** and **5-2).** All of this area is current or former riparian wetlands, containing soils with higher levels of organic carbon. As perchlorate laden groundwater migrates upward through these soils, perchlorate biodegradation is enhanced under anoxic conditions. **Figure 5-3** shows the upward migration of the perchlorate plume as groundwater moves toward Little Elk Creek. In Section 6.0, multiple lines of evidence will be developed to evaluate and document the natural attenuation of perchlorate in groundwater at the Elkton site.

Figure 5-1. Western Bank of Little Elk Creek in Summer in Vicinity of ITF-1.

Figure 5-2. Little Elk Creek in Winter in the Area of Presumed Ground Water Discharge

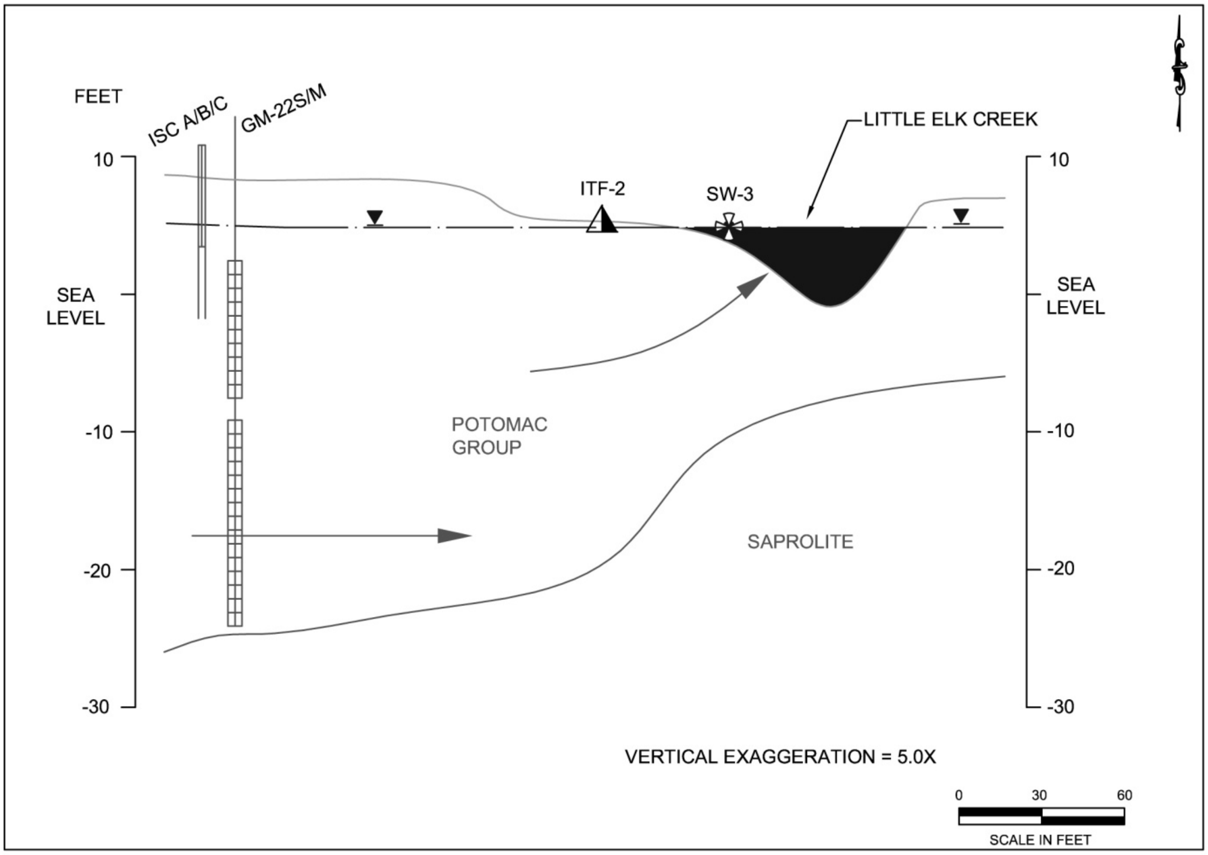

Figure 5-3. Conceptual Model of Discharge of Groundwater Plume to Little Elk Creek

6.0 Field MNA Evaluation Program

Acceptance of MNA as a groundwater remedy requires multiple lines of evidence. Analytical methods are available to monitor the concentration of perchlorate in the environment with high sensitivity and selectivity. Geochemical tests can indicate whether ambient conditions are conducive to perchlorate biodegradation, and MBTs are available to monitor the activity and sustainability of perchlorate-reducing bacterial populations. Using these tools and the direction offered in the MNA Protocol, a tiered approach was used to evaluate the potential for perchlorate MNA at the demonstration site: 1) plume stability and geometry assessment; 2) biogeochemical parameter and biological indicator evaluation; and 3) biodegradation rate estimation (ESTCP, 2008). The following sections summarize this evaluation and the lines of evidence supporting use of MNA as a groundwater remedy.

6.1 Tier 1 Evaluation – Plume Geometry and Stability

6.1.1 Plume Geometry

Historical data can be used effectively to delineate the extent of the contamination and determine the fate of contaminants of concern. With a properly designed monitor well network, trends in the data can successfully illustrate plume geometry and stability. Ideally, the contaminant plume should be stable or retreating. A stable or shrinking perchlorate plume indicates that natural processes are attenuating perchlorate more rapidly than it is released from the source area.

Solutions-IES reviewed historical reports provided by the facility owner to locate data that could be used as part of the MNA evaluation. Some early data related to the TCE SWMU dated back to September 1994, but only included information on chlorinated VOCs. The first sitewide examination of perchlorate in groundwater was conducted in November 2002. Some wells were tested again in March 2004 and November 2006 and the results were used to prepare the Corrective Measures Study (Arcadis, 2007). Solutions-IES performed a sitewide sampling event in May 2006 as the initial field effort for the current project. The results provided a comprehensive pre-demonstration look at the TCE/Perchlorate plume and served to guide the selection of locations for additional monitor wells to be installed (see Section 3.4.1). For most wells, the May 2006 sampling effort was considered the Time 0 baseline from which to compare changes that occurred during the course of the project. Four subsequent groundwater sampling events were performed on or about the dates shown in the **Table 3-3**, covering the approximate 2-year period of the study. Where earlier data were available, these were included in the evaluation.

6.1.2 Plume Stability

6.1.2.1 Groundwater Sampling

During the pre-demonstration baseline testing in May of 2006, Solutions-IES collected groundwater samples from 28 existing wells. Each of the groundwater samples was analyzed for perchlorate, chlorinated VOCs, TOC, chlorate, chlorite, chloride, nitrate, nitrite, bromide, sulfate, and methane. Section 3.4.2 provides details regarding analytical parameters and sampling techniques. After the new well pairs were installed, performance monitoring began and usually included the four new well pairs and 15 existing monitoring wells. **Table 6-1** shows the monitoring wells sampled during the baseline and performance monitoring events. The table also shows the elevation of the mid-point of the well screen. The well construction details are provided in **Table B-1** of **Appendix B**. Wells whose mid-point is shallower than -20 ft msl were considered representative of the shallow aquifer zone. Wells with screen mid-point between -20 and -70 ft msl were in the intermediate zone. Deep wells were screened at depths greater than -70 ft msl.

Table 6-1. Monitoring Wells Sampled During Baseline and Performance Monitoring Tasks

		Mid-Point Screen Elevation (ft msl)*	Pre-Demonstration Baseline (May 2006)	Performance Monitoring
GM-2A	Not specified	-120 (est.)	✓	✓
GM-2B	Intermediate	-70 (est.)	✓	✓
GM-3B	Intermediate	Not specified	✓	
CR-2, CR-3, CR-4	Not specified	Not specified	✓	
GM-14S	Shallow	-15.66	✓	✓
GM-14M	Intermediate	-52.39	✓	✓
GM-14D	Deep	-96.16	✓	
GM-16S	Shallow	-15.62	✓	✓
GM-16D	Deep	-80.87	✓	
GM-21S	Shallow	-12.34	✓	✓
GM-21M	Intermediate	-35.25	✓	✓
GM-22S	Shallow	-5.11	✓	✓
GM-22M	Shallow	-18.8	✓	✓
GM-23S	Shallow	-3.97	✓	✓
GM-23M	Shallow	-14.48	✓	✓
GM-24	Intermediate	-34.4	✓	
GM-25	Intermediate	-48.48	✓	✓
GM-26S	Shallow	-12.40	✓	✓
GM-26M	Intermediate	-38.70	✓	✓
GM-27S	Shallow	+14.14	✓	
GM-28	Shallow	+31.93	✓	
GM-29	Shallow	+18.01	✓	
GM-30S	Shallow	+28.95	✓	
GM-30M	Intermediate	-38.27	✓	✓
GM-32	Shallow	-16.37	✓	
GM-33	Shallow	-19.37	✓	
SMW-8S	Shallow	-3.90		✓
SMW-8M	Intermediate	-33.31		✓
SMW-9S	Shallow	-4.29		✓
SMW-9M	Intermediate	-33.4		✓
SMW-11S	Shallow	-1.82		✓
SMW-11M	Intermediate	-19.78		✓
SMW-13S	Shallow	-0.48		✓
SMW-13M	Intermediate	-30.26		✓
			28	23

Deep = wells with screen mid-point deeper than -70 ft msl.

Figure 6-1 shows an interpretation of the TCE and perchlorate plumes based on the baseline data collected in May 2006. This construction is similar to plume delineation provided by Arcadis (2007). The dissolved perchlorate and TCE plumes overlap and extend over one-half mile from the presumed, but generally undefined, source(s) to Little Elk Creek east of Elkton Rd.

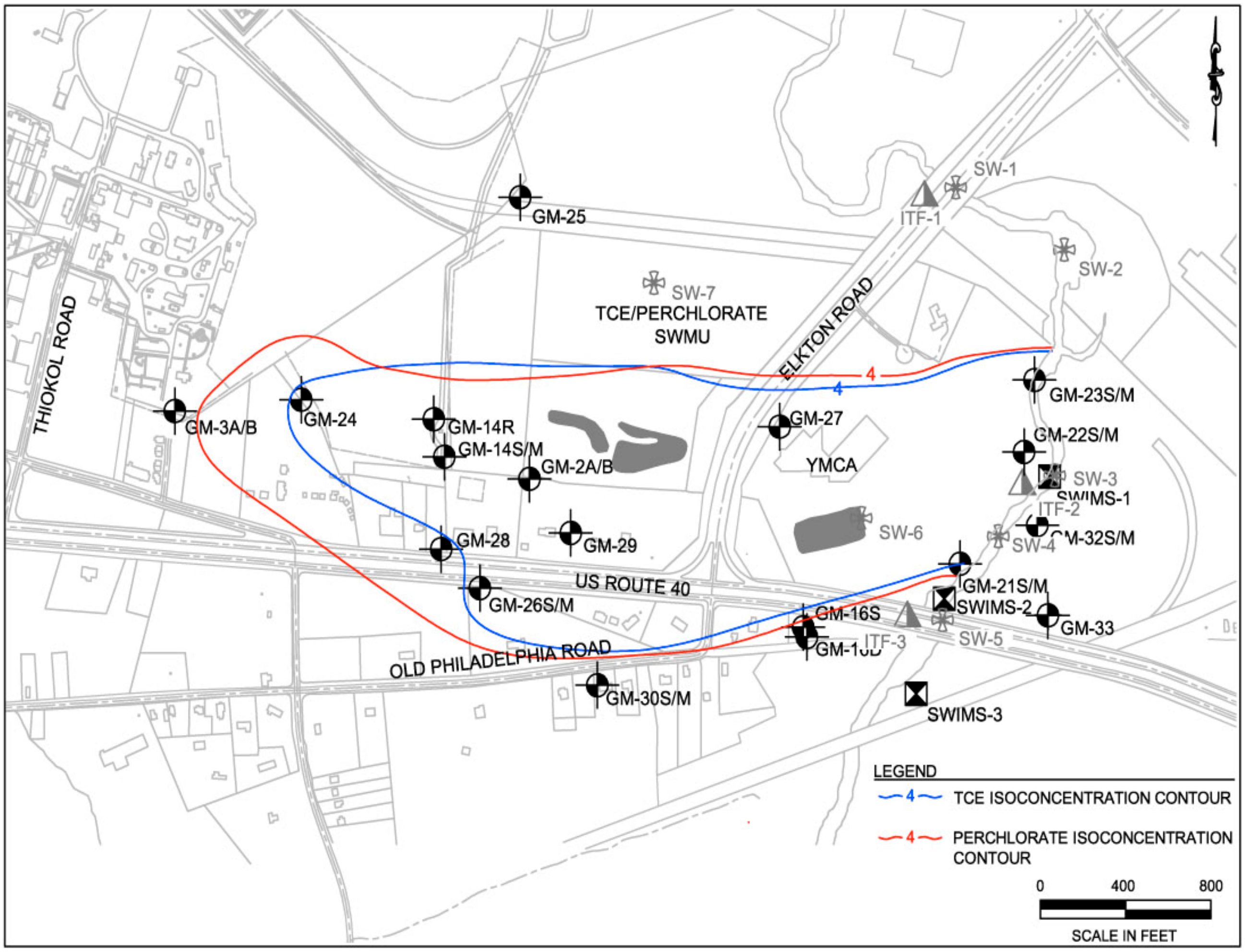

Figure 6-1. Baseline Perchlorate and TCE Delineation in the Intermediate Aquifer in May 2006

For comparison, **Figure 6-2** shows the perchlorate plume delineation during the demonstration activities from sampling performed in October 2007. Samples collected from the newly installed monitoring wells SMW-8M and SMW-9M showed that the plume is wider than previously drawn and extends farther north beyond the utilities easement.

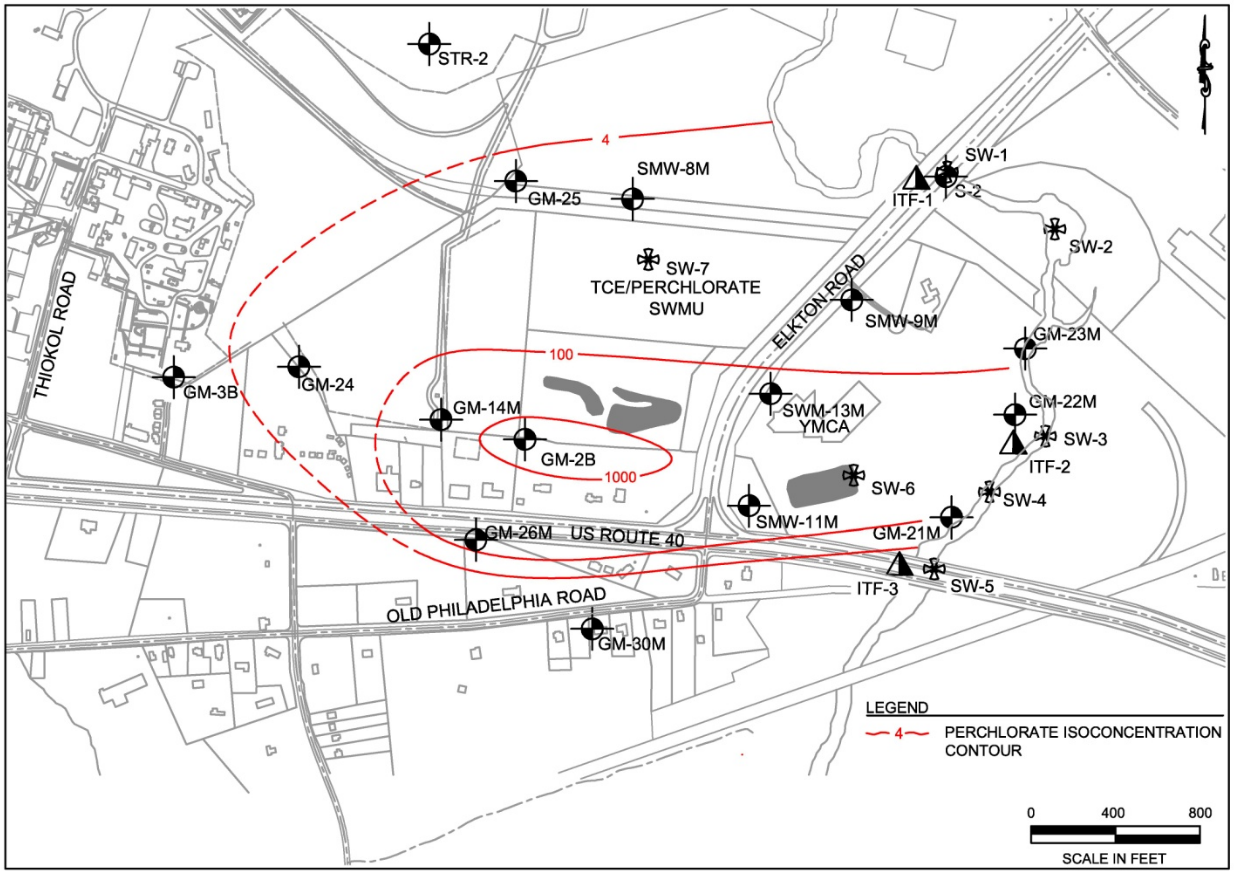

Figure 6-2. Perchlorate Delineation in the Intermediate Aquifer in October 2007

The complete data set for perchlorate, TCE, TCE daughter products and other chlorinated VOCs is provided in **Tables E-1** and **E-2** in **Appendix E.** Isoconcentration plume maps for perchlorate and TCE were constructed for each of the performance monitoring events (not shown) and compared with the baseline maps. With the exception of the plume extending somewhat farther to the north, there was little or no change in the configuration of either plume over the 24-month performance monitoring period of this project. However, it can be noted that the concentrations of both TCE and perchlorate in GM-14M and GM-14S decreased substantially since elevated concentrations were first reported for TCE in 1994 and perchlorate in 2004 (**Tables 6-2a** and **6-2b**). These declines are believed to be due to natural flushing with incoming groundwater and/or enhanced biodegradation associated with the bioremediation pilot test performed in this area by Arcadis in 2004 (see Section 3.2.2.2).

Monitor well pair GM-2A and GM-2B is located approximately 400 ft downgradient from GM-14S/M. The mid-point elevation of the well screen for GM-2A was not reported, but it was constructed as a deep well approximately 145 ft bgs. From the available well construction data, it was estimated that the screen mid-point was approximately -120 ft msl. Similarly, GM-2B was also constructed as a deep well, although finished shallower than GM-2A. The screen mid-point elevation for GM-2B was calculated to be approximately -70 ft msl. As shown in **Table E-2** of **Appendix E,** one detection of TCE and no detections of perchlorate have been reported in GM-2A, but elevated concentrations have been found routinely in GM-2B (**Table 6-2a**). This suggests that contaminated groundwater from the source moves laterally through the deeper portions of the intermediate zone and there is no further downward vertical migration of contamination. This is consistent with the site conceptual model which suggests primary transport of the contaminants away from the source in the intermediate zone of the aquifer. The perchlorate concentration in GM-2B has slowly decreased from about 2,000 µg/L in November 2002 to 1,000 µg/L when sampled in April 2008, representing a natural decrease of ~50% in 5.5 years without active treatment. Conversely, TCE increased by 18% during the same period.

Table 6-2a. Historical TCE and Perchlorate Concentrations in Select Intermediate-Depth Monitoring Wells

	GM-14M		**GM-2B**		**SMW-13M***		**SMW-11M***		**GM-21M**		**GM-22M**	
	Representative Source		400 ft downgradient		1,500 ft downgradient		1,500 ft downgradient		2,500 ft downgradient		2,700 ft downgradient	
Date	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**
1988	-	-	3,500	-	-	-	-	-	-	-	-	-
9/15/94	1,900	-	3,100	-	-	-	-	-	-	-	-	-
11/12/02	1,400	1,300	2,200	2,000	-	-	-	-	190	60	5,100	189
3/17/04	1,000	1,200	2,600	1,700	-	-	-	-	230	87	6,400	258
5/18/06	-	-	3,700	1,000	-	-	-	-	180	74	4,900	174
2/5/07	920	250	2,900	1,000	2,400	24	1,000	14	130	120	3,600	209
5/15/07	500	<1	2,700	1,000	2,500	110	1,400	590	230	140	3,400	122
10/1/07	580	350	-	1,100	-	120	-	800	-	98	3,600	170
4/28/08	360	26	2,600	1,000	2,400	120	2,100	750	170	110	3,900	169
Recent Average	590	160	2,700	1,000	2,400	93	1,500	540	180	120	3,600	167

* SMW-11S/M and SMW-13S/M constructed for this project, therefore no historical data available.
Concentrations reported as µg/L.; concentrations rounded to 2 significant figures.
"Recent average" calculated from performance monitoring events from February 2007 through April 2008.
Blank spaces indicate no sample collected or no data available.

Table 6-2b. Historical TCE and Perchlorate Concentrations in Select Shallow-Depth Monitoring Wells

	GM-14S		SMW-13S*		SMW-11S*		GM-21S		GM-22S	
	Representative Source		1,500 ft downgradient		1,500 ft downgradient		2,500 ft downgradient		2,700 ft downgradient	
Date	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**
9/15/94	2,100	-	-	-	-	-				
11/12/02		-	-	-	-	-	1,100	510	3,000	230
3/17/04	570	230	-	-	-	-	1,500	530	3,200	180
5/18/06	920	58	-	-	-	-	800	280	3,600	160
2/5/07	640	<1	2	<1	<1	<1	1,700	740	3,200	210
5/15/07	450	8	<1	<1	6	<1	1,200	760	2,900	160
10/1/07	170	<1	-	<1	-	<1	-	770	-	170
4/28/08	440	16	2	<1	3	<1	1.600	820	3,500	180
Recent Average	420	6	<2	<1	3	<1	1,500	770	3,200	180

* SMW-11S/M and SMW-13S/M constructed for this project, therefore no historical data available. Concentrations reported as µg/L.; concentrations rounded to 2 significant figures.

"Recent average" calculated from performance monitoring events from February 2007 through April 2008.

Blank spaces indicate no sample collected or no data available.

The absence of perchlorate and TCE in the mid-plume shallow monitor wells SMW-11S and SMW-13S (**Table 6-2b)** compared to the measureable concentrations in the paired intermediate wells (**Table 6-2a**) supports the conceptual model that contamination is migrating through the mid-plume area in the intermediate aquifer zone rather than in shallow groundwater. However, as the groundwater approaches Little Elk Creek, the separation between aquifers becomes less distinct as groundwater flows gradually upward toward eventual discharge into the creek. Well pairs GM-21S/M and GM-22S/M are approximately 30 ft west of Little Elk Creek. These wells are also located in the flood plain just before the 25-ft wide riparian wooded buffer zone bordering the west bank of the creek. There is approximately 15 to 25 ft of vertical difference between the mid-point of the screen interval in each shallow and intermediate well of each pair, but unlike mid-plume, there are elevated concentrations of both perchlorate and TCE in both zones. Interestingly, recent average concentrations of both perchlorate (770 µg/L) and TCE (1,500 µg/L) in GM-21S are 6 to 7 times higher than in GM-21M, whereas average concentrations found in GM-22S (180 µg/L perchlorate and 3,200 µg/L TCE) are very similar to concentrations reported in GM-22M.

6.1.2.2 Surface Water Samples

Previous investigations indicated that low concentrations of both perchlorate and TCE exist in the surface water of Little Elk Creek. Concentrations varied as the creek traversed the facility but were measurable in the vicinity of the eastern-most presumed groundwater discharge zone. As part of the baseline and performance monitoring program, surface water samples were collected from five sampling stations located along the eastern loop of Little Elk Creek (**Figure 6-2**). The sampling stations were designated SW-1 where Little Elk Creek crossed under Elkton

Rd. before turning to the south to SW-5 where the creek flowed under Highway 40 after traversing the discharge area. Surface water samples were also collected from a pond located south of the YMCA building (SW-6) and from standing water seen seasonally in the area of the TCE/Perchlorate SWMU (SW-7).

The results of the sampling from the creek are shown in **Table 6-3**. As surface water enters the eastern loop of the creek, it is minimally impacted with TCE and perchlorate (SW-1), possibly as a result from passage through other areas of the facility unrelated to the TCE/perchlorate SWMU. However as Little Elk Creek flows through the TCE/ClO_4 discharge area, TCE concentrations increase from less than 1 µg/L at SW-1 to 46 µg/L at SW-3. In contrast, there is only a slight increase in ClO_4 from SW-1 to SW-3. While there are a few more detections of ClO_4 in the downstream samples, the 24-month average ClO_4 concentrations at the four downstream sampling locations were not statistically different from SW-1 at the 95% confidence level. By contrast, the 24-month average concentrations of TCE were all statistically significantly different at the 95% confidence level from the concentration in surface water before reaching this portion of the creek. Visual examination of the ClO_4 data suggests that there may be some downward trend in the data. However, this hypothesis could not be statistically evaluated because of the high frequency of below detection samples (ClO_4 < 4 µg/L). TCE or perchlorate was never detected in the pond on the YMCA property (SW-6) or the wetland just west of Elkton Road (SW-7).

Table 6-3. Historical TCE and Perchlorate Concentrations at Downgradient Surface Water Sampling Locations

	SW-1		SW-2		SW-3		SW-4		SW-5	
Date	**TCE***	**ClO_4***	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**
5/18/06	<1.1**	3.0	13	4.0	100	7.0	56	6.0	18	4.0
2/5/07	<1	<4	7.0	4.5	46	4.7	31	4.2	18	4.3
5/15/07	<1	<4	8.0	<4	30	4.0	12	<4	<1	<4
10/1/07	1.5	<4	30	4.2	28	<4	37	5.0	36	6.8
4/28/08	<1	<4	1.7	<4	25	<4	6.9	<4	5.8	<4
24-month Avg.	0.6±	2.2±	11.9±	3.3±	45.8±	3.9±	28.6±	3.8±	15.7±	3.8±
Std Dev.	0.1	0.4	10.9	1.2	31.4	2.1	19.8	1.8	13.7	2.0

* Concentrations reported as µg/L

** Where concentrations reported as "<", one-half the detection limit used in calculating the 24-month average.

6.1.2.3 Groundwater Interface Samples

Groundwater-surface water interface samples were collected at three locations near surface water sampling locations SW-1, SW-3 and SW-5 to monitor groundwater discharge upstream, midstream and downstream of the presumed center of the TCE/ClO_4 plume. These locations are identified as ITF-1, ITF-2 and ITF-3 on **Figure 6-2** and the results of the sampling are summarized in **Table 6-4.**

Table 6-4. Historical TCE and Perchlorate Concentrations at Groundwater-Surface Water Interface Sampling Locations

	ITF-1		ITF-2		ITF-3	
Date	**TCE**	**ClO_4**	**TCE**	**ClO_4**	**TCE**	**ClO_4**
5/18/06	13	<1	1,000	120	-	<1
2/5/07	11	<1	1,000	110	730	240
Avg.	12	<1	1,000	115	730	120

Concentrations reported as µg/L.
Blank spaces indicate no sample collected or no data available

At the upstream interface sampling location, ClO_4 was below detection in all samples, while TCE was consistently detected. In the presumed center of the plume (ITF-2), the average ClO_4 concentration was 115 µg/L compared to 185 µg/L in the closest shallow monitor well GM-22S, indicating limited biodegradation in the 30-ft transport distance from the well. At ITF-3, the average ClO_4 concentration was 120 µg/L compared to 510 µg/L in nearby shallow monitor well GM-21S, suggesting more extensive biodegradation.

6.1.3 Perchlorate Attenuation

The rate that contaminant concentrations change with time in individual wells or with distance between wells may be used to help forecast future behavior and evaluate potential for natural attenuation (Newell et al. 2002). Biodegradation rate constants are discussed in the Tier 3 Evaluation in Section 6.3.

Concentration vs. time rates can be used to characterize current trends and estimate how quickly remediation goals will be met at a particular location within the plume. Calculated rates will be most reliable if data are collected over several years. The performance monitoring period of the current project was 2 years. However, when historical information was available, these data were combined to include in the analysis. **Table 6-5** summarizes computed zero-order rates in individual monitor wells.

Table 6-5. Zero-Order Concentration vs. Time Rates in Monitor Wells

Well	Rate (per µg/L/d)	Correlation Coefficient (R^2)	F Statistic	Observations
GM-14S	**-0.16**	0.87	**0.006**	6
GM-14M	**-0.69**	0.92	**0.003**	6
GM-2B	**-0.54**	0.89	**0.001**	7
GM-21S	+0.16	0.35	0.16	7
GM-21M	+0.03	0.52	0.07	7
GM-22S	-0.02	0.34	0.17	7
GM-22M	-0.03	0.29	0.22	7
GM-23S	**+0.01**	0.68	**0.02**	7
GM-23M	-0.004	0.34	0.17	7

Figure 6-3 shows observed concentrations in three monitor wells near the plume source. All three wells show statistically significant declines in concentration vs. time (F <0.01) and perchlorate concentrations are projected to reach the cleanup standard of 2.6 µg/L in these wells by 2015 if current trends continue. The rapid decline in perchlorate concentration observed in GM-14S and GM-14M has likely been influenced by the continued pumping of the extraction well and the former bioremediation pilot test conducted in this area. GM-2B is located farther downgradient and is not believed to have been directed impacted by the bioremediation pilot test.

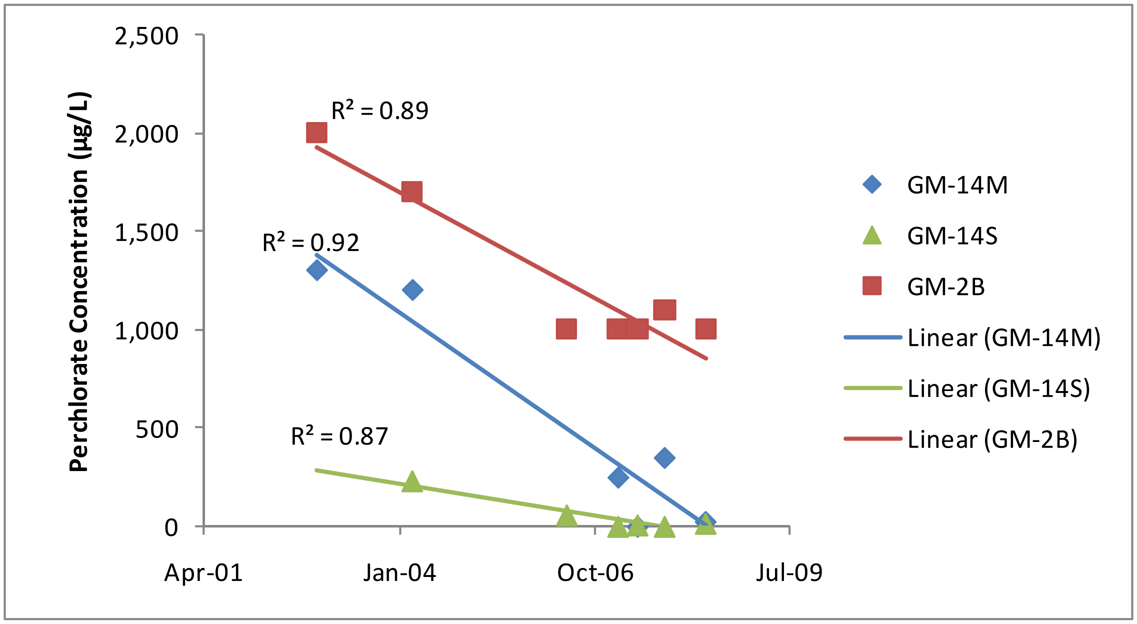

Figure 6-3. Perchlorate Concentration vs. Time in Source Area Wells
(Linear decline in concentration is significant at 99% level for all wells)

Figure 6-4 shows observed concentrations versus time in several shallow and intermediate zone wells near Little Elk Creek. Statistically significant zero-order linear regressions are indicated by a solid line (F < 0.05), while regressions that were not statistically significant are indicated by a dotted line. There is no consistent trend in perchlorate concentrations near Little Elk Creek – three wells show an increasing trend while three wells show a decreasing trend.

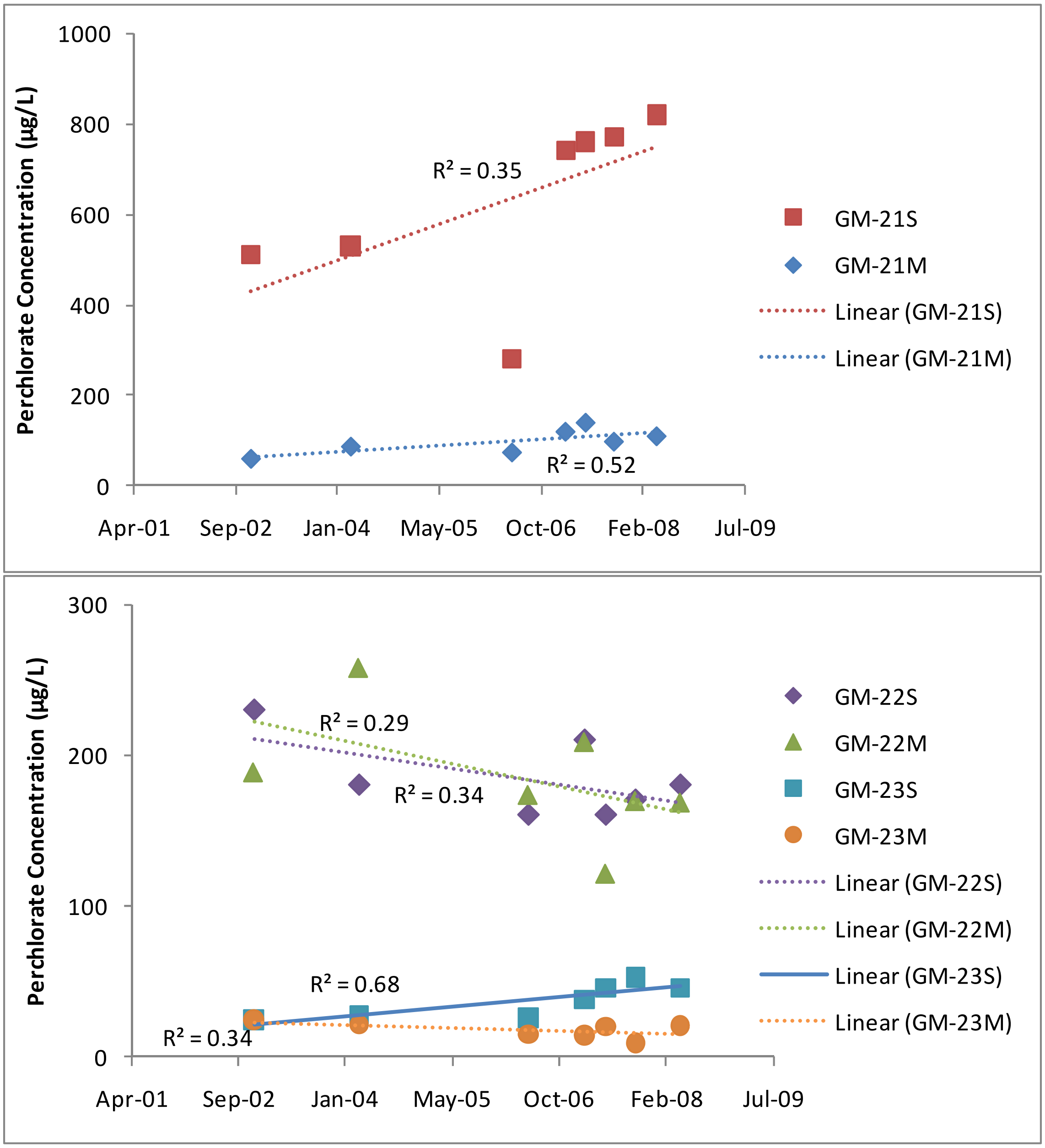

Figure 6-4. Perchlorate Concentration vs. Time in Downgradient Wells
(Only regression line for GM-23S is significant at the 95% level)

Overall results from analysis of concentration versus time trends in individual wells are: (1) concentrations are declining with time in the source area wells and are projected to reach cleanup standards in a few years; and (2) concentrations in wells near Little Elk Creek do not show any consistent trend with concentrations in some wells increasing and other wells decreasing. This overall pattern is consistent with a pulse of dissolved perchlorate migrating through the aquifer towards Little Elk Creek. Travel time from the source area to Little Elk Creek is estimated to be roughly 45 years. If flushing by ambient groundwater flow is removing perchlorate from near the source area, this effect might not be observed in wells near the creek for several decades. Some of the apparent increase in perchlorate near the creek could be due to the arrival of perchlorate that was released in the 1950s – 1960s.

6.1.4 Perchlorate Mass Flux

Contaminant mass flux estimates were determined using the transect method (Borden et al., 1997a; Newell et al., 2003). Three transects were established to analyze groundwater flux. All were oriented approximately normal to the direction of groundwater flow. The locations of each transect are shown on **Figure 6-5**. The mass flux associated with an individual well screen was equal to the measured concentration in the monitor well, times the Darcy velocity for that transect (hydraulic conductivity * gradient), times the cross-sectional area associated with that well. Cross-sectional area for each screen was width * zone thickness. Width associated with each well was defined as either: (a) distance to the mid-point between two adjoining wells; or (b) distance to the edge to the plume. Mass fluxes for the shallow and intermediate zones were calculated separately then summed to get the total flux through each transect. The hydraulic conductivities (K) of the shallow and intermediate zones were estimated to 6.3 ft/d and 10.1 ft/d, resepctively (**Table 4-1**). Hydraulic gradients for each transect were calculated from water table contour maps.

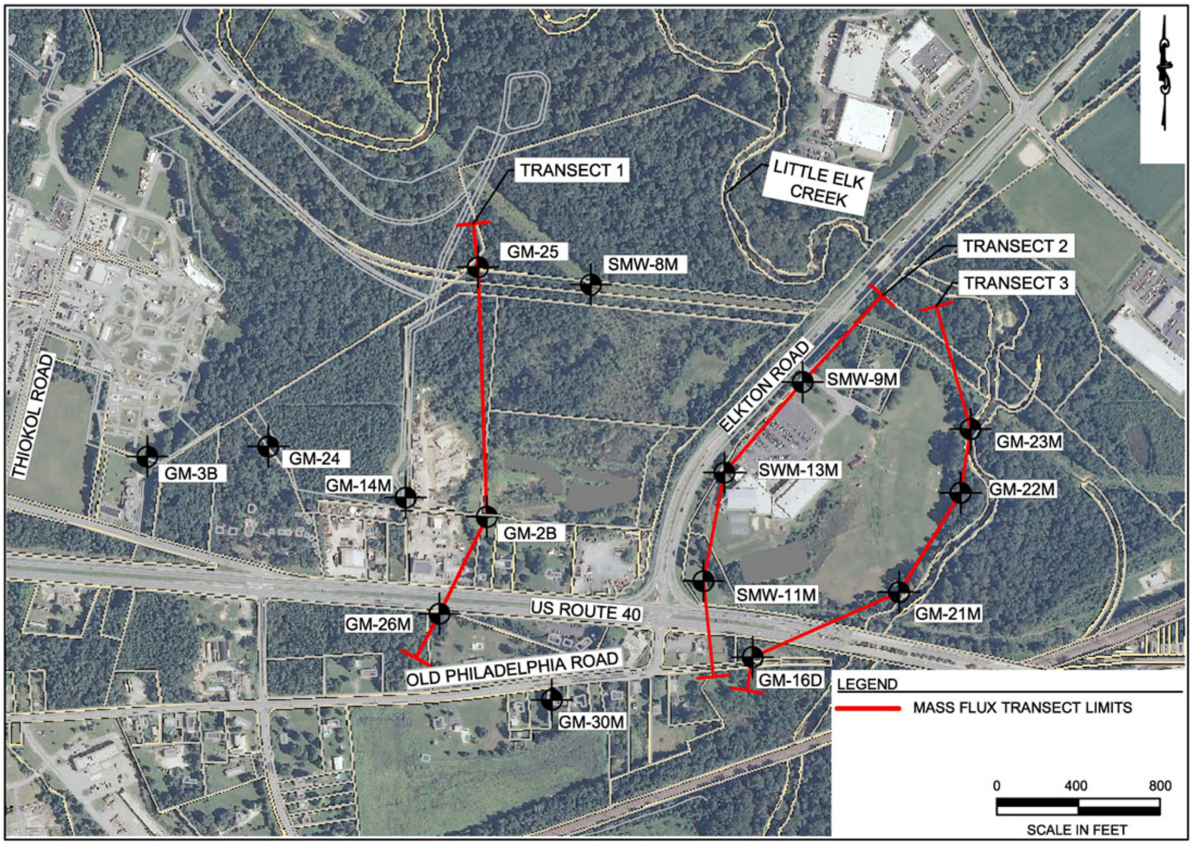

Figure 6-5. Mass Flux Calculation Transects

The characteristics of each transect used in the mass flux calculations are shown in **Table 6-6**. The total width and flow rate through each transect increase as you move downgradient due to dilution and dispersion of the plume.

Table 6-6. Transect Characteristics used to Calculate Mass Flux

Transect Number	1	2	3
Width (ft)	2,100	2,200	2,500
Top (water table) Elevation (ft)	13 to 14	9 to 11	4 to 5
Bottom Elevation (ft)	-70	-70	-50 to -80
Gradient (ft/ft)	0.033	0.044	0.044
Shallow Zone K (ft/d)	6.3	6.3	6.3
Intermediate Zone K (ft/d)	10.1	10.1	10.1
Distance from Representative Source Area near GM-14 S/M (ft)	380	1,750	2,700
Water Flux (cu. ft./d)	4,165	4,301	4,536

Perchlorate mass flux during each of the four performance monitoring events is shown in **Table 6-7** and **Figure 6-6**. Mass flux through Transect 2 was not calculated for the first performance monitoring event (Feb. 2007) because of concerns that perchlorate concentrations in the recently installed wells in that transect had not yet stabilized. Perchlorate mass flux in the intermediate zone declines significantly during groundwater flow from Transect 1 to 3. However, there is a substantial increase in the shallow zone mass flux in Transect 3 as groundwater migrates from the intermediate to the shallow zones near Little Elk Creek. Total mass flux declines from an average of 28 g/d to 18 g/d of perchlorate from Transect 1 to 3. The downward trend in perchlorate mass flux is statistically significant at the 99% level (**Figure 6-6**, F = 0.001).

Table 6-7. Perchlorate Mass Flux through Each Transect During Each Performance Monitoring Event

Transect Number	Feb. 2007	May 2007	Oct. 2007	Apr. 2008	Average (g/d)*
Transect 1					
Shallow	0.0	0.8	1.0	0.9	0.7
Intermediate	23.3	27.3	30.7	28.1	27.3
Total	23.3	28.2	31.7	28.9	28.0
Transect 2					
Shallow		0.0	0.0	0.8	0.2
Intermediate		19.9	25.6	24.6	23.4
Total		19.9	25.6	25.4	23.7
Transect 3					
Shallow	12.8	12.4	12.7	14.6	13.1
Intermediate	4.3	5.2	4.3	4.9	4.7
Total	17.0	17.6	17.0	19.4	17.8

*Mass flux values presented in grams/day (g/d)

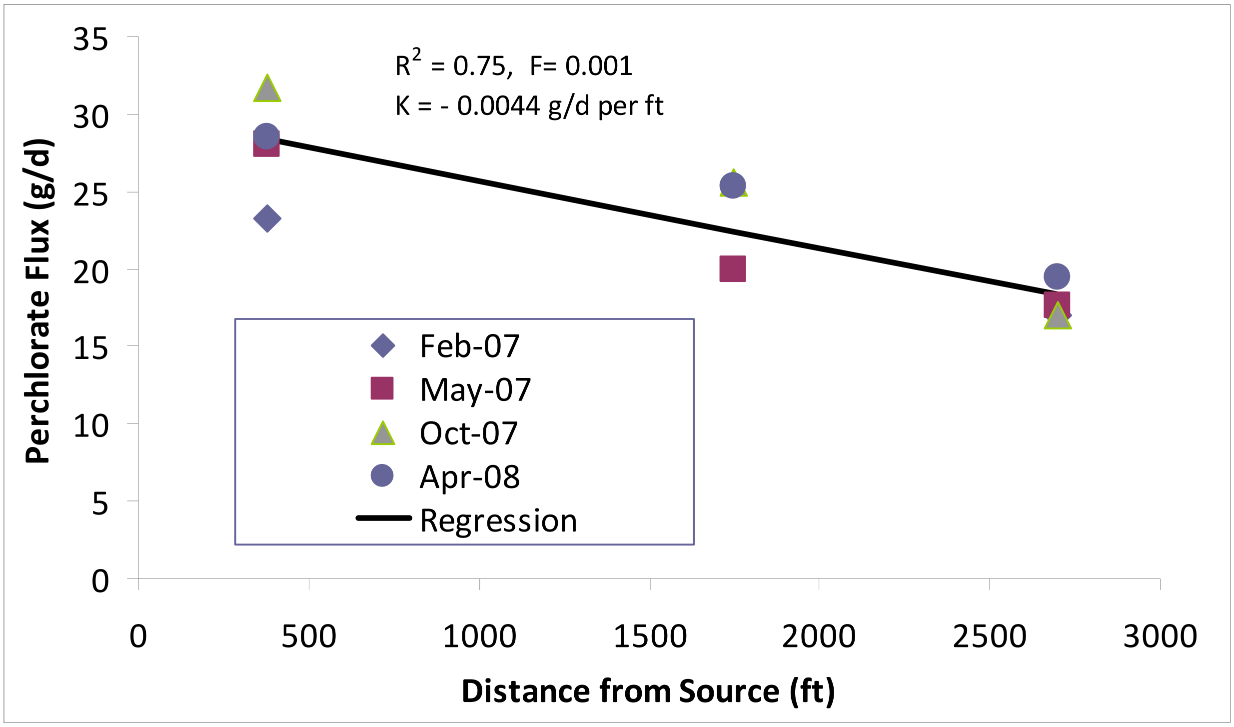

Figure 6-6. Mass Flux vs. Distance from Source

The change in mass flux from Transect 1 to 3 is likely due to two concurrent processes: (a) slow biodegradation of perchlorate; and (b) gradual flushing of dissolved perchlorate through the aquifer which is reducing the mass flux through Transect 1 and possibly increasing the mass flux at Transect 3. Mass flux calculations can only be used to calculate biodegradation rates when the plume is at steady-state. However, **Figure 6-3** shows that the source area wells are not at steady-state. Consequently, it is not possible to calculate biodegradation rates from the mass flux data.

6.1.5 Trichloroethene Attenuation

As part the performance assessment, concentrations of TCE and daughter products were collected from throughout the plume (**Table E-2** in **Appendix E**). Overall trends show a gradual decline in TCE concentrations in the source area vs. time (**Tables 6-2a** and **6-2b).** With the exception of GM-14 (near the former bioremediation pilot test), *cis*-1,2-dichloroethene (*c*DCE) concentrations are low throughout the plume indicating the observed TCE loss is primarily due to dilution, not biodegradation **(Table E-2** in **Appendix E)**. Since TCE does not appear to be readily biodegrading at this site, it was considered possible to use TCE concentrations as a conservative tracer to evaluate the potential degradation of ClO_4.

Figure 6-7a and **6-7b** show the ratio of TCE to ClO_4 in monitor wells screened in the intermediate and shallow zones, resepectively. At each well, replicate measurements are plotted separately. For example, in GM-14M, five separate blue diamonds are plotted for the five sampling events when both TCE and ClO_4 concentrations are available. Overall, there is a great deal of scatter in the data. However, some trends are evident.

In the source area and upgradient portion of the plume, the TCE:ClO_4 ratio is typically between 1 and 3 indicating TCE concentrations are similar to ClO_4 concentrations. Further downgradient, the TCE concentration in many wells is 10 to 30 times the perchlorate concentration. This suggests that ClO_4 is being attenuated more rapidly than TCE, presumably due to biodegradation. The increase in the TCE:ClO_4 ratio is most apparent in the shallow wells, consistent with the hypothesis that elevated levels of organic carbon in the wetland soils enhance ClO_4 degradation. The TCE:ClO_4 ratio is also high in GM-22M (average TCE:ClO_4 ratio = 25:1) indicating strong attenuation of ClO_4 relative to TCE. GM-22M is classified as an intermediate zone well, but is screened at an elevation similar to other shallow wells at the site.

While TCE is elevated relative to ClO_4 in some wells, there are some downgradient wells (e.g., GM-23S and GM-23M) where there is no evidence of perchlorate attenuation. This suggests that perchlorate degradation may be quite variable, possibly associated with spatial variations in the amount of organic carbon in the aquifer.

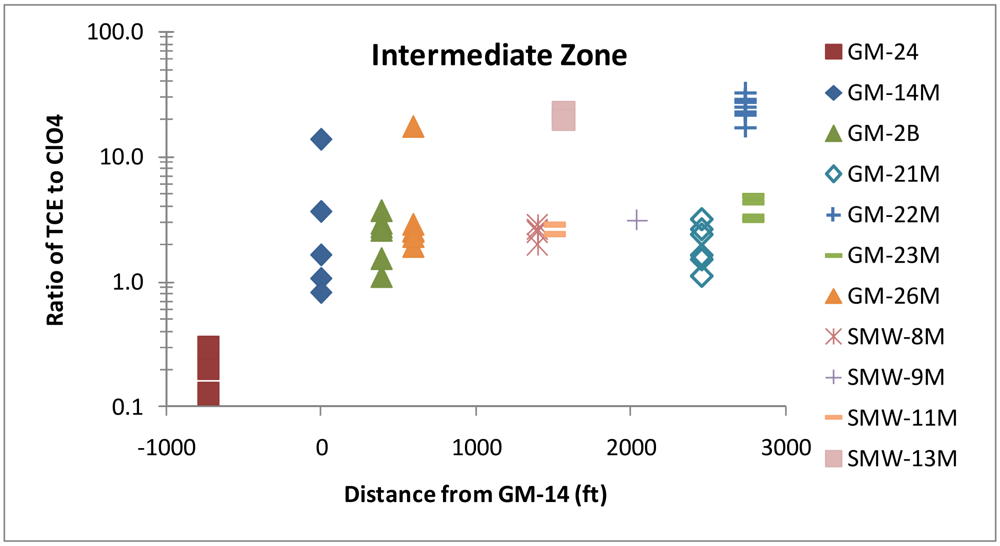

Figure 6-7a. Variation in TCE to ClO_4 Ratio in Intermediate Zone Wells with Distance from Source

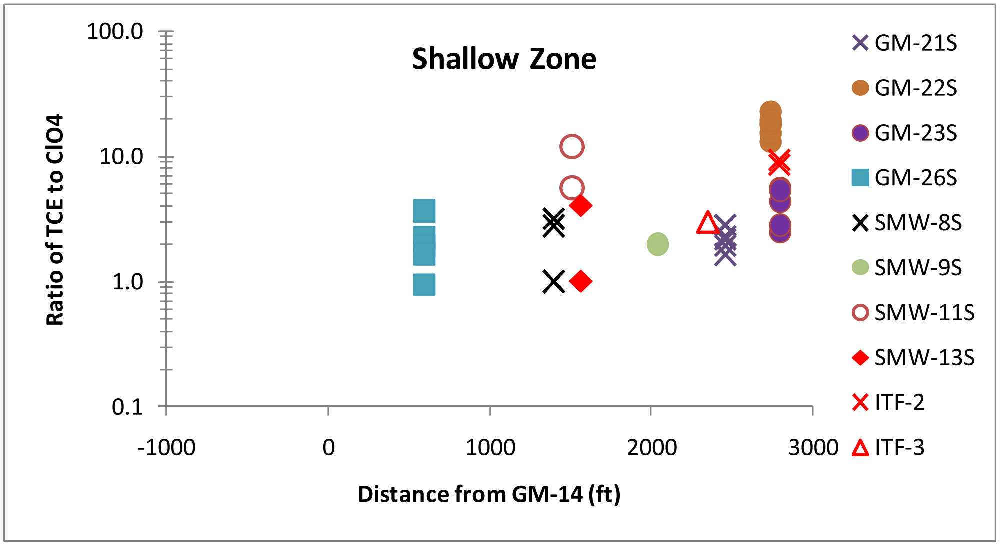

Figure 6-7b. Variation in TCE to ClO_4 Ratio in Shallow Zone Wells with Distance from Source

6.1.6 Summary of Plume Geometry and Stability Evaluation (Tier 1)

Perchlorate and TCE concentration data collected as part of the MNA evaluation indicate the following:

- ClO_4 concentrations are declining with time in the source area monitor wells. In contrast, there is no consistent trend in ClO_4 concentrations with time in wells near Little Elk Creek. This overall pattern is consistent with a pulse of dissolved perchlorate migrating through the aquifer towards Little Elk Creek.

- Perchlorate mass flux in the intermediate zone declines significantly as groundwater flows downgradient. However, there is a substantial increase in the shallow zone mass flux near Little Elk Creek, consistent with upward migration of perchlorate from the intermediate to shallow zones near the creek. The total mass flux through the intermediate and shallow zones declines from an average of 28 g/d of ClO_4 closer to the presumed source to 18 g/d near Little Elk Creek. The downward trend in perchlorate mass flux is statistically significant at the 99% level.

- Changes in the ratio of TCE to ClO_4 throughout the plume suggest some preferential biodegradation of ClO_4. However, these ratios are highly variable and there are some locations with little evidence of ClO_4 biodegradation.

- Perchlorate has not been detected on the eastern side of Little Elk Creek. The perchlorate plume is generally stable and downgradient migration appears to be controlled by discharge to Little Elk Creek. There may be a slight increase in the average ClO_4 concentration in Little Elk Creek during passage through the plume discharge area. However, the apparent increase was not statistically significant at the 95% confidence level.

- Non-biological attenuation mechanisms have resulted in some decreases in perchlorate concentrations over time, but concentrations in some locations appear to be increasing.

6.2 Tier 2 Evaluation – Biogeochemical Parameters and Trends

Site-specific biogeochemical and biological information can often provide an important indication of the potential for MNA of perchlorate. The following section describes collection and interpretation of biogeochemical and biological monitoring results from the Elkton site and how this information was used to evaluate the potential for MNA of perchlorate. The results illustrate the use of a tiered approach for evaluating perchlorate MNA as described in the MNA Prorocol (ESTCP, 2008).

Perchlorate can be rapidly biodegraded under anaerobic or low oxygen conditions when an external electron donor is present. Biodegradation will be most rapid in the absence of nitrate since many perchlorate degraders are also denitrifiers (Robertson et al., 2007; Herman and Frankenberger, 1999; Coates et al., 1999). Tan et al. (2004a) showed the presence of nitrate can slow perchlorate enzyme activity as it is a competing electron acceptor, but concluded that because more than one enzyme is involved in the degradation process, nitrate is not a competitive inhibitor of perchlorate reduction. Tan et al. (2004b) and Tan et al. (2005) concluded that organic substrate availability was the limiting factor under high electron acceptor conditions. As a result, the following conditions are expected to be most favorable for perchlorate biodegradation (ITRC, 2002):

- Available organic carbon;
- ORP between 0 and –100 mV;
- Low levels of dissolved oxygen and nitrate;
- Elevated levels of dissolved iron and/or methane;
- pH between 6.5 and 7.5; and
- Active perchlorate-degrading microbial community.

The key geochemical parameters were evaluated from each well sampled during the four performance monitoring events over 24 months.

The importance of understanding geochemistry of the aquifer materials is often overlooked. Chemical interactions between perchlorate, major aquifer anions and cations along with organic or anthropogenic sources of carbon must be understood before considering an MNA remedial alternative for groundwater. Groundwater samples collected from monitoring wells during performance monitoring were generally analyzed for perchlorate, TOC, chloride, nitrate, sulfate, and methane as well as dissolved iron and manganese. Groundwater samples were also analyzed for chlorite, chlorate, and phosphate during some sampling events. Analytical results can be found in **Table E-1** in **Appendix E**.

The plume dynamics discussed in Section 6.1 indicate that perchlorate (and TCE) are primarily transported downgradient from their origins through the intermediate zone of the aquifer. However, as the groundwater at the distal end of the plume approaches Little Elk Creek, groundwater from the intermediate zone moves vertically upward into the shallow zone, then discharges to Little Elk Creek. To evaluate the potential for MNA of perchlorate as the contaminant migrates downgradient, it is important to examine the geochemical conditions it encounters along the way. To facilitate discussion, the TCE/Perchlorate SWMU was divided into three large zones: Presumed Source Area, Mid-Plume Area, and Presumed Discharge Area (**Figure 6-8**).

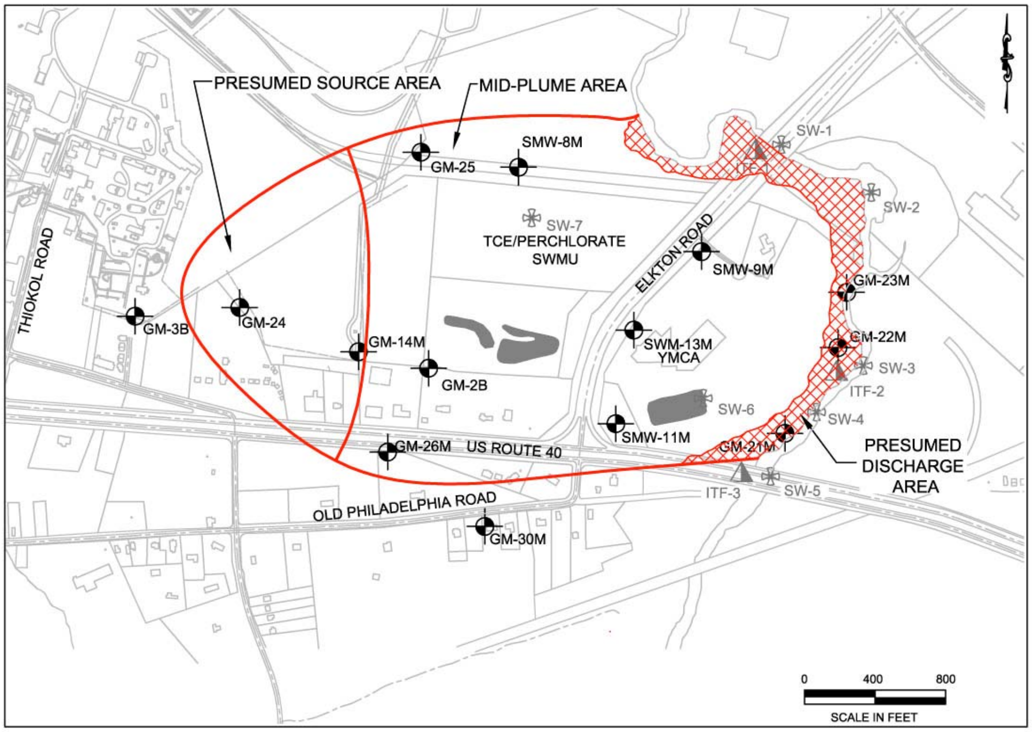

Figure 6-8. Presumed Perchlorate Source Area, Mid-Plume Area, and Discharge Area along Groundwater Flow Path

Table 6-8 summarizes the concentrations of perchlorate, TOC, nitrate, sulfate, methane and chloride in the monitoring zones across the site. It also shows the ORP and pH in each well. The wells were separated into two groups: shallow and intermediate according to the depth of the mid-point of the screen interval as described previously. The approximate distance the mid-plume and discharge area wells are from the representative presumed source is also shown. Most of the data shown were collected during the last performance monitoring event in April 2008 except where noted and are representative of the conditions observed during the 24-month monitoring program. The complete performance monitoring data set is provided in **Table E-1** in **Appendix E**.

The data presented in **Table6-8** illustrate the general absence of perchlorate in the shallow portion of the aquifer beyond the source and throughout the mid-plume areas. In the eastern-most of the wells in the presumed source area, GM-14S, perchlorate concentrations ranged from <1 to 58 µg/L over the 2 years of performance monitoring (**Table E-1** in **Appendix E**). Of the seven shallow wells that were monitored in the mid-plume zone, GM-26S consistently reported low concentrations of perchlorate (<1 to 49 µg/L) as far back as January 2002. However, this well is side-gradient from the general direction of groundwater flow and is south across US Route 40. The other shallow mid-plume well that reported perchlorate was well SMW-9S, located across Elkton Rd. and north of the YMCA. This well has historically been without perchlorate until the duplicates sampled from this well in April 2008 reported 70 and 44 µg/L. However, the laboratory reported some problems with these analyses which make these values suspect. Although absent in the shallow mid-plume wells, perchlorate is reported consistently in the six shallow wells in the presumed discharge area. In April 2008, perchlorate concentrations ranged from 21 to 820 µg/L across this area. Two of the three groundwater interface samples collected in February 2007 showed 110 to 240 µg/L perchlorate. No perchlorate was reported in the two shallow wells across Little Elk Creek.

Perchlorate is generally detected in all the intermediate depth wells from the presumed source area (300 to 350 µg/L), through the mid-plume area (14 to 1,000 µg/L, except GM-25 which is side-gradient north of the primary groundwater flow direction), all the way to the presumed discharge area (110 µg/L).

Table 6-8. Concentrations of Perchlorate, TCE and Geochemical Parameters

Well ID	Distance (ft)[a]	Sample Date	ClO_4^- (µg/L)	TCE (µg/L)	TOC (mg/L)	ORP (mV)	pH (SU)	Methane (µg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
Shallow Groundwater Samples											
Presumed Source Area											
GM-14S	-	4/29/08	16	440	8.3	-23[b]	5.4	200	<0.5	<0.5	28
Mid-Plume Area											
GM-26S	600	4/29/08	21	35	<1	+33	4.7	<4	0.5	6.4	6.9
GM-29	700	5/19/06	<1	<1.1	1.6	+140	5.3	<4	<0.5	30	53
SMW-8S	1,400	4/29/08	<1	1.4	<1	+41[b]	5.5	<4	<0.5	13	7.0
SMW-9S	2,000	4/30/08	44[c]	2.8	1.8	-190	6.2	<4	<0.5	0.7	12.3
SMW-11S	1,500	4/30/08	<1	2.8	<1	+10	4.8	<4	<0.5	9.0	14.0
SMW-13S	1,600	4/30/08	<1	2.0	<1	+19	5.1	<4	<0.5	14	49
GM-27S	1,600	5/17/06	<1	<1.1	<1	+290	4.3	<4	3.8	22	160
Presumed Discharge Area											
GM-21S	2,500	4/29/08	820	1600	<1	+42	4.9	<4	1.3	1.5	18
GM-22S	2,700	4/29/08	180	3,500	1.8	+47	5.4	<4	3.4	6.5	160
GM-22M	2,700	4/30/08	170	3,900	<1	+17	5.5	<4	4.3	9.1	130
GM-23S	2,800	4/30/08	46	130	1.2	+59	5.3	<4	2.6	6.3	9.3
GM-23M	2,800	4/30/08	21	71	1.4	+28	6.5	<4	0.5	18	12
GM-16S	1,800	4/29/08	73	82	<1	+56	4.4	<4	2.6	1.3	8.8
Groundwater Interface Samples											
ITF-1		2/7/07	<1	11	19	-67	5.9	660	0.9	19	74
ITF-2		2/8/07	110	1,000	6.0	+170	5.9	48	14	15	29
ITF-3		2/8/07	240	730	17	NS	NS	2,300	7.3	26	25
Across Little Elk Creek											
GM-32S	2,800	5/18/06	<1	5	<1	+56	5.5	12	<0.5	3.8	3.9

Table 6-8. Concentrations of Perchlorate, TCE and Geochemical Parameters

Well ID	Distance (ft)[a]	Sample Date	ClO_4^- (µg/L)	TCE (µg/L)	TOC (mg/L)	ORP (mV)	pH (SU)	Methane (µg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
GM-33S	2,900	5/18/06	<1	<1.1	<1	+260	4.8	<4	<0.5		4.3
Intermediate Groundwater Samples											
Presumed Source Area											
GM-24	-	5/18/06	300	90	<1	+110	6.2	<4	0.9	18	13
GM-14M	-	10/2/07	350	360	250	+33	4.2	NA	1.6	11	37
Mid-Plume Area											
GB-2B	400	4/29/08	1,000	2,600	<1	+6.7	5.7	<4	12	0.6	19
GM-26M	600	4/29/08	150	350	<1	+96	4.3	<4	3.9	2.0	10
GM-25	1,200	10/4/07	5.6	<1[d]	2.8	+73	13.0	NA	<0.5	25	8.3
SMW-8M	1,400	10/2/07	14	36	<1	+210	4.7	NA	1.1	1.7	18
SMW-9M	2,000	4/30/08	44[c]	190	<1	+99	4.5	<4	<0.5	0.7	13
SMW-11M	1,500	4/30/08	750	2,100	<1	+70	4.8	<4	4.6	2.2	29
SMW-13M	1,600	4/30/08	120	2.0	1.1	+83	4.8	10	1.1	<0.5	24
Presumed Discharge Area											
GM-21M	2,500	4/29/08	110	170	<1	+70	5.3	<4	1.8	1.2	5.1

a) Approximate distance measured parallel to groundwater flow direction from west to east from interpreted eastern edge of Source Area Zone shown in Figure 6-6.
b) Data from October 2, 2007.
c) Perchlorate concentrations from Duplicate samples collected from the well.
d) Data from April 29, 2008
e) Concentrations rounded to 2 significant figures.

6.2.1 Total Organic Carbon

Soil TOC levels were measured at various depths during the installation of four new monitor wells in December 2006. The results summarized in **Table 6-9** show that TOC is measurable throughout the soil column at mid-plume locations 1,400 to 2,000 feet downgradient of the presumed source area, and 500 to 1,000 ft from Little Elk Creek. Substantial amounts of organic carbon are present at a few depths (2% in SMW-9M) suggesting the potential for development of anoxic conditions in isolated zones. However, TOC was below 0.1% in many of the samples which will likely result in more oxidizing conditions. TOC in soils closer to Little Elk Creek were not measured.

Table 6-9. Concentrations of Total Organic Carbon in Soil (December 2006)

SMW-8M		SMW-9M		SMW-11M		SMW-13M	
Depth	**TOC**	**Depth**	**TOC**	**Depth**	**TOC**	**Depth**	**TOC**
ft bgs	%	ft bgs	%	ft bgs	%	ft bgs	%
NA	NA	10	0.46%	8	0.36%	14	0.09%
25	0.04%	19	0.69%	18	0.26%	25	0.76%
34	0.03%	27	2.00%	28	0.36%	34	0.14%
45	0.03%	42	0.13%	42	0.51%	45	0.28%
57	0.25%	54	0.05%	52	0.08%	55	0.16%

Elevated levels of organic carbon in groundwater (TOC > 2 mg/L) will enhance perchlorate biodegradation by providing a terminal electron acceptor for ClO_4 reduction and reducing levels of other competing electron acceptors including oxygen and nitrate (ESTCP, 2008). Naturally occurring sources of carbon can be found in wetlands, stream bottoms and riparian buffers. Where perchlorate plumes discharge into these features, the opportunity for MNA increases; in mineral soils with little TOC, this may be limited.

TOC data shown in **Table 6-8** indicates organic carbon is low throughout most of the plume. However, elevated levels TOC levels were detected in a few wells (SMW-9S, GM-25, GM-30M), presumably due to isolated high organic carbon layers in the aquifer. TOC was also elevated in GM-14S (8.3 mg/L) and GM-14M (330 mg/L) due to carry over from the former bioremediation pilot test performed in 2004. There was no evidence of an increase in TOC in GM-2B, 400 feet downgradient from GM-14S/M.

Elevated levels of TOC were also detected in the groundwater collected from the shallow interface wells emplaced along the Little Elk Creek stream bank. The concentrations ranged from 6.0 mg/L in ITF-2 to 19 mg/L in ITF-1. This result is consistent with the deposition and decay of organic material from the wooded areas on either side of the creek.

6.2.2 Oxidation-Reduction Potential

ORP is a measure of the oxidizing or reducing conditions in groundwater. The ORP of a groundwater system depends upon and influences rates of biodegradation (Wiedemeier et al., 1998). The ORP of groundwater generally ranges from -400 mV to +800 mV. As illustrated in **Figure 6-9**, some processes operate most effectively within a prescribed range of ORP conditions.

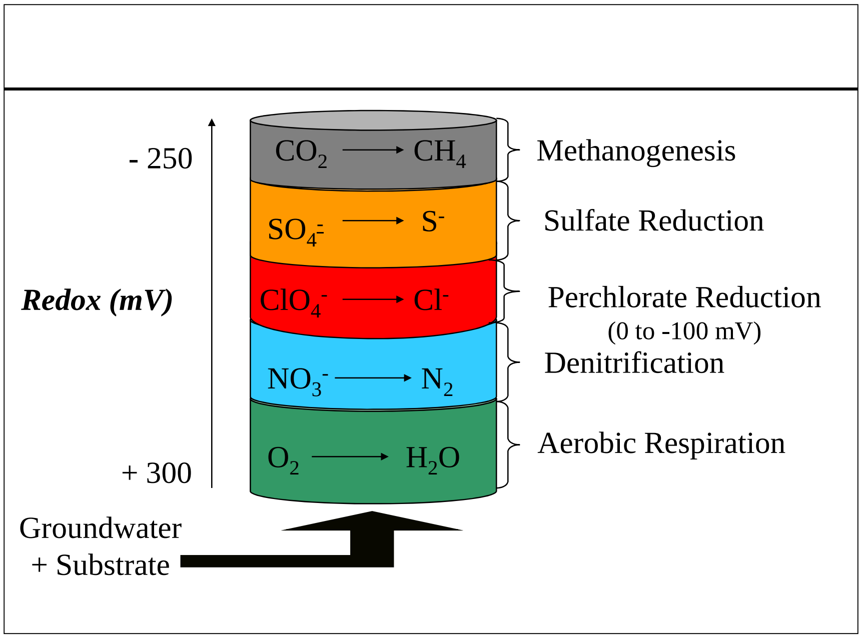

Figure 6-9. Redox Potential for Degradation Processes (ITRC 2002)

Table 6-8 shows the ORP measurements in shallow and intermediate groundwater in the monitoring network during representative sampling dates. The historical data set for field parameters is provided in **Table E-3** in **Appendix E.** ITRC (2002) reported that conditions would be most favorable for perchlorate degradation when the Eh was between ORP 0 and –100 mV (**Figure 6-7**). However, in the evaluation of perchlorate MNA at NSWC, Indian Head, MD performed as part of this project (ESTCP, 2010), perchlorate biodegradation was rapid at ORP values between 0 and +100 mV. At the demonstration site, most ORP values are less than +100 mV suggesting some potential for perchlorate biodegradation.

6.2.3 Dissolved Oxygen

Although many perchlorate-reducing bacteria are versatile, DO concentrations greater than 2 mg/L are expected to inhibit perchlorate biodegradation, and DO concentrations less than 1 mg/L are expected to be more favorable for natural attenuation of perchlorate (ESTCP, 2008). The DO concentrations across the site ranged from 0.3 to 3.5 mg/L with no discernible difference between shallow and intermediate groundwater. The data did not indicate significant measureable depletion of DO as a result of residual TOC near the source in GM-14M or in the interface zone adjacent to Little Elk Creek. The DO data are provided in **Table E-3** in **Appendix E.** Perchlorate biodegradation can occur under strict anaerobic conditions as well as facultative anaerobic and microaerophilic conditions (Rikken et al., 1996; Chaudhuri et al., 2002; Coates and Achenbach, 2004).

6.2.4 Nitrate

The same conditions that are required for denitrification (the conversion of nitrate to nitrogen gas) are favorable for perchlorate reduction. Many perchlorate reducing bacteria can reduce nitrate as well as perchlorate (Herman and Frankenberger, 1998). As stated in Nzengung et al. (2007), "… evidence for the reduction of nitrate (e.g., decrease of nitrate), or observance of nitrite production (a step in the denitrification of nitrate), along with a decrease in perchlorate concentration along the flow path, may be good indicators of the natural attenuation of perchlorate." However, high levels of nitrate can inhibit perchlorate reduction (Chaudhuri et al., 2002; Krauter et al., 2005). For natural bioattenuation of perchlorate to occur most efficiently, low levels of nitrate (< 5 mg/L) are preferable.

Representative nitrate concentrations in individual wells are shown on **Table 6-8**. The only well with nitrate concentrations consistently greater than 5 mg/L was GM-2B which averaged 11.7 mg/L during the performance monitoring period (**Table E-3** in **Appendix E).** The only other wells across the site with nitrate concentrations greater than 3 mg/L included GM-28 (12.2 mg/L), GM-22S (3.9 mg/L), GM-22M (4.5 mg/L), SMW-11M (4.6 mg/L) and GM-26M (4.1 mg/L).

6.2.5 Iron and Manganese

Increases in dissolved iron (Fe^{2+}) and dissolved manganese (Mn^{2+}) can be indicators of a reducing environment that is conducive to perchlorate degradation. Dissolved iron concentrations greater than 0.5 mg/L suggest conditions favorable for perchlorate biodegradation.

Fe^{2+} and total Mn were measured frequently during the performance monitoring using field test kits (CHEMetrics Inc., Calverton, VA). These colorimetric tests are semi-quantitative and can be influenced by natural coloration of the water sample. Dissolved iron was only measurable in GM-14M, near the source and the former bioremediation pilot test. Neither dissolved iron nor manganese was detectable in any other groundwater sample collected during the project. The absence of iron and manganese from groundwater is shown via the historical data set provided in **Table E-3** in **Appendix E**.

6.2.6 Methane

Methane can be formed biologically in strongly reducing groundwater as a result of anaerobic biodegradation of organic matter and the reduction of carbon dioxide (CO_2). Methanogenesis is not a direct indicator of the biodegradation of perchlorate, but can be used as a line of evidence for reducing conditions that favor perchlorate reduction. Methanogenesis is not a prerequisite condition for perchlorate biodegradation to occur.

Appreciable levels of methane were detected in GM-14S and the three interface samples (**Table 6-8)**. The methane in GM-14S is presumably due to carry over from the former bioremediation pilot test conducted in that area. Methane in the interface samples collected near Little Elk Creek is presumably the result of anaerobic bioactivity supported by slightly increased TOC, lower ORP and more-neutral pH. This level of bioactivity could contribute to the biodegradation of perchlorate leading to its natural attenuation prior to groundwater discharging into the creek.

6.2.7 pH

The groundwater beneath the site generally ranges from pH 4.1 to 6.5 with no discernible difference between the shallow and intermediate portions of the aquifer (**Table 6-8**). The historical data from 15 shallow wells and 9 intermediate wells were used to calculate overall averages for each zone. The complete historical data set is provided in **Table E-3** of **Appendix E**. The average pH in the shallow groundwater was pH 5.5±1.0 (n=32); the average pH in the intermediate aquifer was 5.4±0.9 (n=33). The groundwater in GM-25 and GM-30 has historically ranged from pH 9.60 to 13.0 and was not used in calculating the averages. Although these wells have been anomalously high compared to the remaining wells on site, the measurements have been consistent over the performance monitoring period. These wells are located 1,200 or more feet from the source and have been impacted minimally by the release of perchlorate. The reason for the elevated pH is unknown.

The groundwater in the interface samples just prior to discharge to the creek was pH 5.9 when measured in May 2006. The entire set of pH data from five surface water sampling stations collected over the 24-month performance monitoring period was used to calculate the average pH of the surface water in Little Elk Creek. The average pH was 6.5±0.7 (n=25). The historical pH data for the interface and surface water samples are provided in **Table E-3** in **Appendix E.**

The perchlorate-reducing bacteria generally grow optimally at pH values near neutrality. However, field studies have shown that some species are capable of growth and perchlorate respiration can occur at values as low as pH 5 (Coates and Achenbach, 2004). In evaluating the potential for MNA of perchlorate, pH values between 5 and 8 are preferable. The groundwater within the TCE/perchlorate plume is somewhat acidic, and is generally at the low end of the optimal range. Conditions closer to pH 6 occur nearer to Little Elk Creek, which could potentially better support perchlorate-reducing bacterial activity.

6.2.8 Temperature

The presence and metabolic vitality of microorganisms can be affected by temperature. Warmer temperatures promote increased activity. As stated by Wiedemeier et al. (1995, 1998), “groundwater temperature directly affects the solubility of oxygen and other geochemical species…Groundwater temperature also affects the metabolic activity of bacteria. Rates of hydrocarbon biodegradation roughly double for every 10°C increase in temperature over the temperature range between 5 and 25°C.” This general rule is expected to apply to species capable of reducing perchlorate in the environment.

Temperatures in the groundwater plume change relatively little across the well network. Some minor seasonal variations were observed, but, groundwater temperatures generally stayed between 12 and 19ºC.

6.2.9 Chloride, Chlorate and Chlorite

If starting chloride concentrations are low and perchlorate is high, increased levels of chloride can provide a direct indication of perchlorate biodegradation. However, when background chloride is higher than the level of contamination, as observed in the TCE/perchlorate plume, it can be difficult to attribute changes in chloride to biodegradation of the contaminant(s). The complete chloride data set is provided in **Table E-1** in **Appendix E**. The chloride concentration in each well during the four or five performance monitoring events was averaged and compared spatially across the plume. In the presumed source area, chloride concentrations in shallow and intermediate groundwater were significantly different ($P = .02$), ranging from 23±4.1 mg/L ($n=5$) in GM-14S to 45±17 mg/L ($n = 4$) in GM-14M. However, the chloride concentration in GM-2B (23±4.4 mg/L), which is from the intermediate depth, was most similar to the concentration in shallow well GM-14S. The source of this difference is unknown.

Chloride concentrations in the mid-plume area are consistent within each well over time, but some spatial variation can be observed. For example, well pair SMW-9S/M located along Elkton Rd north of the YMCA averaged 11 and 9 mg/L chloride, respectively, whereas well pair SMW-11S/M along Elkton Rd. south of the YMCA averaged 32 and 33 mg/L, respectively, and SMW-13S/M directly in front of the YMCA and in the middle of the plume was 49 and 26 mg/L, respectively. The difference in chloride concentrations between SMW-9S/M and the other two well pairs is significant ($P < .0003$), but the source of the increase is unclear. The highest chloride concentrations (148 and 138 mg/L) were recorded in GM-22S/M located in the middle of the discharge zone near the creek. These concentrations are significantly higher than any of the chloride concentrations across the site or the average concentration in the stream which was 32±3.5 mg/L. Although there is no obvious reason for the increases observed across the site, it is possible that use of salt or brine for ice control along Elkton Rd. and in the parking lot of the YMCA has resulted in stormwater runoff containing elevated chloride that has infiltrated the flood plain behind the YMCA or directly impacted the stream.

The biodegradation of perchlorate occurs through sequential, enzymatic removal of oxygen atoms from the perchlorate anion. As shown in **Figure 1-1**, the intermediate breakdown products are chlorate (ClO_3^-) and chlorite (ClO_2^-), leading to the formation of chloride and oxygen. EPA Method 300.1 (Rev 1.0) is an ion chromatography method approved for testing chlorate and chlorite in drinking water. A modification of this ion chromatography method was employed at the NCSU-CCEE laboratory to analyze for anions including chlorate and chlorite. The detection limit was 0.5 mg/L. Chlorate was detected in well GM-14S at a concentration of 0.6 mg/L during the May 2006 pre-demonstration sampling. No chlorate was reported during any of the remaining sampling events. Chlorite was detected in well GM-14M at a concentration of 4.7 mg/L in October 2007 and 5.2 mg/L in May 2008. Chlorite was also reported in well SMW-11S at a concentration of 0.8 mg/L in October 2007. No other chlorite was reported during any of the sampling events in any of the wells.

The rate controlling step in the biodegradation process is the reduction of perchlorate to chlorate by a perchlorate-reductase enzyme. Chlorate reducers are up to 50 times more abundant than perchlorate reducers, so once formed, chlorate is readily converted to chlorite at rates up to three times faster than the initial step. Chlorite formation could be problematic as it is toxic to bacteria, but the CD enzyme that catalyzes the disproportionation of chlorite to O_2 and Cl^- is the fastest acting enzyme in the sequence. Therefore, intermediates do not ordinarily accumulate in solution during perchlorate biodegradation **(**Magnus XC, 2005; Logan et al., 2001**)**. Thus, like chloride, these intermediates may only be useful indicators when very high concentrations are being degraded, leaving sufficient time for residual concentrations to accumulate.

6.2.10 Microbial Populations

Monitoring of microbial populations and their spatial distributions can provide important evidence about contaminant biodegradation. The MNA Protocol (ESTCP, 2008) describes several methods for enumeration of perchlorate-reducing bacteria including anaerobic plate counts, most probable number enumeration, and MBTs. Several different types of MBTs were used to monitor the activity and spatial distribution of perchlorate reducing bacteria at the site.

A wide diversity of microorganisms can degrade perchlorate to chloride and oxygen (Coates et al., 1999; Coates and Pollock, 2003). The perchlorate biodegradation pathways are well understood and the microorganisms involved in perchlorate biodegradation are known to use a variety of different organic substrates as electron donors (Nzengung, 2008) including simple organic acids and alcohols, aromatic hydrocarbons, hexoses, reduced humic substances, both soluble and insoluble ferrous iron and hydrogen sulfide (Coates and Achenbach, 2006). Dissimilatory Perchlorate-Reducing Bacteria (DPRB) are widespread in the environment (Coates et al., 1999; Logan, 2001) and bioaugmentation is not usually required to stimulate perchlorate reduction (Coates and Achenbach, 2006). The metabolic versatility of these organisms allows many to function as strict or facultative anaerobes and survive and degrade perchlorate even in microaerophilic environments or environments with low levels of other competing electron acceptors.

As noted during the pre-demonstration testing (Section 3.2.3), DNA-based PCR assays were used initially to qualitatively monitor for organisms with the genetic capability to biodegrade perchlorate. The PCR assay used during site screening targeted the chlorite dismutase gene (*cld*) which codes for the CD enzyme. The CD enzyme mediates dismutation of chlorite, the final step in reduction of perchlorate to chloride and oxygen (Gunawan, 2007). During site screening, saturated soil was collected from the shallow aquifer from a hand-auger boring immediately adjacent to GM-22S and tested for the presence of the *cld* genes (Section 3.2.4). Groundwater samples were not tested. The shallow aquifer sample was reported as “++”, a moderately strong indication of the presence of the *cld* genes (ESTCP, 2007).

As part of the Tier 2 evaluation, the CD enzyme assay was again applied as a screening tool. In October 2007, groundwater samples were collected from 23 monitoring wells and shipped to Microbial Insights to be screened quantitatively for the overall microbial population census (“eubacteria”) and qualitatively for the CD enzyme. Total eubacteria (EBAC) provides an index of the total bacterial biomass and is generally greater than 10^6 cells/mL in the absence of factors inhibiting microbial growth. As shown in **Table 6-10**, this threshold was reported in only 4 of the 23 samples, suggesting less than optimal conditions supporting biological growth throughout the aquifer. Six out of 23 samples were reported as strongly positive (“+++”) and four others as moderately positive (“++”) for the CD enzyme. There appeared to be greater positive response in intermediate and deep groundwater samples than in shallow samples. This would be expected as a response to the presence of perchlorate in the deeper groundwater compared to the shallower zones.

After conducting their analyses, Microbial Insights sent the samples to the Soil Microbial Ecology Laboratory at the University of California at Davis under the direction of Dr. Kate Scow where the qPCR assay was used to estimate populations of perchlorate-degrading microorganisms in the samples. The DNA-based qPCR assay was performed on each of the samples targeting the *pcrA* gene which is one of the gene subunits that codes for the perchlorate-reductase enzyme known to mediate the initial breakdown of perchlorate to chlorate and chlorite.

Table 6-10 shows the number of gene copies in groundwater from each of the wells that were tested during the performance monitoring event conducted October 2, 2007. The *pcrA* gene was absent in 19 of the 23 samples. The strongest indications were in GM-14S and GM-14M located in the source area where perchlorate reduction had been stimulated by the bioremediation pilot test. Otherwise, *pcrA* gene copies were quantifiable just above the detection limit only in shallow groundwater from GM-23S and GM-16S. GM-23S is close to the riparian woodlands near the discharge to Little Elk Creek; GM-16S is in a natural area south of US Hwy 40, but also in the presumed discharge area somewhat close to Little Elk Creek. In an evaluation of perchlorate MNA at Indian Head (ESTCP, 2010), rapid perchlorate biodegradation was associated with *pcrA* levels greater than 100 gene copies per mL. The MBT analyses indicate that perchlorate biodegradation will be limited in most of the aquifer at Elkton. However, some perchlorate biodegradation may occur in areas near Little Elk Creek where organic carbon levels are higher.

Table 6-10. Enzyme Assay Results from October 2, 2007

Chlorite Dismutase Gene (cld)		**Eubacteria (EBAC)**	***Perchlorate Reductase Gene (pcrA)***
	pos/neg	**gene copies/mL**	**gene copies/mL**
Shallow Groundwater Samples			
GM-14S	+++	4.60E+06	11,000
GM-26S	-	5.34E+04	<10
SMW-8S	+/-	1.20E+05	<10
GM-30	+	2.13E+04	<10
SMW-9S	-	9.13E+04	<10
SMW-11S	+/-	2.46E+02	<10
SMW-13S	+	2.54E+02	<10
GM-21S	-	3.84E+04	<10
GM-22S	+	1.06E+05	<10
GM-22M	+	3.12E+05	<10
GM-23S	+++	1.50E+06	28
GM-23M	+	3.77E+02	<10
GM-16S	++	1.93E+05	11
Intermediate & Deep Groundwater Samples			
GM-14M	+++	2.40E+07	1,200
GM-26M	-	3.18E+03	<10
GM-2A	++	5.79E+05	<10
GM-2B	+++	5.48E+03	<10
GM-25	+	1.29E+06	<10
SMW-8M	++	2.59E+04	<10
SMW-9M	++	3.34E+02	<10
SMW-11M	+++	2.44E+05	<10
SMW-13M	+++	1.80E+05	<10
GM-21M	+	1.90E+05	<10

6.2.11 Summary Biogeochemical Evaluation (Tier 2)

The results of the Tier 1 and Tier 2 analyses can be summarized by reviewing the interaction of key parameters that are needed for perchlorate biodegradation to occur. These include:

- Presence of microbial populations with perchlorate-reducing capability;
- Presence of available organic carbon measured as TOC as substrate for growth and energy of perchlorate reducing microorganisms;
- Absence of competing electron acceptors;
- Favorable pH for bioactivity; and
- Evidence of reducing conditions with minimal oxygen present.

The following sections discuss the conditions at the Maryland manufacturing site as contaminated groundwater moves from the TCE/Perchlorate SWMU to the east toward Little Elk Creek and encounters zones with different biogeochemical conditions.

6.2.11.1 Presumed Source Area

The data shown in **Table 6-8** illustrate the conditions in the shallow and intermediate aquifer in the vicinity of the presumed source as represented by wells GM-14S/M and GM-24. There are low concentrations of perchlorate in the groundwater at both depths. In March 2004, prior to the bioremediation pilot test, the concentration of perchlorate in GM-14M was 1,240 µg/L (data not shown). It appears that the introduction of organic substrate stimulated perchlorate reduction resulting in an 80 to 90% decrease in concentration. These wells are slightly acidic but contain some residual TOC and show evidence of reducing conditions that could promote further perchlorate degradation over time. These source area wells also contain measurable populations of bacteria with *cld* and *pcrA* activity.

6.2.11.2 Mid-Plume Area

The mid-plume wells located approximately 400 to 600 feet downgradient of the representatitve source area begin to show the contamination pattern that is most prevalent throughout the plume. There is virtually no perchlorate in the shallow portion of the aquifer (<1 to 21 µg/L), but there is elevated perchlorate in the intermediate groundwater (150 to 1,050 µg/L). The pH is somewhat acidic, the ORP is oxidative, and TOC is low.

Although the pH is somewhat acidic and below optimal for many bacteria, there are measureable populations of microorganisms (i.e., 10^3 to 10^5 eubacteria/mL) in both the shallow and deep portions of the aquifer. However, levels of perchlorate-reducing bacteria were below detection, although the *cld* assays did indicate some capacity. In this portion of the aquifer, flushing by uncontaminated groundwater is expected to be the primary attenuation mechanism.

Geochemical conditions in the shallow and intermediate aquifer zones are similar at 600 to 1,750 feet downgradient from the source. However, perchlorate levels are much higher in the intermediate zone. This is presumably due to more rapid flushing in the shallow zone.

6.2.11.3 Discharge Area and Interface Samples

The Tier 1 and 2 evaluation shows that groundwater conditions are most conducive to perchlorate biodegradation immediately adjoining Little Elk Creek. In wells located within the playing fields, ORP levels are generally oxidizing and TOC levels are low. However immediately adjacent to Little Elk Creek, TOC is elevated (6 to 19 mg/L), pH has increased to 5.9, and methane is present indicating favorable conditions for perchlorate biodegradation.

Tier 3 investigations are focused on the area adjoining Little Elk Creek because of the more favorable conditions for biodegradation.

6.3 Tier 3 Evaluation – Biodegradation Rates

Laboratory and field experiments can be used to demonstrate contaminant biodegradation and estimate the rate and extent of perchlorate biodegradation. Macrocosm and *in situ* biodegradation studies were employed at the site to provide direct evidence of biodegradation.

Microcosms were also performed, but were used during the site-screening process as described in Section 3.2.3.2 and the Treatability Study (ESTCP, 2007). These tests were used to attempt to determine rates of perchlorate degradation that could be applied to the evaluation of MNA as a potential groundwater remedy.

6.3.1 Macrocosm Study

Macrocosms were constructed on June 26, 2007, during the demonstration to evaluate perchlorate biodegradation using saturated soil collected from the shallow aquifer zone adjacent to well pair GM-22S/M. The macrocosms were prepared as described in Section 3.6.2. The carboys were incubated in the dark at room temperature. The macrocosms were sampled for perchlorate and nitrate immediately after setup and approximately every two weeks thereafter for 121 days.

The nitrate and perchlorate sample results for each macrocosm repetition are depicted in the **Figure 6-10**. The average starting concentration for nitrate was 4.6 mg/L and the perchlorate was 0.17 mg/L. The data suggest that there might have been a lag of approximately one month in the biodegradation of perchlorate until nitrate dropped below 4.0 mg/L, possibly a result of competition with denitrifying bacteria. Overall, nitrate decreased by 88% over 98 days to below the analytical detection limit (0.5 mg/L) and perchlorate decreased by 58% over 121 days to 0.07 mg/L.

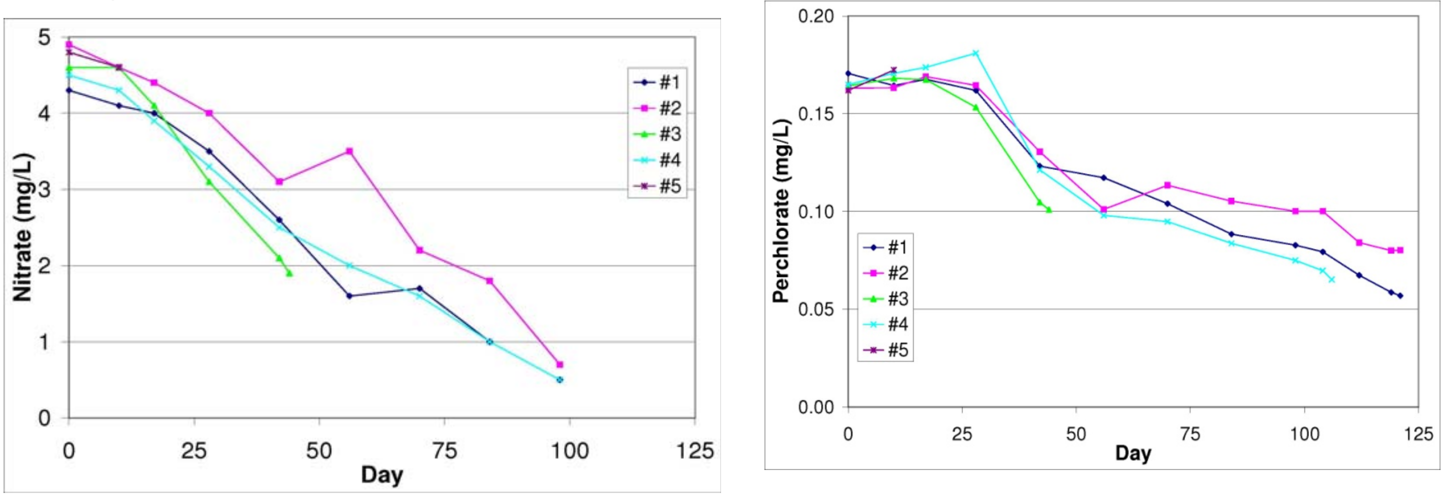

Figure 6-10. Concentrations of Nitrate (a) and Perchlorate (b) in Five Replicate Macrocosms

Macrocosm results were evaluated by determining reaction rate constants by fitting zero-order (Eq. 1) and first-order (Eq. 2) rate equations to temporal concentration data for perchlorate.

$$[C] = [C_0] + kt \qquad \text{(Eq. 1)}$$

$$[C] = [C_0]e^{-kt} \qquad \text{(Eq. 2)}$$

Figures 6-11a and 6-11b show the results from the macrocosm study where the slope of the regression line was statistically significant at the 90% level (F statistics <0.10).

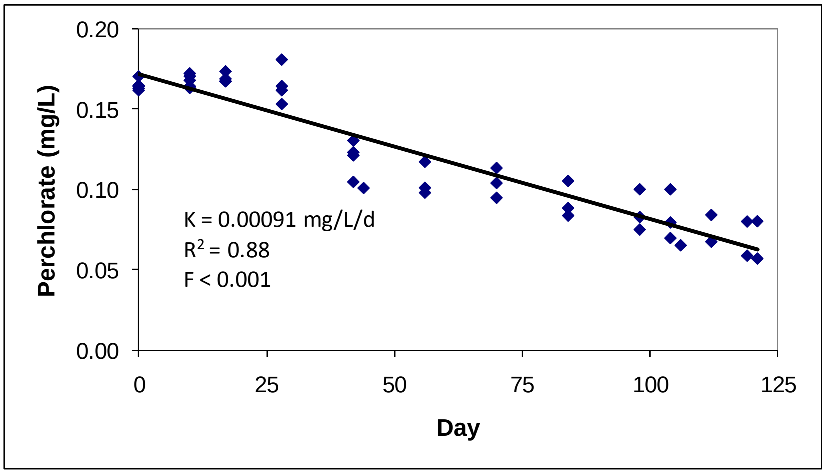

Figure 6-11a. Zero-Order Regression of Perchlorate Concentration vs. Time in Macrocosms

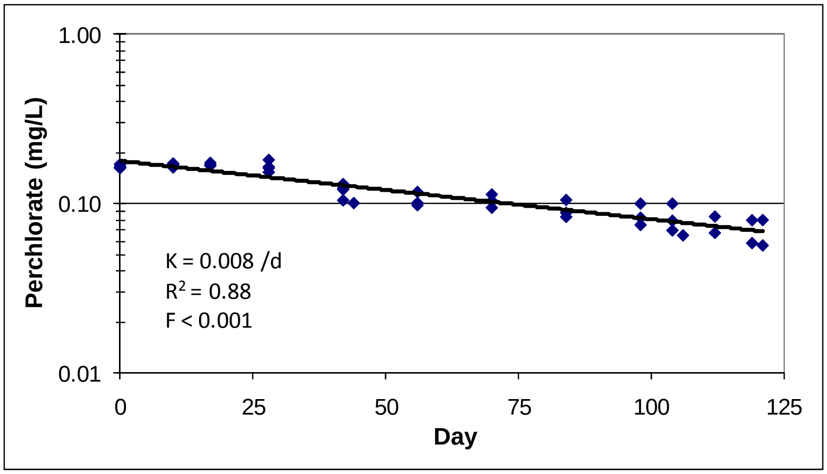

Figure 6-11b. 1st-Order Regression of Perchlorate Concentrations vs. Time in Macrocosms

6.3.2 *In Situ* Column Biodegradation Study

In situ column (ISC) experiments were run to measure perchlorate biodegradation rates under representative field conditions. Three *in situ* columns were installed in June 2007 adjacent to well pair GM-22S/M (**Figure 6-12**). Two columns (ISC-B and ISC-C) were operated as live replicates. The experiment was initiated on October 2, 2007 by collecting anoxic groundwater from GM-22M, amending with sodium bromide (NaBr; 140 mg/L as Br^-) to serve as a non-reactive tracer, and then injecting the solution into the columns. Prior to collecting the groundwater from GM-22M, the well headspace and collection bottles were purged with argon to displace air, then the well was purged a minimum of five well volumes prior to filling the groundwater collection bottles. The third column, ISC-A, was operated as a poisoned control column for comparison with the two live columns. Perchlorate degradation was inhibited by aerating the ISC-A injection solution and spiking with 15 mL of 13% (v/v) nitric acid (HNO_3) solution to generate an aerated, low pH and high NO_3 environment.

Immediately after injection was complete, the ISCs were sampled for pH, DO, perchlorate and anions. Samples were again collected on Day 1, Day 43, Day 65 and Day 198. Perchlorate changes as a result of other abiotic attenuation mechanisms were observed by monitoring perchlorate in ISC-A. The *in situ* biodegradation rates were calculated by comparing perchlorate concentrations with the bromide non-reactive tracer.

Figure 6-12. Amending *In Situ* Column ISC-A near GM-22S/M

The data collected from the ISC study are provided in **Table F-1** in **Appendix F. Figure 6-13** illustrates the decrease in perchlorate concentrations in ISC-B and ISC-C compared with the abiotic control column ISC-A. The initial perchlorate concentrations in the columns averaged 148 µg/L. After 6.5 months, the perchlorate concentration in both live columns was below detection. This represented a 100% decrease compared to only a 47% decrease in ISC-A.

This evaluation does not account for dilution that occurred when the sample was withdrawn at each event and replaced with unamended groundwater from below. To correct for these influences, the ratio of perchlorate concentration in each live column to perchlorate in the abiotic column was calculated for each sampling day. The ratios are shown in **Table F-1** of **Appendix F**. The 1st-order biodegradation curves are shown in **Figure 6-12**. Thus, correcting for abiotic losses, the 1st-order biodegradation rate in columns were 0.021 and 0.023/day. Both regressions were significant at the 95% level.

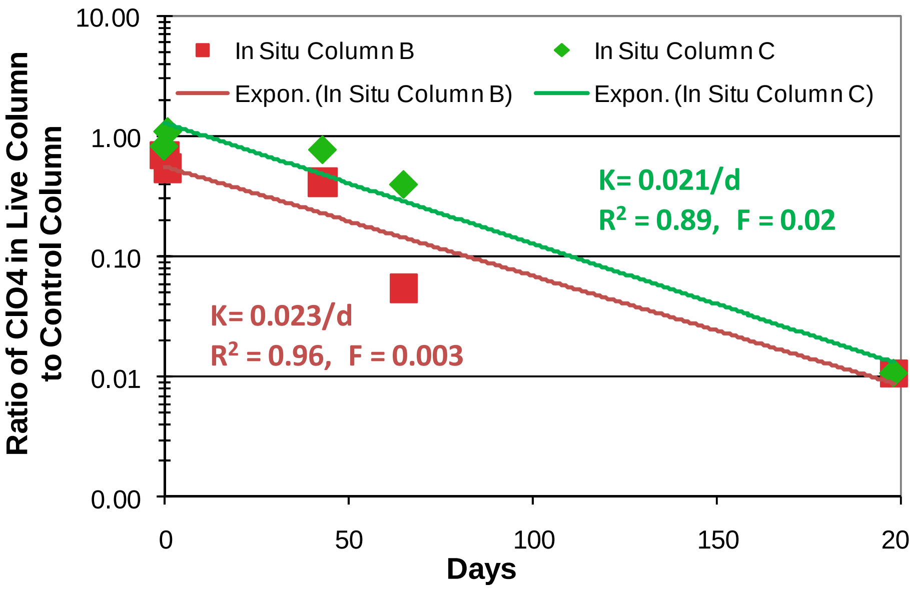

Figure 6-13. Ratio of Perchlorate Concentrations in Live *In Situ* Columns to Abiotic Control Column

6.3.3 Summary of Biodegradation Rates

The biodegradation rates estimated from microcosm, macrocosm, and *in situ* column studies are summarized in **Table 6-11**. The matrices used in these tests were from a similar area of the site which is close to the woods that border Little Elk Creek near GM-22S/M. The microcosm, macrocosm and ISC rates shown in the table suggest a biological component to attenuation in the location near the creek, although the actual rates in the wells located in that vicinity are much slower. Nonetheless, the tests offer a positive line of evidence supporting the potential for MNA of perchlorate to occur in this area of the TCE/Perchlorate contaminant plume.

Table 6-11. Summary of Biodegradation Rates

Test	Type	Rate Constant	Half-Life ($t_{½}$)
Microcosms	Zero-Order	0.92 mg/L/yr	--
Macrocosms	1st-Order	2.9/yr	87 days
In Situ Column B	1st-Order	8.4/yr	30 days
In Situ Column C	1st-Order	7.7/yr	33 days

6.4 Summary of MNA Evaluation

The Tier 1, 2 and 3 evaluations show that some attenuation of perchlorate is occurring in the upgradient portion of the plume. Geochemical conditions are not optimal for perchlorate biodegradation in much of the aquifer. However, in the forested riparian buffer, geochemical conditions are much more conducive to perchlorate biodegradation. This is supported by the relatively rapid degradation of perchlorate observed in the macrocosms and *in situ* columns.

The perchlorate mass flux declined from 28 g/d near the source area to 18 g/d near Little Elk Creek, a decline of 36%. To put this number in perspective, it may be useful to compare the decline in mass flux due to natural attenuation to the perchlorate removal achieved by the current pump and treat system. For over 10 years, groundwater has been extracted from GM-14R and treated by air stripping, prior to discharge to Little Elk Creek. The average pumping rate from 1998 to 2004 was 14.6 gpm (2,800 ft^3/d) or about 67% of the water flow through the first mass flux transect. However, extraction rates have declined over time, reaching a low of 3.6 gpm in 2008 (17% of groundwater flow). Since air stripping is not effective for removal of perchlorate, any perchlorate removed from the aquifer likely entered the creek. Perchlorate was not consistently reported. However, the mass of perchlorate extracted from the aquifer was estimated with what data was available. In 2003, 14 kg of perchlorate was removed from the aquifer. Perchlorate removal declined to 5.5 kg/yr in 2007. In 2007 and 2008, natural attenuation processes in the aquifer reduced the mass of perchlorate transported from Transect 1 to 3 by 10 g/d (3.7 kg/yr). This indicates that monitored natural attenuation processes are currently somewhat less effective than the groundwater system in removing perchlorate from the aquifer. However, as perchlorate concentrations in the source area decline, the groundwater extraction system is expected to become less and less effective and MNA processes will provide a greater proportion of the overall perchlorate removal.

Field monitoring results indicate that perchlorate biodegradation will be more rapid in the forested riparian buffer, downgradient of Transect 3. Unfortunately, the monitoring well network was not constructed in a manner to allow accurate estimate of perchlorate removal within this buffer. To provide some estimate of the impact of biodegradation in the buffer, biodegradation rates measured in the macrocosms and *in situ* columns were used to estimate the mass of perchlorate that may be removed. The forested buffer is typically about 30 ft wide and the average groundwater velocity is approximately 60 ft/yr, so the average travel time through the buffer should be about 0.5 yr. Measured biodegradation rates varied from 2.3 to 8.5/yr, which would result in a 68 to 99% reduction in perchlorate. This would be equivalent to reducing the mass flux entering Little Elk Creek from the aquifer from 3.7 kg/yr to between 1.2 kg/yr and 0.1 kg/yr.

The potential impact of the perchlorate discharge on water quality in Little Elk Creek can be evaluated by estimating the potential increase in perchlorate concentration in the creek during average and drought conditions. The average flow in Elk Creek is 1.1 cfs/sq. mi. and the 7-day/10-year (7Q10) low flow rate 0.18 cfs/sq. mi. (Sloto, 2002). Based on a 36 square mile watershed area at the site, that average flow in of Little Elk Creek is estimated to be 41 cfs and the 7Q10 is 6.9 cfs. Assuming no biodegradation in the forested buffer, the total mass flux to the creek would be 18 g/d which would result in a 0.2 µg/L increase in ClO_4 during average conditions, and a 1 µg/L increase during the 7Q10 drought. Including biodegradation believed to occur within the buffer would reduce perchlorate to non-detectable levels in the creek. Results of this analysis are generally consistent with the very low concentrations of perchlorate measured in Little Elk Creek.

7.0 Performance Assessment

Primary and secondary performance objectives were established in the Technical Demonstration Plan (Solutions-IES, 2006). The ability of MNA to meet these objectives at the Maryland manufacturing site is discussed below.

7.1 Primary Performance Objectives

Criterion: Reduce Perchlorate Concentration
The perchlorate plume was delineated from the presumed source area to Little Elk Creek. New monitor well pairs were installed to provide additional coverage across the plume. The well network provided sufficient coverage to monitor changes along the entire length of the contaminant plume from the presumed source area to the distal end of the plume near its discharge to Little Elk Creek. Concentrations in the intermediate aquifer zone declined by 85% between monitoring well GM-2B and the presumed discharge area as defined by GM-21M and GM-22M, a distance of approximately 2,400 ft. The observed declines in perchlorate concentration in individual wells and over the length of the plume are likely due to a combination of dispersion, dilution, flushing by incoming groundwater and biodegradation.

Criterion: Reduce Contaminant Mass Flux
The mass flux of perchlorate declines from 28 g/d near the source area to 18 g/d near Little Elk Creek, a decline of 36%. This slow rate of decline is consistent with the mildly oxidizing conditions in much of the plume.

Criterion: Factors Affecting Performance
The biogeochemical evaluation showed that conditions within the intermediate aquifer zone are not optimal for perchlorate biodegradation. Groundwater is characterized by low pH, low TOC, and oxidative ORP. Within the riparian buffer adjoining Little Elk Creek, geochemical conditions are more conducive to perchlorate biodegradation including lower ORP, more neutral pH, increased levels of TOC, and evidence of methane production.

Criterion: Ease of Use
The monitor well network was expanded to include eight additional monitoring wells. New monitor well pairs were installed to provide additional coverage across the plume. The installation of the new wells to fill in “gaps” in the well network was routine and required no extraordinary operation and/or maintenance. The well network provided sufficient coverage to monitor changes along the entire length of the contaminant plume.

Criterion: Maintenance
No special operation and/or maintenance steps were needed to maintain the network for the duration of the study.

7.2 Secondary Performance Objectives

Criterion: Biodegrade Perchlorate

There are a variety of conventional and innovative methods available to demonstrate perchlorate biodegradation including biogeochemical monitoring, MBTs, microcosm and macrocosm studies, *in situ* column experiments, and monitoring for compound specific stable isotopes. Except for stable isotopes, these techniques were used extensively and effectively in the current demonstration to evaluate the significance and extent of perchlorate biodegradation. Biogeochemical parameters indicated that conditions were not optimal for biodegradation throughout the upgradient portion of the plume and microbial populations containing the *cld* and *pcr*A enzymes were low. However, the highest population densities were reported in groundwater closer to Little Elk Creek where geochemical conditions are more appropriate for biodegradation. Macrocosms and *in situ* column experiments demonstrated that perchlorate will biodegrade in the presence of aquifer material from the riparian buffer zone, given sufficient contact time. First-order perchlorate biodegradation rates varied from 2.9 to 8.5/yr in the macrocosm and *in situ* column tests.

Criterion: Meet Regulatory Standards

Historical data were used to estimate natural attenuation rates. Groundwater within the source area is projected to reach the MDE Drinking Water Standard (2.6 µg/L) by 2015, if current trends continue. However, the long travel time through the aquifer will cause perchlorate to remain above drinking water standards in some portions of the plume for decades.

Natural attenuation processes of dilution, dispersion and biodegradation are reducing the concentration of perchlorate in Little Elk Creek. Currently, there is no surface water standard for perchlorate.

Criterion: Contaminant Mobility

Implementation of the MNA evaluation did not have any detectable impact on contaminant mobility. Significant amounts of water were not withdrawn or injected into the aquifer, so assessment activities did not contribute to any further dispersion or dilution.

Criterion: Process Waste and Hazardous Materials

MNA is a passive remedial strategy. Therefore, waste generation was limited to soil cuttings from well installation and groundwater from well development and purging. Perchlorate assessment and remediation activities can be conducted without extraordinary health and safety handling precautions. MNA does not produce or use hazardous materials as part of the treatment technology. Level D PPE provides adequate protection.

Criterion: Reliability, Versatility and Scale-up Constraints

When site conditions are appropriate, MNA can provide a reliable and versatile approach for management of perchlorate plumes. The successful demonstration of MNA requires a monitoring well network sufficient to illustrate attenuation downstream from the source and prior to intercepting sensitive receptors. There are no scale-up constraints since the MNA evaluation is conducted at full scale.

8.0 Cost Assessment

8.1 Cost Drivers

Costs associated with various *in situ* remediation technologies for perchlorate are discussed in Stroo and Norris (2009) and Krug et al. (2009), but neither directly addresses or compares potential costs to MNA. There are many similarities, particularly associated with up-front assessment and long-term monitoring activities, but the difference with MNA is the absence of any designed intervention with the groundwater conditions. To employ MNA, the goals of the assessment should merge with the goals of MNA. When considering MNA as a remedial alternative, an expanded network of monitoring wells may be installed during the assessment phase to characterize the contaminant distribution and site hydrogeology. Once installed, altering the site monitoring program may be needed to gather additional data to complete the Tier 1 and Tier 2 evaluations. Tier 3 biodegradation rate studies may be helpful for demonstrating perchlorate biodegradation at unusual sites, but may not be necessary in all cases.

The Remedial Action Objectives (RAO) for a site also can have a significant impact on cost and potential applicability of MNA as a remedial alternative. End users should work closely with regulators during the evaluation process to determine realistic objectives for perchlorate remediation that are agreeable to the stakeholders. Results should be achievable for the regulatory agency involved in the cleanup. Cost estimates in the following sections use the federal TBC of 24.5 µg/L as the target RAO. More and more agencies are promulgating standards for perchlorate to take the place of the TBC concentration. For example, during the course of this demonstration, the MDE established a perchlorate drinking water standard of 2.6 µg/L (MDE, 2008).

8.2 Elkton Demonstration Costs and Long-Term Cost Model

The primary capital costs were associated with preparing the Technology Demonstration Plan, designing the evaluation, and installation of permanent wells to fill out the network downgradient of the presumed source area and installation of the *in situ* biodegradation columns. Factors that impact capital costs include off-site access, concentrations and mass of target and co-contaminants, depth of impacted aquifer, site-specific lithology and hydrogeology.

Many of the operating costs that are associated with MNA are often incurred during site assessment when the goals of a thorough assessment merge with the goals of MNA. As an example, during the assessment phase, a network of monitoring wells is installed to thoroughly evaluate the nature of the contaminants present and the hydrogeology of the site in question.

Altering the site monitoring plan and perhaps frequency is often all that is necessary to gather data for the Tier 1 and Tier 2 portions of the MNA evaluation. If the Tier 3 evaluation is necessary to prove biodegradation is occurring and to obtain rate estimates, additional lab and or field work may be required. Specialized laboratory costs for CD enzyme and *q*PCR analyses add to the operating costs. When estimating the cost of implementing MNA for the base case, we assumed that a tiered evaluation including all three tiers is required. However, at many sites, a Tier 3 evaluation may not be required. The number of performance monitoring events used to develop the case for MNA also influences cost. After the tiered evaluation, and assuming the monitoring well network is in place, the primary cost driver for MNA of perchlorate is long-term monitoring.

Table 8-1 summarizes the life cycle cost components of the demonstration at the Maryland manufacturing site. The layout of the table is derived from Krug et al. (2009). The table includes both known costs associated with implementing the demonstration and estimated costs for going forward with MNA at this site. The costs associated with the tiered evaluation are also included.

The costs for preparing the present report overlap with an estimate of the costs that would be incurred to take the data derived from this demonstration and use them to prepare a permit application for MNA for the site and gain regulatory approval of this technology as the long-term groundwater remedy. Long-term costs include semi-annual monitoring and reporting. The Net Present Value of the estimated costs is calculated for up to 30 years using a 2.7% interest rate.

Table 8-1. Actual and Estimated Future Costs for Implementation of Perchlorate MNA at the Maryland Site(1)

	2005	2006	2007	2008	2009	2010						
	Yearly Costs Incurred											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10 to 30**	**NPV of Cost**	**Total Costs**
CAPITAL COSTS												
Design/Planning	10,000	11,000										
Additional Assessment		45,000										
CAPITAL SUBCOST ($)	10,000	56,000		0	0	0	0	0				
TIERED EVALUATION												
Tier 1		10,000										
Tier 2		11,000										
Tier 3	15,000		25,000									
Evaluation Reporting/Permitting			24,000									
TOTAL ($) (capital &evaluation)	25,000	77,000	59,000								152,000	161,000
PERFORMANCE MONITORING COSTS												
Sampling/Analysis/Reporting	15,000	15,000	15,000	35,000	30,000(2)	30,000(3)	30,000	30,000	30,000	30,000 Per year		
SUBCOST ($)	15,000	15,000	15,000	35,000	30,000	30,000	30,000	30,000	30,000	630,000	573,000	860,000
TOTAL PROJECT COST ($)	40,000	92,000	74,000	35,000	30,000	30,000	30,000	30,000	30,000	630,000	725,000	1,021,000

Notes:

(1).The cost summarized in this table are meant to illustrate cost associated with evaluating and performing MNA at the Maryland manufacturing site, so cost associated site selection, and white papers, as an example, are not included in these cost.

(2) Project Semi-annual monitoring starting in 2009

(3) Average monitoring cost

NPV-Net Present Value; calculated based on 2.7% discount rate

8.3 Cost Comparison: MNA vs. Passive *In Situ* and Active Pumping Technologies

To compare costs directly between the several remediation scenarios, a base case was prepared using hypothetical site conditions. The characteristics summarized in **Table 8-2** are those used by Krug et al. (2009) and were used for this evaluation in order to simplify the comparison with MNA.

Table 8-2. Summary of Site Characteristics and Design Parameters for Biological Treatment of Perchlorate-Impacted Groundwater

(Source: Krug et al., 2009)

Design Parameter	Units	Characteristics
Plume Width	feet	400
Plume Length	feet	800
Porosity		0.25
Gradient		0.008
Hydraulic Conductivity	ft/day	2.83
Upgradient Perchlorate Concentrations	mg/L	2
Downgradient Perchlorate Concentrations	mg/L	1.1
Nitrate Concentration	mg/L	15
Dissolved Oxygen Concentration	mg/L	5
Depth to Water	ft bgs	10
Vertical Saturated Thickness	ft	30
Groundwater Seepage Velocity	ft/year	33
Perchlorate Treatment Objective	mg/L	0.0245
Assumed Number of Pore Volumes to Flush Plume		2
Number of Barriers Perpendicular to Groundwater Flow		1
Groundwater Travel Time to Barriers	years	24
Years to Clean Up Groundwater	years	48

The cost estimate for the base case includes an estimate of capital cost, operations and maintenance, and long-term monitoring for the treatment of base case perchlorate plume. Capital costs for the engineered remediation systems include system design, well installation, start-up and testing. Pre-remedial investigations including treatability studies were not included in the capital cost for the engineered remediation systems. However, a tiered evaluation (Tier 1, 2 & 3) and reporting were included with the capital costs for the perchlorate MNA estimate because the tiered evaluation may not be included in typical pre-remedial activities.

Tables 8-3 through 8-5 summarize the life cycle cost for the Passive Injection Biobarrier, a Groundwater Extraction and Treatment System, and Perchlorate MNA alternatives, respectively, as applied to the Base Case site conditions.

Table 8-3. Cost Components for Passive Injection Biobarrier Treatment of Perchlorate-Impacted Groundwater for Base Case

(Source: Krug et al., 2009)

	Year Cost is Incurred							**NPV of Cost**	**Total Costs**
	1	**2**	**3**	**4**	**5**	**6**	**7 to 30**		
CAPITAL COSTS									
System Design	68,100							68,100	68,100
Well Installation (30 1" PVC Wells)	32,713							32,713	32,713
Substrate Injection	175,784							175,784	175,784
Start-up and Testing**								0	0
SUBCOST ($)	276,597	0	0	0	0	0	0	276,597	276,597
OPERATION AND MAINTENANCE COSTS									
Substrate Injection				166,284			166,284 every 3 yrs	985,956	1,496,556
SUBCOST ($)	0	0	0	166,284	0	0	166,284	985,956	1,496,556
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	35,240	35,240	35,240	35,240	35,240	11,780	11,780 every yr	348,483	470,700
SUBCOST ($)	35,240	35,240	35,240	35,240	35,240	11,780	11,780	348,483	470,700
TOTAL COST ($)	311,837	35,240	35,240	201,524	35,240	11,780	178,064	1,611,036	2,243,853

Notes:

NPV-Net Present Value

* NPV calculated based on a 3% discount rate

Table 8-4. Cost Components for Extraction and Treatment of Perchlorate-Impacted Groundwater for Base Case

(Source: Krug et al., 2009)

	Year Cost is Incurred							NPV of Cost	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	90,611							90,611	90,611
Well Installation	86,292							86,292	86,292
System Installation	292,362							292,362	292,362
Start-up and Testing**	25,000							25,000	25,000
SUBCOST ($)	494,265	0	0	0	0	0	0	494,265	494,265
OPERATION AND MANTENANCE COSTS									
System Operation and Maintenance	49,009	74,009	74,009	74,009	74,009	74,009	74,009 every year	1,469,127	2,195,270
SUBCOST ($)	49,009	74,009	74,009	74,009	74,009	74,009	74,009	1,469,127	2,195,270
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	35,240	35,240	35,240	35,240	35,240	11,780	11,780 every year	348,483	470,700
SUBCOST ($)	35,240	35,240	35,240	35,240	35,240	11,780	11,780	348,483	470,700
TOTAL COST ($)	578,514	109,249	109,249	109,249	109,249	85,789	85,789	2,311,875	3,160,235

Notes:

NPV-Net Present Value

* NPV calculated based on a 3% discount rate

Table 8-5. Perchlorate MNA for Base Case

	Year Cost is Incurred						NPV of Cost	Total Costs
	1	2	3	4	5	6 to 30		
CAPITAL COSTS								
Tiered Evaluation- Design & Planning	$15,000							
Tier 1	$11,000						$10,711	$11,000
Tier 2	$ 4,000						$3,792	$4,000
Tier 3		$5,000					$4,616	$5,000
Evaluation Reporting		$24,000					$22,156	$24,000
SUBCOST ($)	$30,000	$29,000					$41,275	$44,000
LONG TERM MONITORING COSTS								
Sampling/Analysis/Reporting/Well Maintenance								
(Quarterly for 5 years, then annually)	$94,800	$94,800	$94,800	$94,800	$94,800	$23,000 every yr	$811,500	$1,065,500
SUBCOST ($)	$94,800	$94,800	$94,800	$94,800	$94,800		$811,500	$1,065,500
TOTAL COST ($)	$105,800	$98,000	$123,800	$94,800	$94,800		$852,775	$1,110,500

Notes:

NPV-Net Present Value

* NPV calculated based on a 2.7% discount rate

** "No Start-up and Testing" costs are included because no operating equipment is left behind following substrate injection

Table 8-6 summarizes the estimated costs for the three technologies described in **Tables 8-3, 8-4** and **8-5**. Perchlorate MNA is approximately one half the life-cycle cost of the Passive Injection Biobarrier alternative, and approximately one-third the cost the Extraction and Treatment alternative even though the cost of monitoring is almost double the long-term monitoring for the engineered systems. Even with the additional cost of assessment and demonstration activities associated with the demonstration, the total remedy cost is approximately $1,600,000, and less than the project life cycle cost of the Passive Injection Biobarrier and Extraction and Treatment alternatives.

Table 8-6. Summary of Capital Costs and NPV of costs for Operation, Maintenance and Monitoring for Biological Treatment of Perchlorate-Impacted Groundwater

Alternative	Capital Costs	NPV of 30 Years of O&M Costs	NPV of 30 Years of Monitoring Costs	NPV of 30 Years of Total Remedy Costs	Total 30-Year Remedy Costs
Perchlorate MNA	$40	--	$810	$850	$1,110
Passive Injection Biobarrier	$280	$990	$350	$1,610	$2,240
Extraction and Treatment	$490	$1,470	$350	$2,310	$3,160

Note: Costs in thousands of dollars.

When costing MNA of perchlorate for the Base Case, an evaluation including all three tiers was assumed. One baseline and four performance monitoring events were conducted over 24 months. After the evaluation itself is complete, and assuming the remedy would be accepted, the primary cost driver for MNA of perchlorate would be long-term monitoring, with continued data evaluation, interpretation and reporting.

9.0 Implementation Issues

9.1 Environmental Checklist

The environmental checklist includes a number of items that are useful both before and during the evaluation of a perchlorate-contaminated site for MNA. In general, before proceeding, it is important to plan an approach to obtain the following key information:

- Identification of the source area
- Time of release
- Historical Data
- Plume Delineation
- Sensitive Receptors
- Subsurface Geochemistry
- Subsurface Microbiology

Once a plan has been developed, data gaps can be addressed in order to complete the steps outlined in the tiered evaluation of MNA.

9.2 Regulatory Issues

The groundwater criteria for many contaminants of concern is well documented, but the recent information gathered about perchlorate at a wide range of sites nationwide has lead to new interest in the issues associated with its environmental fate and transport as it pertains to risks to human health. However, regulatory standards for perchlorate in groundwater have not been established in all states. For example, at the beginning of this project, Maryland did not have a drinking water or groundwater standard for perchlorate. The federal TBC remains 24.5µg/L. Maryland issued a drinking water advisory limit 1.0 µg/L which was recently replaced with a standard of 2.6 µg/L (MDE, 2008). Other states are in the process of developing standards.

The TCE SWMU at the Maryland manufacturing site from which the Perchlorate/TCE plume emanates is regulated under RCRA. Ms. Linda Holden of USEPA-Region 3 is the project manager for the facility. Dr. Amin Yazdanian, Public Health Engineer, MDE, Waste Management Administration, Waste Permitting Division, provides regulatory oversight of environmental operations at the facility. This report has focused on the evaluation steps to demonstrate the potential for MNA of perchlorate as an applicable groundwater remedy for this plume. However, perchlorate is co-mingled plume with TCE and approval to implement MNA for perchlorate independent of TCE may be problematic. Site conditions throughout the majority of the plume are less than optimal for TCE biodegradation, but there is evidence that favorable conditions for perchlorate biodegradation can be demonstrated closer to the creek.

9.3 End-User Issues

Potential end-users of the technology include a variety of agencies within the federal government (DoD, DoE and USEPA), state and local governments and private industry. Potential end-user concerns may include:

- Permitting
- Community acceptance
- Receptors
- Achievable state-specific target concentrations when considering MNA.
- Potentially long life cycles

Local concerns about perchlorate, the threat of perchlorate and the acceptance of MNA of perchlorate may vary. We have demonstrated that under the proper conditions and with a strategically planned, step-wise approach, end-users can gain assurance that MNA of perchlorate will be protective of human health and the environment.

10.0 References

ARCADIS G&M, Inc., 2003. *Interim Site-Wide Investigation Technical Report and Work Plan*. Prepared by ARCADIS G&M, Inc., May 2003.

Arcadis, 2007. *Site-Wide Corrective Measures Study Report.* Prepared by ARCADIS, Inc. February 2007.

Bender, K.S., S.M. O'Connor, R. Chakraborty, J.D. Coates, and L.A. Achenbach, 2002. Sequencing and Transcriptional Analysis of the Chlorite Dismutase Gene of *Dechloromonas agitata* and Its Use as a Metabolic Probe. *Appl. Environ. Microbiol.* 68(10): 4820-4826.

Borden, R.C., R.A. Daniel, L.E. LeBrun IV, and C.W. Davis, 1997a. Intrinsic Biodegradation of MTBE and BTEX in a Gasoline-Contaminated Aquifer. Water Resources Res., 33(5):1105-1115.

Borden, R.C., M.J. Hunt, M.B. Shafer and M.A. Barlaz, 1997b. Environmental Research Brief - Anaerobic Biodegradation of BTEX in Aquifer Material. EPA/600/S-97/003, US Environ. Protect. Agency, Washington, DC, pp. 9.

CDHS (California Department of Health Services), 2007. Maximum Contaminant Levels – Inorganic Chemicals. 22 California Code of Regulations §64431.

Chaudhuri, S.K., S.M. O'Connor, R.L. Gustavson, L.A. Achenbach, and J.D. Coates, 2002. Environmental Factors that Control Microbial Perchlorate Reduction. *Appl. Environ. Microbiol.* 68(9): 4425-4430.

Coates, J.D. and L.A. Achenbach, 2004. Microbial Perchlorate Reduction: Rocket Fuelled Metabolism. *Nat. Rev. Microbiol*. 2: 569-580.

Coates, J.D. and L.A. Achenbach, 2006. Chapter 12: The Microbiology of Perchlorate Reduction and its Bioremediative Application. *In:* B. Gu and J.D. Coates (eds.), Perchlorate: Environmental Occurrence, Interactions, and Treatment, Springer. pp. 279-295. ISBN: 978-0-387-31114-2.

Coates, J.D and W.A. Jackson, 2009. Chapter 3, Principles of Perchlorate Treatment. *In:* H.F. Stroo, H.F and C.H. Ward (eds), *In Situ* Bioremediation of Perchlorate in Groundwater. Doi:10.1007/978-0-387-84921-8_1, SERDP and ESTCP Remediation Technology Monograph Series, Springer Science+Business Media, LLC, New York, NY, pp. 29-52.

Coates, J.D., U. Michaelidou, R.A. Bruce, S.M. O'Connor, J.N. Crespi, and L.A. Achenbach, 1999. Ubiquity and Diversity of Dissimilatory (Per)chlorate-Reducing Bacteria. *Appl. Environ. Microbiol.* 65 (12): 5234-5241.

Coates, J.D. and J. Pollock, 2003. Potential for *In Situ* Bioremediation of Perchlorate in Contaminated Environments. Presented at: *In Situ* and On-Site Bioremediation, the Seventh International Symposium, Orlando, FL, June 2003, Battelle, Columbus, OH.

ESTCP, 2007. Field and Laboratory Evaluation of the Potential for Monitored Natural Attenuation of Perchlorate in Groundwater, Final Technical Report. Prepared by Solutions-IES, Inc. and North Carolina State University, Project No. ER-0428, Environmental Security Technology Certification Program, Arlington, VA, July 2007.

ESTCP, 2008. Protocol Report. Natural Attenuation of Perchlorate in Groundwater: Processes, Tools and Monitoring Techniques. Prepared by Solutions-IES, Inc., Project No. ER-0428, Environmental Security Technology Certification Program, Arlington, VA, August 2008.

ESTCP, 2010. Perchlorate Monitored Natural Attenuation in Groundwater, Building 1419 Site, Naval Surface Warfare Center, Indian Head, MD. Prepared by Solutions-IES, Inc., Project No. ER-0428, Environmental Security Technology Certification Program), Arlington, VA, July 2010.

Farhat, S.K., C.J. Newell and E.M. Nichols, 2006. User's Guide: Mass Flux Tool Kit. (http://www.estcp.org/Technology/upload/ER-0430-MassFluxToolkit.pdf)

Gunawan, 2007. Bioremediation for Perchlorate-containinated Groundwater. Michigan State Univ., Microbiology & Molecular Genetics, Course 445. *Basic Biotechnology eJournal* 3: 6-13. (http://www.taxonomicoutline.org/index.php/mmg445/article/view/220/274).

Hatzinger, P.B., 2005. Perchlorate Biodegradation for Water Treatment. *Environ. Sci Technol*. 39: 239A-247A.

Herman, D.C. and W.T. Frankenberger, Jr., 1998. Microbial-Mediated Reduction of Perchlorate in Groundwater. *J. Environ. Qual.* 27: 750-754.

Higgins, M.W. and L. B. Conant, 1990. The Geology of Cecil County, Maryland. Maryland Geological Survey, Bulletin 37.

ITRC, 2002. A Systematic Approach to *In Situ* Bioremediation in Groundwater Including Decision Trees on *In Situ* Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate. *In Situ* Bioremediation Team, Interstate Technology & Regulatory Council, August 2002.

ITRC, 2005. Perchlorate: Overview of Issues, Status, and Remedial Options. ITRC Perchlorate Team, Interstate Technology & Regulatory Council, September 2005. (http://www.itrcweb.org).

Kendall, G.S., M.P. Kladias, and J.P. Sgambat, 2004. Conceptual Site Model of Groundwater Flow and Transport at the (Confidential) Facility, ARCADIS G&M, Inc., September, 2004.

Kladias, M.P.and J.P. Sgambat, 1999. Perchlorate Investigation Sampling Plan, ARCADIS Geraghty & Miller, Inc., April 15, 1999

Krauter, P.W., B. Daily, V. Dibley, H. Pinkart, and T. Legler, 2005. Perchlorate and Nitrate Remediation Efficiency and Microbial Diversity in a Containerized Wetland Bioreactor. *Int. J. Phytoremediation* 7: 113-128.

Krug, T.A., C Wolfe, R.D. Norris, and C.J. Winstead, 2009. Chapter 10, Cost Analysis of *In Situ* Perchlorate Remediation Technologies. In: Stroo, H.F. and Ward, C.H. (eds.), *In Situ* Bioremediation of Perchlorate in Groundwater. SERDP and ESTCP Remediation Technology Monograph Series, Springer Science+Business Media, LLC, New York, NY, pp 199-218.

Logan, B.E, 2001. Assessing the Outlook for Perchlorate Remediation. *Environ. Sci. & Technol*. 35 (23): 482A- 487A.

Logan, B.E., J. Wu, and R.F. Unz, 2001. Biological Perchlorate Reduction in High-Salinity Solutions. *Wat. Res*. 35 (12): 3034-3038.

MADEP (Massachusetts Department of Environmental Protection), 2006. Inorganic Chemical Maximum Contaminant Levels, Monitoring Requirements and Analytical Methods. 310 Code Massachusetts Regulations §22.06.

Magnus XC, 2005. Energetics Degradation. phA Environmental Restoration, Inc. (http://pha-er.com/magnusXC.html).

MDE (Maryland Department of the Environment), 2008. Cleanup Standards for Soil and Groundwater, Type I and II Aquifers, Interim Final Guidance (Update No. 2.1), June 2008.

Newell, C.J., H.S. Rifai, J.T. Wilson, J.A. Connor, J.A. Aziz, and M.P. Suarez, 2002. Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. United States Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH, EPA/540/S-02/500, November 2002.

NRC, 2005. Health Implications of Perchlorate Ingestion. National Academies Press, Washington, DC, USA, 276p.

Nzengung, V.A., M.T. Lieberman, H.F. Stroo, and P.J. Evans, 2008. Chapter 11, Emerging Technologies for Perchlorate Bioremediation. In: Stroo, H.F.and C.H. Ward (Eds), *In Situ* Bioremediation of Perchlorate in Groundwater. doi: 10.1007/978-0-387-84921-

8_11. SERDP and ESTCP Remediation Technology Monograph Series, Springer Science+Business Media, LLC, New York, NY.

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. *Appl. Micrbiol. Biotechnol.* 45: 420-426.

Robertson, W.D., C.J. Ptacek and S.J. Brown, 2007. Geochemical and Hydrogeological Impacts of a Wood Particle Barrier Treating Nitrate and Perchlorate in Ground Water. *Ground Water Monit. & Remed.* 27 (2): 85-95, Spring 2007.

Sloto, R.A., 2002. Geohydrology and Ground-water Quality, Big Elk Creek Basin, Chester County, Pennsylvania and Cecil County, Maryland: U.S. Geological Survey Water-Resources Investigations Report 02-4057, 81 p.

Solutions-IES, 2006. Evaluation of Potential for Monitored Natural Attenuation of Perchlorate in Groundwater, Technology Demonstration Plan for Perchlorate/TCE SWMU, ATK Elkton, LLC, Elkton, MD. Prepared for Environmental Security Technology Certification Program, Arlington, VA., May 2006.

Stroo, H.F., R.C. Loehr, and C.H. Ward, 2009. Chapter 1, *In Situ* Bioremediation of Perchlorate in Groundwater: An Overview. *In:* Stroo, H.F and Ward, C.H. (eds), *In Situ* Bioremediation of Perchlorate in Groundwater. Doi:10.1007/978-0-387-84921-8_1, SERDP and ESTCP Remediation Technology Monograph Series, Springer Science+Business Media, LLC, New York, NY,, pp. 1-13.

Stroo, H.F. and R.D. Norris, 2009. Chapter 5, Alternatives for *In Situ* Bioremediation of Perchlorate. *In:* Stroo, H.F and Ward, C.H. (eds). *In Situ* Bioremediation of Perchlorate in Groundwater. Doi:10.1007/978-0-387-84921-8_1, SERDP and ESTCP Remediation Technology Monograph Series, Springer Science+Business Media, LLC, New York, NY, pp. 79-90.

Tan, K., T.A. Anderson, and W.A. Jackson, 2004a. Degradation Kinetics of Perchlorate in Sediments and Soils. *Water, Air and Soil Pollut* 151: 245 – 259.

Tan, K., W.A. Jackson, T.A. Anderson, and J.H. Perdue, 2004b. Fate of Perchlorate-Contaminated Water in Upflow Wetlands. *Water Research* 38: 4173-4185.

Tan, K., T.A. Anderson, and W.A. Jackson, 2005. Temporal and Spatial Variation of Perchlorate in Streambed Sediments: Results from In-Situ Dialysis Samplers. *Environmental Pollution* 136: 283–291.

USEPA, 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. EPA/600/R-98/128. Washington, DC: ORD.

USEPA, 1999. Final Directive: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17P. (http://www.epa.gov/swerust1/directiv/d9200417.htm).

USEPA, 2005. *Perchlorate Treatment Technology Update*: Federal Facilities Forum Issue Paper. EPA No. 542-R05-015. InfoNational Service Center for Environmental Protection, Solid Waster and Emergency Response (5102G), Cincinnati, OH, May 2005 (www.epa.gov/tio/tsp).

USEPA, 2006. Assessment Guidance for Perchlorate. Memorandum from S.P. Bodine, Asst. Administrator, to Regional Administrators, January 26, 2006.

USFDA (U.S. Food and Drug Administration), 2007. 2004-2005 Exploratory survey data on perchlorate in food. Posted May 2007. (http://www.cfscan.fds.gov/~dms/clo4data.html).

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen, 1995. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater, Volume II. Air Force Center for Environmental Excellence, Brooks Air Force Base, TX. November 1995.

Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, P.E. Haas, R.N. Miller, J.E. Hansen, and F.H. Chapelle, 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater. EPA 600-R-98-128.

Wilson, J.T. J.S. Cho, F.P. Beck, 1997. Field Estimation of Hydraulic Conductivity for Assessments of Natural Attenuation. *In:* Volume 2: Fourth International *In Situ* and On Site Bioremediation Symposium New Orleans, April 28 – May 1, 1997. Battelle Press, Columbus, OH. pp 309 - 314

APPENDIX A

Soil Boring Logs

APPENDIX B
Monitor Well Construction Details

APPENDIX C
Hydrogeologic Cross-Sections

APPENDIX D
Historical Water Level Data

APPENDIX E
Performance Monitoring Analytical Data

APPENDIX F

In Situ Column Biodegradation Study Data

APPENDIX G
Points of Contacts

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