Field and Laboratory Evaluation of the Potential for Monitored Natural Attenuation of Perchlorate in Groundwater
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LIST OF ABBREVIATIONS USED IN THIS DOCUMENT

ACRONYMS

1. ACE – Army Corps of Engineers
2. AFB –Air Force Base
3. BOD – Biochemical Oxygen Demand
4. CAH – Chlorinated Aliphatic Hydrocarbons
5. CD – Chlorite Dismutase
6. CVOC – Chlorinated Volatile Organic Compound
7. COPC – Compound of Primary Concern
8. DO – Dissolved Oxygen
9. DoD – Department of Defense
10. DOC – Dissolved Organic Carbon
11. EOD – Explosive Ordnance Disposal
12. EOS® - Emulsified Oil Substrate
13. ESTCP – Environmental Security Technology Certification Program
14. FID – Flame Ionization Detector
15. ft bgs – Feet Below Ground Surface
16. GC – Gas Chromatography
17. HSWA – Hazardous and Solid Waste Amendments
18. IDW – Investigation-Derived Waste
19. ITRC – Interstate Technology & Regulatory Council
20. MCL – Maximum Contaminant Level
21. MNA – Monitored Natural Attenuation
22. NCSU – North Carolina State University
23. ORP – Oxidation-Reduction Potential
24. OU – Operable Unit
25. PCE – Tetrachloroethene (Tetrachloroethylene)
26. RCRA – Resource Conservation Recovery Act
27. RfD – Reference dose

28. SVOCs – Semivolatile Organic Compounds
29. TOC – Total Organic Carbon
30. USEPA – United States Environmental Protection Agency
31. UST – Underground Storage Tank
32. VOA – Volatile Organic Analysis
33. VOC – Volatile Organic Compound

CHEMICALS

1. 1,1-DCA – 1,1-Dichloroethane
2. 1,2-DCA – 1,2-Dichloroethane
3. *cis*-DCE – *cis*-1,2-Dichloroethene
4. PCE – Tetrachloroethene
5. *trans*-DCE – *trans*-1,2-Dichloroethene
6. 1,1,1-TCA – 1,1,1-Trichloroethane
7. 1,1,2-TCA – 1,1,2-Trichloroethane
8. TCE – Trichloroethene
9. RDX - Cyclotrimethylenetrinitramine (Cyclonite)
10. VC – Vinyl Chloride

SITE NAMES

1. ATK – Alliant Techsystems, Inc.
2. LMTA – Little Mountain Test Annex
3. NSWC – Naval Surface Warfare Center
4. RSA – Redstone Arsenal
5. SSC – Stennis Space Center

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EXECUTIVE SUMMARY

As an emerging technology, the promise of using monitored natural attenuation (MNA) as a remediation approach for perchlorate is significant. There is extensive laboratory documentation that perchlorate is biodegradable under anaerobic conditions and can be expected to naturally attenuate in some aquifers. However, besides an apparent decrease in concentrations often seen downgradient of many source areas, there are essentially no data showing mechanisms responsible for the observed changes and the conditions where attenuation is most likely to occur. Without clear, convincing evidence for the natural attenuation of perchlorate, there may be a tendency to push for aggressive remediation approaches whenever perchlorate is detected. While aggressive remediation is warranted at some sites, there are probably many other sites where MNA is a very appropriate approach.

Before the MNA of perchlorate becomes an accepted technology, evidence must be obtained to confirm the informal observations in the field. In addition, the approach should be demonstrated in the field at multiple sites. The field and laboratory evaluation (treatability study) that is the subject of this report was conducted as a preliminary task in answering the question about the suitability and practicality of using MNA as a viable treatment remedy for perchlorate-contaminated groundwater. This report, funded by the Environmental Security Technology Certification Program (ESTCP) as part of a larger project (ESTCP ER-0428), describes the results of the process used to: 1) identify perchlorate sites; 2) select a subset of these contaminated sites for field characterization and sampling; 3) characterize the sites in the field, and 4) test the site conditions in the laboratory.

This report describes the three levels of evaluation that were conducted. Screening Level 1 (site identification) initially reviewed 123 sites across the United States identified from public sources (e.g., internet), as well as personal contacts with the U.S. Army Corps of Engineers offices and the Interstate Technology Regulatory Council (ITRC) Perchlorate Team. Approximately 40 direct contacts were initiated and site-specific information was obtained from 13 base managers who responded to a detailed questionnaire, leading to Screening Level 2 (data review and initial site selection). In Screening Level 2, seven locations were selected for field characterization and sample collection based on historical information regarding contaminant fate and transport, groundwater biogeochemistry, and hydrogeological conditions. These sites included: Little Mountain Test Annex (LMTA) near Hill Air Force Base, UT; Alliant Techsystems, Inc (ATK) in Elkton, MD; Naval Surface Warfare Center, Indian Head, MD; Stennis Space Center, MS; Redstone Arsenal (RSA), AL; ATK Thiokol in Promontory, UT; and Beale Air Force Base, CA.

Screening Level 3 included actual collection and analysis of samples from the seven field sites, testing innovative measures of enzyme activity to assist in identifying microbial activity on perchlorate and use of microcosm tests to examine rates of degradation under ambient and augmented conditions. The sampling locations focused on areas of each site where the concentration of perchlorate suggested there were conditions already supporting natural attenuation. These locations were generally toward the leading edge of well-defined plumes, downgradient from known sources, or in the vicinity of a discharge feature such as a creek, swamp or riparian buffer. Groundwater and sediment or soil samples obtained from the field were subjected to a full range of field measurements and laboratory analytical tests including depth to water, pH, temperature, specific conductance, oxidation-reduction potential (ORP), dissolved oxygen (DO), dissolved iron, and dissolved manganese, total organic carbon (TOC), light hydrocarbon gases (methane, ethane, and ethene), chlorinated volatile organic compounds (CVOCs), perchlorate, and other common anions including chloride, nitrite, nitrate, sulfate and phosphate. Samples were also sent to specialized laboratories and tested for the presence of the chlorite dismutase (CD) enzyme.

In-depth laboratory evaluations were performed in the Laboratory of Environmental Engineering in the Department of Civil, Construction and Environmental Engineering at North Carolina State University (CCEE-NCSU). Two studies were conducted: a six-month biochemical oxygen demand (BOD_6) study to measure the ambient oxygen demand of site-matrix groundwater and microcosm treatability tests to measure the rate of perchlorate degradation under natural and enhanced conditions.

At all locations, the perchlorate concentration decreased between the source and the downgradient well or wells that were tested. However, the differences were not as pronounced at LMTA or RSA. The extent of the decrease in concentration depended to some extent on the plume geometry and the distance between the source and downgradient wells that were sampled. At most of the locations, based on historical site-specific information, it is likely that higher residual concentrations of perchlorate could be found in other wells. The pH at all the sites except ATK Elkton and Stennis Space Center was generally favorable to microbial activity. Perchlorate-reducing microorganisms are not believed to be as sensitive to ranges of pH as are Dehalococcoides-like microorganisms that are needed for dehalorespiration of aliphatic chlorinated hydrocarbons.

The groundwater in the perchlorate plumes at ATK Elkton and Stennis Space Center was more oxidative than observed at the other five sites. At the other sites, oxidation-reduction conditions varied widely, but tended to be more reducing, especially in the downgradient portions of the plume. Nitrate ranged from up to 46 mg/L at ATK Thiokol, but was not much greater than 10 mg/L at the other sites. The presence of nitrate has been shown to interfere with perchlorate degradation. Sulfate concentrations varied widely and were generally much higher than nitrate ranging from 1.1 to 116 mg/L. Sulfate concentrations reportedly do not influence perchlorate biodegradation.

The CD enzyme test was run on either sediment or groundwater from wells on six of the seven sites. The results of this study showed that regardless of the background conditions, there was evidence of microbial communities that were genetically capable of perchlorate reduction. This observation was further confirmed in the microcosm studies. The addition of electron donors (lactate and acetate mixture or EOS® vegetable oil emulsion) quickly stimulated perchlorate degradation in aquifer material from each of the seven sites.

The TOC measurements and 6-month BOD test were used to provide additional information about the availability of background carbon to indigenous microorganisms. The TOC in groundwater from each of the sites was highest at Indian Head (4.4 mg/L), but generally less than 2 mg/L at the other sites. The BOD test also gave an indication of the rate at which indigenous microorganisms can consume oxygen using the background organic carbon as electron donor. The BOD_6 ranged from below detection at ATK Elkton to 19 mg O_2/L at ATK Thiokol. This test did not infer the relationship between background available organic carbon and degradation of perchlorate.

Under conditions of natural attenuation, results varied widely. A degradation rate was calculated for each site and fitted to one of two kinetic models. Zero-order kinetics implies that the rate of degradation is independent of the perchlorate concentration; first-order kinetics implies that the rate is dependent on the perchlorate concentration. The degradation rates were zero-order at two of the seven sites (ATK Elkton and ATK Thiokol), 1st order at two sites (NSWC Indian Head and Redstone Arsenal) and could be fitted to both models at one site (Stennis Space Center). At two sites (LMTA and Beale AFB), apparent zero-order biodegradation rates were less than 0.01 mg/L per year indicating no measureable perchlorate degradation. When measurable, zero order rates ranged from 0.13 mg/L/yr at Stennis Space Center to 33 mg/L/yr at ATK Thiokol. The first order rates ranged from 1.75 yr^{-1} at Stennis Space Center to 5.1 yr^{-1} at NSWC Indian Head.

Results of the treatability studies were used to help select sites for more detailed field demonstrations. The data show the difficulty in predicting the potential for the MNA of perchlorate to occur. Consequently, the selection of two sites for further study is not an “absolute science”. One of the most important pieces of evidence was the observed disappearance of perchlorate along the axis of the plume. At most locations evaluated, perchlorate appeared to attenuate. However, at LMTA and Beale AFB, the declines in perchlorate concentration with distance were not large enough to warrant further study. The same argument could be made to eliminate NSWC Indian Head, but additional data not used in this study suggested that higher concentrations of perchlorate were present in other parts of the plume, so this site was not eliminated.

LMTA and Beale AFB were also eliminated from further consideration based on site conditions, lab performance, hydrogeological or site access conditions. RSA was then eliminated because of difficulty defining the plume geometry and complex karst hydrogeology which greatly increased the difficulty in accurately characterizing groundwater flow paths. Results from the microcosm studies from Stennis Space Center showed some potential for natural attenuation, but the geochemical conditions throughout the plume weighed against selecting this site for the field demonstration.

The site conditions at ATK Thiokol were generally favorable for demonstration MNA of perchlorate. There is TOC, a measurable rate of degradation in the microcosm studies, a low DO, mostly reducing environment and a neutral pH. The slightly elevated nitrate concentrations would be a concern in this plume. However, the depth to groundwater and logistics of working at this site increased the cost for the demonstration dramatically, thus removing it from further consideration.

The two sites selected for detailed field studies are both located in Maryland: ATK Elkton and NSWC Indian Head. Throughout most of the plume at ATK Elkton, groundwater is oxidative with low levels of organic carbon and a low pH. However, in the downgradient portion of the plume near Little Elk Creek, microcosm studies showed relatively rapid biodegradation of perchlorate suggesting the potential for MNA within the riparian buffer of this stream. At NSWC Indian Head, nitrate concentrations are low and there is some TOC in the groundwater. There is a large decrease in perchlorate concentration from the source to the downgradient portion of the plume. Laboratory microcosms showed evidence for reasonably rapid biodegradation of perchlorate. Thus, the treatability studies were useful in selecting two sites for field demonstrations to evaluate the potential for the MNA of perchlorate in groundwater.

1.0 Introduction

1.1 Background

Until recently, water supplies were rarely monitored for perchlorate (Logan 2001). However, several new regulatory initiatives at the State and Federal levels now require sampling of soils, surface water and groundwater for perchlorate. With this increased level of monitoring, it is inevitable that perchlorate will be detected at many more locations.

Groundwater and surface water contaminated with perchlorate (ClO_4^-) has become a major environmental issue for the US Department of Defense (DoD) due to the use, release and/or disposal of solid rocket fuel and munitions containing ammonium perchlorate. At some locations, releases have resulted in extensive contamination of surface and groundwater supplies. In the western United States, over 15 million people consume water with some level of perchlorate. The increasing detection of perchlorate, which is known to interfere with idodide uptake by the thyroid (USACHPPM), indicates a significant environmental problem that will require aggressive control measures to prevent adverse human and environmental impacts. While perchlorate appears to persist at many sites, at other sites, perchlorate may naturally attenuate with little environmental impact. Based on the apparent magnitude of the problem, any attenuation of perchlorate is significant.

Natural attenuation is defined by the US EPA 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.” The term Monitored Natural Attenuation (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. The primary challenge of MNA as a remedial alternative is to make the determination that the transformation processes are taking place at a rate that is protective of human health and the environment (Azadpour-Keeley *et al.* 2001a).

As an emerging technology, the promise of using monitored natural attenuation (MNA) as a remediation approach for perchlorate is significant. There is extensive laboratory documentation that perchlorate is biodegradable under anaerobic conditions and can be expected to naturally attenuate in some aquifers. However, besides an apparent decrease in concentrations often seen downgradient of many source areas, there are essentially no data showing mechanisms responsible for the observed changes and the conditions where attenuation is most likely to occur. Without clear, convincing evidence for the natural attenuation of perchlorate, there may be a tendency to push for aggressive remediation approaches whenever perchlorate is detected. While aggressive remediation is warranted at some sites, there are probably many other sites where MNA is a very appropriate approach.

1.2 Goals and Objectives

The present work is funded by the Environmental Security Technology Certification Program (ESTCP) as part of a larger project titled "Evaluation of the Potential for Monitored Natural Attenuation of Perchlorate in Groundwater" (ESTCP ER-0428). As an emerging process, there is a good understanding of the microbiology of the perchlorate-reduction process and some of the conditions that might influence perchlorate biodegradation in the field. However, at this time there is a little or no evidence of perchlorate natural attenuation at field sites (Wu *et al*. 2001; Jackson 2003; Coates and Pollock 2003). This is not necessarily because perchlorate biodegradation does not occur, but may be because it hasn't been investigated in any systematic fashion.

Before the MNA of perchlorate becomes an accepted technology, evidence must be obtained to confirm the informal observations in the field. In addition, the approach must be demonstrated in the field at multiple sites. The overall goals of the project are as follows:

1. Provide DoD managers with the tools needed to evaluate whether MNA may be appropriate for management of perchlorate releases on their site(s); and
2. Demonstrate to regulatory agencies that perchlorate MNA is effective for controlling adverse impacts to the environment.

To achieve these goals, several project objectives were established.

a. Evaluate the rate and extent of perchlorate biodegradation in aquifer material and groundwater from a variety of sites that potentially received perchlorate.
b. Develop multiple lines of evidence to evaluate the monitored natural attenuation of perchlorate at two field sites.
c. Evaluate the use of isotopic ratios as an indicator of perchlorate biodegradation in laboratory incubations.
d. Develop a protocol for monitoring the natural attenuation of perchlorate.
e. Transfer the knowledge gained about perchlorate MNA to the regulatory community.

The field and laboratory evaluation (treatability study) that is the subject of this report was conducted as the initial task for answering questions about the suitability and practicality of using MNA as a viable treatment remedy for perchlorate-contaminated groundwater. This report describes the results of the process used to: 1) identify perchlorate sites; 2) select a subset of these contaminated sites for field characterization and sampling; 3) characterize the sites in the field, 4) test the site conditions in the laboratory; and 5) select two sites for field demonstrations of the technology. Reports on the results of the field studies and the protocol for monitoring the natural attenuation of pechlorate will be provided under separate cover.

1.3 Regulatory Drivers

The regulatory climate for perchlorate contamination continues to change as new information is learned and states consider the perchlorate risk. Currently, there is no federal drinking water Maximum Contaminant Level (MCL) for perchlorate in groundwater although a “guidance” level of 24.5 ppb has been issued (CPEO 2006). In July 2006, Massachusetts promulgated a drinking water MCL of 2 ppb, becoming the first state to do so. Perchlorate soil and groundwater standards for hazardous waste site cleanup under the Massachusetts Contingency Plan are alos being established, along with adoption of a reference dos (RfD) of 7 X 10 -5 mg/kg-day to be used for site-specific risk assessments (MassDEP 2006). Several states have identified advisory levels that range in concentration from 1 µg/L to 52 µg/L. California and New Jersey are currently considering standards of 6 ppb and 5 ppb, respectively. Maryland, the location of the demonstration sites, has an advisory level of 1 µg/L for groundwater (ITRC 2005). Maryland does not have a surface water standard for perchlorate[1].

1.4 Stakeholder/End-User Issues

A stated above, an important goal of this project is to produce a protocol that can be used by scientists, engineers and regulators as a guide to implement the MNA of perchlorate as a remedial strategy in whole or in part for the site in question. Demonstrating MNA of perchlorate may be difficult because of large plume areas, poorly defined source areas, and absence of easily monitored degradation products. Assuming that the demonstration is successful and the lines of evidence evaluated are useful, stakeholders such as local regulators and the general public will gain confidence that MNA of perchlorate is an effective remediation option to implement while protecting the public welfare and environmental health.

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[1] Personal communication from John McGillen, Maryland Department of the Environment, to M. Tony Lieberman, Solutions-IES, January 26, 2006.

The protocol will provide end-users with guidance for designing monitoring well networks in locations to optimize gathering useful information about plume movement and attenuation. The protocol will also present guidance for obtaining appropriate analytical data from the site and evaluating the data to understand its meaning with regard to indicating if MNA of perchlorate is the best remedial strategy.

2.0 Technology Description and Demonstration Design

2.1 Monitored Natural Attenuation (MNA)

In the 1980s and early 1990s, over a million sites were identified where groundwater was impacted by leaking petroleum underground storage tanks (USTs). The initial response to this problem was to implement high cost, high maintenance corrective measures to control the downgradient migration of contaminated groundwater. However, circumstantial evidence began to accumulate that dissolved petroleum plumes might naturally attenuate without active human intervention. In response, industry and government supported a variety of studies to determine the extent and significance of this process. Results of this work demonstrated that: (1) the primary soluble constituents of petroleum fuels are biodegradable under aerobic and anaerobic conditions; and (2) dissolved hydrocarbon plumes do biodegrade under ambient conditions in the subsurface (Borden and Bedient 1986, 1987; Borden et al. 1986, 1989, 1995, 1997a, 1997b; Johnston et al. 1996; Kao and Borden 1997; Hunt et al. 1998; Lee et al. 1988). Based on this information, the USEPA adopted a policy allowing natural attenuation to be used as remedy for groundwater contamination (USEPA OSWER Directive 9200.4-17, 1997). MNA has now gained widespread acceptance and is the most commonly adopted remedial technology for management of groundwater contamination at UST sites (USEPA 1998).

MNA for management of petroleum releases is now widely accepted by regulators because: (1) the microbiology of petroleum biodegradation is well understood; (2) there are a number of well documented case studies in the peer-reviewed literature demonstrating that petroleum hydrocarbon plumes do biodegrade without production of toxic intermediates; and (3) there are also well documented, scientifically sound protocols for evaluating the rate and extent of natural attenuation. Site owners have accepted MNA because it works and, where conditions are appropriate, it is much less expensive than most other approaches.

2.2 Perchlorate Biodegradation

In recent years, an extensive body of information has been developed demonstrating that a wide diversity of microorganisms can degrade perchlorate to chloride and oxygen (Coates *et al*. 1999; Coates and Pollock 2003). Perchlorate-reducing organisms are widespread in the environment (Coates *et al*. 1999; Logan 2001) and can use a variety of different organic substrates (e.g. acetate, propionate and lactate) as electron donors for perchlorate reduction (Herman and Frankenberger 1998; Coates *et al*. 1999). Perchlorate reduction occurs under facultative anaerobic conditions and but is inhibited by dissolved oxygen concentrations in excess of 2 mg/L (Rikken *et al.* 1996; Chaudhuri *et al.* 2002). In the presence of biodegradable organic substrates, available oxygen will be consumed resulting in reducing conditions and perchlorate reduction. This suggests that perchlorate may naturally degrade at some sites without human intervention. The biodegradation pathway of perchlorate is illustrated in **Figure 2-1**.

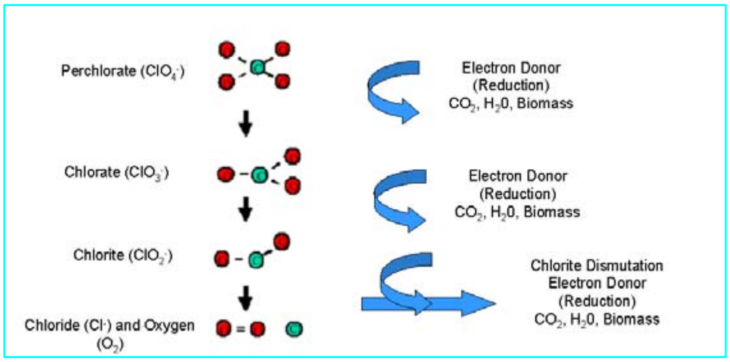

Figure 2.1. Perchlorate Biodegradation Pathway

Work by Coates et al. (1999), Chaudhuri et al. (2002), and Bender et al. (2002) indicate that the Dechloromonas and Dechlorosoma groups represent the primary chlorate and perchlorate reducing bacteria (PRB) in the environment, but more that 30 different strains of perchlorate-reducing microbes have been identified (EPA 542-R-05-015). The rate-limiting step in the three-step degradation process is the conversion of perchlorate to chlorate by a perchlorate reductase enzyme. 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. Results by O'Connor and Coates (2002) indicate that the CD enzyme: (1) is present in organisms grown anaerobically with perchlorate; (2) is not present in these same organisms grown aerobically; and (3) is not present in closely related organisms that cannot grow by (per)chlorate reduction. These results suggest that the presence and specificity of the CD enzyme in environmental samples could be used as a direct indicator of active perchlorate reduction, not just that organisms capable of perchlorate reduction are present.

There is a strong potential for MNA of perchlorate at some sites. There are extensive data on biological denitrification under ambient conditions (ITRC 2002; Martin *et al*.1999). Nitrate, like perchlorate, is very mobile, nonsorptive and resistant to biodegradation in many aquifers. While denitrifying bacteria are ubiquitous in soils and groundwater, denitrification can be very slow due to the lack of a carbon energy source for bacterial growth. However, in aquifers with higher levels of naturally occurring or anthropogenic organic carbon, nitrate is rapidly removed under anaerobic conditions. For example, studies have documented extensive nitrate removal during groundwater flow through organic-rich riparian buffers prior to surface water discharge (Fennessy and Cronk 1997;

Martin *et al*. 1999; Borin and Bigon 2002; Schoonover and Williard 2003). At other sites, organic materials released to the subsurface have resulted in anaerobic conditions with depletion of dissolved oxygen, nitrate, and sulfate, and the creation of methanogenic conditions. These conditions are ideal for nitrate and perchlorate reduction.

Field studies at a wide variety of sites have demonstrated at least partial biodegradation of chlorinated solvents under anaerobic conditions (Wiedemeier *et al*. 1998). This indicates that the anaerobic conditions required for perchlorate biodegradation are present at a significant number of sites.

2.3 Demonstration Design

To identify sites for participation in the project, three levels of site evaluation were conducted. The first level of site identification (Screening Level 1) was performed in the office and involved gathering information from as many sites across the United States as possible. The second level of site identification (Screening Level 2) included reviewing the gathered information, and selecting seven sites for initial and comparative field characterization. The third level of screening (Screening Level 3) included actual collection and analysis of samples from the selected field sites, use of microcosm tests to examine rates of degradation under ambient and augmented conditions, and testing innovative measures of enzyme activity to assist in identifying microbial activity on perchlorate. The rigorous screening process was designed to enable the selection of two field sites where the preliminary field and laboratory findings could be tested. The results of each screening level are discussed in the following sections.

2.3.1 Screening Level 1 - Site Identification

A master list of sites with perchlorate contamination and contacts was compiled from an Internet search, personal contacts and other available resources. The master list consisted of approximately 123 sites with documented perchlorate contamination, and was used as an initial pool of information from which contacts were obtained. The master list was also cross-checked with the Environmental Protection Agency (EPA) document, Known Perchlorate Releases in the U.S. (EPA 2004), and additional sites were found that were included on the master list. In addition, the project needs were identified to over 50 environmental managers in seven U.S. Army Corps of Engineers (ACE) offices nationwide through in-person presentations at ACE offices and direct phone calls. Another 30 persons, including state regulators, academics, industrial and military representatives, were asked for information about sites via a presentation by the project's Principle Investigator to the Interstate Technology Regulatory Council (ITRC) Perchlorate Team.

Using the master list, personal contacts, and the other solicited sources for information, over 50 telephone calls were made to gather information about potential sites of interest. Some of the contacts were "direct", meaning contact with personnel likely responsible for management of perchlorate issues at a particular site. Other contacts were "indirect", indicating that these contacts could provide leads to responsible site personnel. Of the telephone calls, approximately 40 direct contacts were initiated. During the telephone calls, responsible personnel were generally provided with the objectives of the project, the benefits of participating in the project and the mechanism for taking the next step to participate in the project which was completing a questionnaire about their site conditions.

The Solutions-IES questionnaire consolidated the desired information into a concise format that base or remediation managers could complete with relatively little time commitment. The questionnaire is provided in **Appendix A**. **Table 2.1** summarizes the number of sites identified by state, the number of direct contacts made, the number of questionnaires sent to interested managers, and the number of questionnaires returned.

Of the 40 direct contacts initiated, 13 questionnaires were received from responsible personnel. This information was utilized in Screening Level 2 to select sites for field characterization.

2.3.2 Screening Level 2 – Preliminary Site Selection

After site information was gathered, this information was then reviewed and sites were selected for field characterization. The goal was to examine a broad range of conditions that might influence the natural attenuation of perchlorate. At many of these sites, the perchlorate concentrations tend to decline as they move downgradient from the known or presumed source area. Where base managers indicated that they had reasonable expectation that natural attenuation processes were occurring, the site was given additional consideration. However, the mechanisms responsible for the observed attenuation were not clear, and historical data sets that could be used to evaluate the potential for natural attenuation of perchlorate were limited.

Based on industry experience with implementing MNA for chlorinated volatile organic compounds (CVOCs), sites with available data on multiple monitoring parameters such as levels of natural and/or anthropogenic organic carbon, DO concentration and ORP, nitrate and sulfate concentrations, and pH (Wiedemeier *et al.*, 1998) were preferred over sites with minimal or no data on these parameters. Secondarily, because of the presumption that conditions similar for natural attenuation of CVOCs would be similar to those favorable for attenuation of perchlorate, any evidence of reductive dechlorination [e.g., production of 1,2-*cis*-dichloroethene (*cis*-DCE) from trichloroethene (TCE)] was also noted and considered valuable. Finally, in order for a site to be considered further, the aquifer needed to have been characterized and information readily available and complete regarding the location of the perchlorate in the aquifer, size of the area of impact, groundwater flow direction and velocity, and type of geological formation and sediment material that would be encountered.

Table 2.1
Summary of Site Screening Process

State	Number of Sites Identified	Number of Contacts	Questionnaires Requested	Questionnaires Returned
Alabama	2	2	1	1
Arizona	8	2		0
Arkansas	2			
California	27	14	5	4
Florida	1	1		0
Georgia	2			
Indiana	1			
Iowa	5			
Illinois	1	1		0
Kansas	2			
Louisiana	1			
Maryland	5	2	2	2
Massachusetts	1	1	1	1
Minnesota	2			
Mississippi	1	1	1	1
Missouri	2	2		0
Nebraska	3			
New Jersey	2			
New Mexico	15	3		0
New York	6	1		0
Nevada	3	1		0
North Carolina	1			
Oregon	2			
Pennsylvania	5			
Tennessee	1	1		0
Texas	16	4	2	1
Utah	3	3*	2	3
Virginia	1			
Washington	3	1	1	0
West Virginia	1			
	123	40	14	13

Note:* Three sites in Utah were contacted. Two responded with questionnaires. One contact forwarded two questionnaires, and one contact forwarded one.

Based on the information obtained from the base managers and the questionnaires, the following seven sites were chosen for preliminary testing:

1. Little Mountain Test Annex Sludge Drying Beds, Hill AFB, Utah
2. Alliant Techsystems, Inc. (formerly ATK Tactical Systems), Elkton, Maryland
3. Naval Surface Warfare Center (NSWC), Indian Head, Maryland
4. John C. Stennis Space Center, Mississippi
5. Redstone Arsenal, Alabama
6. ATK Thiokol, Inc., Utah
7. Beale Air Force Base, California

Table 2-2 summarizes some of the geological and analytical information gathered about these sites. As seen in the table, at many sites there was limited characterization and many parameters considered to be important for an evaluation of the potential for MNA had not been collected. The objective of Screening Level 3 was to fill in the data gaps at these sites and perform additional laboratory testing in order to pick two sites for field demonstrations of the technology.

Table 2.2
Historical Data from Sites Selected for Field Characterization

Site & Location	**Little Mountain, Utah**	**ATK Elkton, Maryland**	**Indian Head, Maryland**	**Redstone Arsenal, Alabama**	**Stennis Space Center, Mississippi**	**ATK Thiokol, Utah**	**Beale Air Force Base, California**
Characteristics							
Perchlorate (mg/L)	1.1	230(maximum)	8 to 430	0.280 to 220 (maximum)	0.004 to 12.7	0.001 to 50	0.492
Dissolved oxygen (mg/L)	NA	2.88	1.49 to 1.64	NA	NA*	NA	0.6 to 9.13
Nitrate (mg/L)	NA	NA	4 to 50	NA	NA	0.01 to 53.5	12 to 14
Iron-total (mg/L)	17.2	NA	NA	NA	NA	0.002 to 50	NA
Iron-dissolved (Fe^{2+}) (mg/L)	NA	NA	NA	NA	NA	NA	2.8 (highest)
Manganese (mg/L)	11.1	NA	NA	NA	NA	NA	NA
Manganese-dissolved (mg/L)	NA	NA	NA	NA	NA	NA	1.9 (highest)
Sulfate (mg/L)	42.6	NA	NA	NA	NA	0.02 to 711	12 to 15.7
Methane (mg/L)	5.58	NA	NA	NA	NA	NA	NA
Ethane/Ethene	0.003/0.447	NA	NA	NA	NA	NA	NA
Oxidation/reduction potential (mV)	NA	+73.5 to +117	NA	NA	NA	NA	-57 to +197
pH (S.U.)	NA	5.7 to 6.2	5.0 to 6.8	NA	NA	6.0 to 8.0	6.2 to 9.1
TOC (mg/L)	4420	NA	NA	NA	NA	NA	NA
Temperature (ºC)	NA	NA	NA	NA	NA	13 to 18	20 to 27
Alkalinity (mg/L)	1130	NA	NA	NA	NA	1 to 530	96 to 104

Table 2.2
Historical Data from Sites Selected for Field Characterization

Site & Location	**Little Mountain, Utah**	**ATK Elkton, Maryland**	**Indian Head, Maryland**	**Redstone Arsenal, Alabama**	**Stennis Space Center, Mississippi**	**ATK Thiokol, Utah**	**Beale Air Force Base, California**
Depth to Water (ft below ground surface)	5 to 10 ft @ property boundary	6	5	12 to 40	10	0 to 250	10 to 20
Seepage Velocity (ft/d)	NA	NA	NA	0.001	0.07	Highly variable	Unknown
Aquifer Lithology Summary	Fractured bedrock	Mixture of clay, silt, sand, & gravel	Fill; sandy silts and sand and gravel seams		Poorly graded fine sand	Fractured carbonates	Silt & clay w/ some sand & gravel
Reported potential for natural attenuation of perchlorate*	Yes	NA	Yes	Unknown	Unknown	Unknown	Yes

NA – data unavailable or not readily available from site personnel
* - Anecdotal information obtained from base manager or site personnel

2.3.3 Screening Level 3 – Site Characterization and Laboratory Studies

In Screening Level 3, a field characterization and laboratory microcosm study was completed at the seven sites to further evaluate the potential for MNA of perchlorate and assist in selecting two sites for a much more extensive field demonstration. The objective of the field sampling activities was to collect representative groundwater samples from existing monitoring wells and soil to characterize current conditions from the same general area that would be analyzed in the eventual field demonstrations. The sampling locations focused on areas of each site where the concentration of perchlorate suggested there were conditions already supporting natural attenuation. These locations were toward the leading edge of well-defined plumes, downgradient from known sources, or in the vicinity of a discharge feature such as a creek, swamp or riparian buffer. Site-specific hydrogeology was also thoroughly reviewed to evaluate the impact of abiotic factors on the observed attenuation.

The field and laboratory studies included the following activities: (1) biogeochemical evaluation of selected field samples to determine current site conditions in areas of the site suspected to support the MNA of perchlorate; (2) enzyme assays on field samples to determine the presence of perchlorate-reducing microorganisms and, if possible, assess their activity; (3) a six-month biochemical oxygen demand (BOD_6) study to measure the background biochemical oxygen demand of site-matrix groundwater; and (4) microcosm treatability tests to measure the rate of perchlorate degradation under natural and enhanced conditions. Details of the field and laboratory procedures are described in the following sections.

2.4 Biogeochemical Characterization

Up to five monitor wells at each site were sampled to provide a general characterization of biogeochemical conditions in the aquifer. The wells were selected based on historical information provided to Solutions-IES by site representatives and chosen by Solutions-IES to generally cover the range of biogeochemical conditions at the site including highly contaminated locations, moderately contaminated locations, and uncontaminated background locations. The following parameters were measured in the field for each well sampled: depth to water, pH, temperature, ORP, DO, dissolved iron, and dissolved manganese. The following parameters were measured in the laboratory for each well: TOC, permanent gases (methane (CH_4), ethane, ethene, and vinyl chloride (VC)), CVOCs (PCE, TCE, *cis/trans*-DCE, 1,1,1-TCA and dichloroethane (DCA)), perchlorate (ClO_4^-) and other anions (Cl^-, NO_2^-, NO_3^-, SO_4^{+2}, PO_4^{+3}).

All laboratory analyses were performed in the Environmental Engineering Laboratory in the Department of Civil, Construction and Environmental Engineering at North Carolina State University (NCSU) under the direction of Dr. Robert C. Borden, P.E. Perchlorate was analyzed by ion chromatography following Method 314.0. Other anions were also analyzed by ion chromatography following Method 300. Chlorinated VOCs were analyzed by purge and trap gas chromatography with flame ionization detection (FID) following methods equivalent to SW-846 5030 and 8015B with a Tekmar LSC 3000 Purge and Trap with a Tekmar 2016 autosampler connected to a Shimadzu 14a Gas Chromatograph (GC) fitted with a FID detector and a 50-m DB-VRX column (J&W Scientific). The quantitation limit for all compounds is 5 μg/L or less using a 5-mL water sample. Permanent gases (methane, ethane, ethene, VC) were analyzed by headspace gas chromatography with flame ionization detection (headspace GC/FID) following methods equivalent to SW-846 5021 and 8015B using a Tekmar 7000 Static Headspace autosampler connected to a Hewlett Packard Gas Chromatograph.. The quantitation limit for all compounds was 5 μg/L or less using a 2-mL water sample.

2.5 Chlorite Dismutase (CD) Enzyme Analysis

Sediment and/or groundwater samples collected from the sites were sent to commercial laboratories to be assayed for the chlorite dismutase (CD) enzyme. Samples were collected in autoclaved 40-mL VOA vial, filled with groundwater to exclude entrapped air, and shipped to either Microbial Insights, Inc. (Rockford, TN) or BioInsites, Inc. (University of California at Berkeley, under the direction of Dr. John Coates), or both, to be assayed for levels of the CD enzyme. Results by O'Connor and Coates (2002) indicate that the CD enzyme: (1) is present in organisms grown anaerobically with perchlorate; (2) is not present in these same organisms grown aerobically; and (3) is not present in closely related organisms that cannot grow by (per)chlorate reduction. These results indicate that the CD enzyme is only present in organisms that are actively reducing perchlorate or chlorate. As a consequence, detection of the CD should provide a direct indication that perchlorate is currently being degraded under *in situ* conditions.

2.6 Six-month Biochemical Oxygen Demand (BOD_6) Test

The standard 5-day BOD test (APHA 1999) was adapted for use in this study. BOD can be used to evaluate the amount of background available organic carbon in a matrix. The traditional 5-day test was modified to extend the duration to six months and directly observe oxygen utilization rates under ambient groundwater conditions from each of the sites. To prepare the modified test, instead of diluting groundwater samples into a known BOD salts solution, the BOD_6 bottles were prepared using solely groundwater from each site. Two liters of groundwater were collected in the field with no headspace and shipped to NCSU for preparation of the BOD assays. At the laboratory, a volume of groundwater was placed in a large bottle and aerated by vigorously shaking the half-filled bottle. Then, the aerated groundwater was used to fill 60-mL serum bottles leaving no headspace and each bottle was sealed with a thick butyl-rubber stopper. All bottles were incubated at room temperature in the laboratory. Multiple bottles were prepared.

At time zero and sampling events performed 7 days, 21 days, 2 months and 6 months after setup, triplicate bottles were sacrificed and the dissolved oxygen (DO) concentration in the bottles was measured using a modified Winkler Titration (Appendix A). Oxygen loss in the bottles was then compared to parallel deionized water blanks to determine the amount of oxygen lost due to biological activity. The rate constant (k) and ultimate BOD_6 (L_o) were computed using a linear best fit regression of the data to compute the slope (b) and intercept (a), which were input into the Thomas Method (1950) equations. The ultimate BOD_6 is expressed as mg O_2/L. Higher ultimate BOD_6 values suggested the presence of higher amounts of available organic carbon and are presumed more likely to support microbial activity. Higher rates suggest sites where DO can be consumed more quickly, anaerobic conditions can be established, and there is increased potential for MNA of perchlorate to occur.

2.7 Laboratory Microcosms

Laboratory microcosms were constructed to monitor perchlorate biodegradation with the following experimental treatments:

Treatment 1: Groundwater plus sediment - ambient low-level perchlorate (triplicate)
Treatment 2: Groundwater plus sediment – ambient high-level perchlorate (triplicate)
Treatment 3: Groundwater plus sediment - killed control - ambient low-level perchlorate (duplicate)
Treatment 4: Groundwater plus sediment - killed control – ambient high-level perchlorate (duplicate)
Treatment 5: Groundwater plus sediment - added organic carbon (single)
Treatment 6: Groundwater plus sediment - added EOS® solution[2] (triplicate)

2.7.1 Sediment and Groundwater Collection for Laboratory Microcosms

Aquifer material and groundwater were collected from one or two locations at each site for potential use in microcosm construction. The sampling locations were selected based on previous groundwater sampling results indicating presence of detectable perchlorate and biogeochemical monitoring results indicating a combination of low dissolved oxygen and/or low ORP with some organic carbon.

Sediment samples for the microcosm study were collected in the field using hand augers, Geoprobe® and/or by pumping accumulated sediment from the bottom of monitor wells. When sampling by Geoprobe®, sediment samples were collected

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

in new plastic MacroCore sleeves. When using a hand auger, the auger was carefully cleaned with phosphate-free soap solution, tap water and a deionized water rinse before a final rinse with methanol. The sampling tool was air-dried prior to use to prevent carry over of methanol into the soil sample. Sediment samples were collected from a location and depth expected to be representative of groundwater conditions at the location of interest. Sediment samples were collected in sterile mason jars, covered immediately with groundwater with no headspace, and shipped on ice to the Environmental Engineering Laboratory at NCSU for use in the microcosm studies.

Groundwater for use in microcosm construction was collected from an adjoining monitor well using peristaltic, Whale™ or Grundfos submersible sampling pump. The groundwater was pumped into autoclaved 1-L bottles with no headspace to exclude entrapped air. One sediment sample was also collected from each location in an autoclaved 40-mL VOA vial for sediment TOC analysis by an outside commercial laboratory.

2.7.2 Microcosm Construction and Sampling

The groundwater monitoring results were reviewed to select one location at each facility for microcosm construction. The objective of this process was to identify sediment and groundwater samples with the highest potential for natural attenuation of perchlorate. Prior to microcosm construction, the sediment collected from the field was sieved with a #4 sieve to remove large pebbles and blended. Microcosms were constructed using 245-mL serum bottles filled with 100 g of wet aquifer sediment and 150 mL of groundwater and were sealed with thick butyl rubber stoppers, sleeve stopper or equivalent, in triplicate, duplicate, or single repetitions as specified by the treatment plan. At some sites, it was not possible to obtain large volumes of aquifer material for use in microcosm construction. In these cases, microcosms were constructed with 200 mL of sediment-groundwater slurry. Prior to sealing, the microcosm headspace was flushed with hydrogen-free nitrogen to remove oxygen.

After the basic microcosms had been assembled, the bottles received different amendments to evaluate the effects of environmental conditions on perchlorate biodegradation. In the ambient conditions treatment (Treatment 1), nothing was added to the microcosm bottles so that natural changes to ambient conditions could be observed. This treatment contained the low level of perchlorate already in the contaminated sample matrix. If not, this treatment was amended with a concentrated sodium perchlorate ($NaClO_4$) solution to achieve a starting concentration of approximately 100 to 200 µg/L perchlorate.

Regardless of the ambient starting concentration, the high-level perchlorate treatment (Treatment 2) was amended with a concentrated $NaClO_4$ solution to achieve a starting concentration of approximately 5,000 µg/L perchlorate.

Abiotic (killed) controls (Treatments 3 and 4) were set up identical to Treatments #1 and #2, then amended with 500 mg/L sodium azide and autoclaved at 121^{o}C for 30 minutes on two consecutive days. In the added organic carbon treatment (Treatment 5), the microcosm was amended with 50 mg/L Na lactate and 50 mg/L Na acetate, as a positive control. In the EOS-amended treatment (Treatment 6), the microcosm was amended with sufficient EOS® to provide approximately 500 mg/L emulsified soybean oil, as an additional positive control.

Microcosms were incubated at room temperature and monitored at regular intervals for up to a year for perchlorate, other anions, VOCs, and permanent gases following analytical methods described under biogeochemical characterization. Microcosms were sampled after thoroughly mixing by inverting three times and then allowing sediment to settle out of solution. A 10-mL syringe and 26.5 gauge needle was flushed with nitrogen and inserted through the rubber stopper. Ten mL of nitrogen injected into the bottle enabled withdrawal of 10 mL of aqueous sample. A portion of the sample was then used for the analysis of perchlorate, anions and VOCs. DO was measured by using a Chemetrics 0 - 1 mg/L self-filling DO ampoule. DO concentration was then determined by visual comparison to color standards. If DO exceeded 1 mg/L, this process was repeated with the 1 – 12 mg/L DO ampoules.

2.8 Biodegradation Rate Analysis

The sum of electron acceptors was calculated by adding the milliequivalents of electron acceptors, NO_3^- and ClO_4^-. Dissolved oxygen was not included in sum of electron acceptors as most of the times the DO value was below 0.5 ppmv and DO analysis is not very reliable below 0.5 ppmv. The following equation was used to calculate sum of electron acceptors:

$$\text{Sum of electron acceptors (meq/L)} = 5[NO_3^-] + 8[ClO_4^-] \qquad [1]$$

The concentration of nitrate (mg/L) was divided by its equivalent weight to get meq/L of nitrate. The concentration of perchlorate (µg/L) was divided by 1000 and then by its equivalent weight to get meq/L of perchlorate.

Microcosm results were evaluated by determining reaction rate constants by fitting zero-order (eq. 2) or first-order (eq. 3) rate equations to temporal concentration data for nitrate, perchlorate and sum of electron acceptors.

$$[C] = [C_0] + kt \qquad [2]$$

$$[C] = [C_0]e^{-kt} \qquad [3]$$

3.0 Field and Laboratory Results – Little Mountain Test Annex, UT

This section presents results from the field and laboratory studies conducted at the Little Mountain Test Annex (LMTA) of Hill Air Force Base (Hill AFB), near Ogden, UT.

3.1 Background information

Solutions-IES initially contacted Mr. Kyle Gorder, Environmental Engineer, at the Base about the potential for including the LMTA in the study. Mr. Gorder provided information about the history and site conditions, as well as guidance regarding operational issues at the site. Mr. Gorder also provided a copy of the Health and Safety Plan prepared by Parsons Engineering Science for previous assessment and monitoring work performed at the site. These two resources were used as primary sources of information about the site that are paraphrased below.

3.1.1 Location and Layout

The 740-acre LMTA is located on Little Mountain, a large, isolated hill in Weber County, UT, approximately 20 miles northwest of the Hill AFB. The LMTA is located at the farthest western extension of 12th Street in Ogden, UT. A former water treatment plant, sludge drying beds, and a water-investigation-derived waste (IDW) treatment system building are located on top of a small hill located approximately 0.25 mile southeast of the main LMTA complex. The sludge drying bed site is situated on a flat-lying saddle atop a west–northwest trending ridge at the southern portion of Little Mountain. The sludge drying beds were originally constructed in 1958 to dry clarified sludge from the adjacent water treatment plant. Maps showing the general site layout and monitor well locations are shown in **Figures 3.1 and 3.2**. The LMTA complex is approximately 165 feet above the maximum shoreline of the Great Salt Lake.

The sludge drying beds cover an area of approximately 0.25 acre and have the approximate dimensions of 70 feet by 140 feet by 4 feet deep. Both beds are fenced around most of the bed area perimeter. A drainage ditch is located immediately east and south of the beds and was an overflow channel. Both beds are connected to the overflow ditch by concrete outflow structures. Hill AFB has designated the former sludge drying beds (source area) and related dissolved contaminant plume as Operable Unit (OU)-A.

The surficial geology at the site consists of a thin topsoil layer typical of terrace and shoreline deposits of ancient Lake Bonneville. These deposits overlie fractured, generally non-porous bedrock. In several locations surrounding the sludge drying beds, the fractured bedrock is exposed at the surface. The Great Salt Lake shoreline varies from 0.25 to 1 mile from the site. The groundwater table is at an elevation of approximately 4,208 feet, which is approximately 150 ft below ground surface and about 10 feet above lake level.

3.1.2 Site Contaminants

In the mid-1970s, paint strippers, consisting of TCE and other solvents including methylene chloride, phenols, benzyl alcohol, petroleum hydrocarbons and potentially other compounds also were disposed in the inactive drying beds. Chlorinated solvents were the primary contaminants, but semi-volatile organic compounds (SVOCs) including phenol and benzyl alcohol are evident, along with perchlorate and RDX.

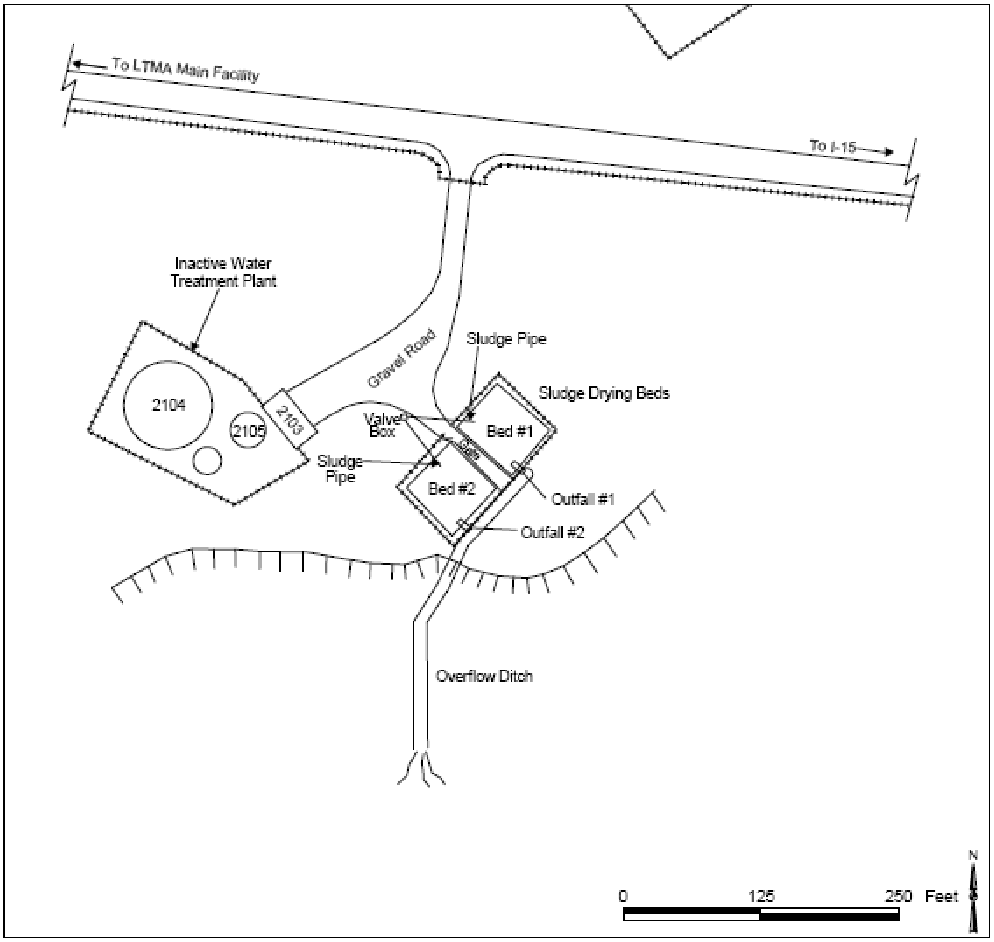


Figure 3.1 LMTA Operable Unit A Site Features

More recent groundwater investigations have detected concentrations of methylene chloride (MC) up to 1,350,000 μg/L and TCE up to 89,800 μg/L. The TCE degradation product *cis*-1,2-dichloroethene (*cis*-1,2-DCE) has been detected at concentrations up to 245,000 μg/L. Some contaminant information available from previous investigations of the site performed in 1986 and 1990 identified total phenols and metals as compounds of primary concern (COPCs); however, the compounds discussed above are the primary COPCs. Perchlorate has been identified at the site at a concentration of approximately 1,100 μg/L.

Figure 3.2 LMTA Operable Unit A Monitor Well Locations

Representative groundwater conditions of the OU-A area were obtained from previous monitoring results. **Table 3.1** summarizes the conditions at three representative wells along the OU-A groundwater plume.

Table 3.1
Representative Conditions in OU-A Groundwater Plume
LMTA, Hill AFB

	Units	**LM-036A (Source Area)**	**LM-035 (Source Area)**	**LM-012 (Downgradient)**
Anions				
Perchlorate	μg/L	NA	1,100	NA
Chloride	mg/L	1,120	2,240	2,000
Nitrate – N	mg/L	1.4	BDL	8.8
Sulfate	mg/L	89	6.2	441
Volatile Organic Compounds				
1,1-Dichloroethane	μg/L	135	7,780	32.2
1,1-Dichloroethene	μg/L	32.9	600	6.8
1,2-Dichloroethane	μg/L	156	2,310	15.7
Cis-1,2-Dichloroethene	μg/L	12,500	245,000	1,180
Methylene Chloride	μg/L	2.82	26,100	<5
Tetrachloroethene	μg/L	4.83	BDL	<5
Trichloroethene	μg/L	1,620	12,500	776
Toluene	μg/L	1.75	2,460	<5
Explosives				
RDX		NA	3650	NA
HMX		NA	20.2	NA
Semi-Volatile Organic Compounds				
Benzyl Alcohol	μg/L	<2	4,190	NA
2,4-Dimethylphenol	μg/L	<4.9	63.6	NA
2-Methylphenol	μg/L	<2.9	315	NA
Phenol	μg/L	<5.9	14,300	NA
3- & 4-Methyl phenol	μg/L	<0.98	3,050	NA
Dissolved Gases				
Methane	μg/L	4420	6,200	7.9
Ethene	μg/L	34	466	<0.1
Petroleum Hydrocarbons				
Petroleum hydrocarbons	mg/L	1.03	50.3	0.19
PHC as Gasoline	μg/L	10,700	224,000	2160
PHC as Diesel Fuel	mg/L	0.25	16	<0.095
Water Quality				
Total Organic Carbon	mg/L	7.68	497	1.53
pH	SU	7.70	6.75	7.54
Dissolved Oxygen	mg/L	0.25	0.57	0.5
Oxid.-Red. Potential	mV	-38	-147	-55

NA = Not analyzed.

3.1.3 Site Hydrogeology and Plume Geometry

The superposition of rock formations at the LMTA shows a sequence consisting of slate or phyllitic shale, a clastic, greenstone that includes a congruent, mafic (iron/magnesium mineral) igneous unit (mostly intrusive diabase) within the upper part of the shale, and a tillite (lithified glacial deposit) overlying the greenstone. The greenstone appears to be local to the immediate area of the sludge drying beds site and is not present elsewhere at Little Mountain. According to Mr. Kyle Gorder, the Hill AFB site representative, drilling in the area of the sludge drying beds is difficult and bedrock is encountered within 4 to 6 feet of the surface.

The maximum COPC plume length is greater than 1,200 feet from the source and the plume is up to 750 feet wide. Groundwater is found approximately 160 feet below ground surface (ft bgs) in the source zone, but topography drops off steeply to the south along the plume and groundwater is only 5 to 10 ft bgs at the property boundary. The maximum depth of contamination is greater than 200 feet below the water surface (i.e., 360 ft bgs) and the maximum aquifer thickness is up to 200 feet. The direction of groundwater flow across the site generally follows the topographical gradient which declines from north to south.

3.2 Biogeochemical Characterization

Field monitoring activities were conducted by Solutions-IES on December 14 - 15, 2004. Because of the documented depth to groundwater and anticipated difficult drilling, Solutions-IES opted not to collect soil from the site. Instead, sediment was collected from monitoring wells LM-012, LM-026A, and LM-35 by pumping using a Grundfos pump set near the bottom of each well. The sediment was collected prior to purging the wells. Groundwater samples were then collected from monitoring wells LM-012, LM-026A, LM-35, LM-36A, and LM-10 using a Grundfos pump set on the lowest setting to produce a non turbulent flow. Field parameters (pH, conductivity, temperature, and ORP) were measured during the low-flow sampling process. The field and laboratory results for each well sampled are presented in **Table 3.2**.

Table 3.2 **Field Monitoring Results– December 14-15, 2004** **LMTA, Hill AFB**						
	Units	**LM-010**	**LM-035**	**LM-036**	**LM-026A**	**LM-012**
Analyte or Test Parameter		**Up-gradient**	**Source**	**Down-gradient**	**Down-gradient**	**Down-gradient**
Perchlorate	µg/L	<10	34	NA	<10	<10
1,1-Dichloroethene	µg/L	<1	76,000	<1	2	<1
trans-1,2-Dichloroethene	µg/L	<1	770	64	54	1
Dichloroethane	µg/L	<1	6,300	40	127	7
cis-1,2-Dichloroethene	µg/L	<1	250,000	4,300	4,630	275
1,1,1-Trichloroethane	µg/L	<1	<1	79	10	<1
Trichloroethene	µg/L	<1	13,000	960	4,010	187
Tetrachloroethene	µg/L	<1	94	5	34	1
Vinyl Chloride	µg/L	<1	93	7	4	<1
Ethene	µg/L	<1	230	3	1	<1
Methane	µg/L	<5	12,000	3,200	910	<5
Chloride	mg/L	566	2,100	550	1,700	1,700
Nitrate	mg/L	131	<.5	31	24	45
Sulfate	mg/L	208	5	64	290	410
Total Organic Carbon	mg/L	1	14	2	1	2
Chlorite Dismutase (BioInsite)	pos/neg	NA	NA	NA	-	+
Chlorite Dismutase (Microbial Insights)	pos/neg	NA	+/-	NA	+++	++
pH	SU	7.6	6.3	7.3	7.5	7.3
Dissolved Oxygen	mg/L	0.2	<0.1	0.2	0.2	1.0
Oxidation-reduction potential	mV	-22	-78	-22	-9	-129
Manganese	mg/L	<1	<1	<1	<1	<1
Iron	mg/L	<1	250	<1	<1	10

NA = Not Analyzed

3.3 Chemical Oxygen Demand (BOD) Results

The 6-month BOD test was prepared on groundwater samples from LM-012 and LM-026. Both LM-012 and LM-026 were located downgradient of the source. In ambient groundwater from these wells, the starting perchlorate and DO concentrations were low (**Table 3.2**). Conversely, nitrate was elevated. The BOD_6 results, presented in **Table 3.3**, suggest a limited amount of BOD available as an electron donor for consumption of oxygen, nitrate and perchlorate. Given the high levels of nitrate present in these wells (24 and 45 mg/L), it is unlikely that the nitrate would be consumed before the available BOD is exhausted, limiting the potential for anaerobic biodegradation of perchlorate.

Table 3.3
BOD_6 Results, LMTA, Hill AFB

Wells	slope	intercept	R^2	k	L_o
	b	A		2.61(b/a)	1/(2.3*k*a3)
LM-012	0.00586	1.75	0.23	0.00876	9.3
LM-026	0.00721	1.60	0.66	0.0118	9.0

3.4 Microcosm Results

Laboratory microcosms were constructed to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added organic substrates. Because of the large depth and presence of fractured rock, it was not feasible to obtain large amounts of sediment for microcosm construction. Consequently, microcosms were constructed with a groundwater-sediment slurry collected from the bottom of monitor well LM-012, located approximately 800 ft downgradient of the sludge drying beds. Initially, perchlorate was not detected in the LM-012 well and, thus microcosms were spiked with 25 µL of 750 mg/L $NaClO_4$ to achieve a starting perchlorate concentration of approximately 75 µg/L.

All the microcosms were tested for the changes in concentration with time of vinyl chloride, methane, ethene, TCE, *cis*-DCE, dissolved oxygen, nitrate, sulfate, chloride, and perchlorate. In all LMTA microcosms, all monitoring results for VC, methane, and ethene were below the method quantitation limit.

In the EOS-amended microcosms (Treatment 6), perchlorate was reduced in the three replicates from a starting average of 86µg/L to 13 µg/L in 271 days. The relatively slow perchlorate degradation may have been associated with the low pH of the unbuffered EOS product used to prepare these microcosms. As expected, DO and nitrate dropped to below detection within 34 days. Sulfate was reduced by 90% in two of the three replicates; the average sulfate concentration in all three replicates decreased from 420 mg/L to 172 mg/L within 271 days

In Treatment 5, the microcosm with added lactate and acetate as organic carbon amendment, perchlorate was below detection limit until day 34 when the bottle was amended with ~75 µg/L of perchlorate (actual starting concentration was 70 µg/L). Within 29 days after the injection, perchlorate declined to below the laboratory detection limit (<1 µg/L) indicating the presence of an active population of perchlorate degraders. There was an increase in chloride content from 1,586 mg/L to 1,818 mg/L. Nitrate was reduced to below detection within 34 days, but the sulfate content remained unchanged.

The concentration of all contaminants and indicator parameters decreased slightly over time in the high perchlorate microcosms (Treatment 2) and killed microcosms (Treatments 3 and 4). The concentration of sulfate increased slightly with time.

The average concentrations of perchlorate and indicator parameters in the ambient condition microcosms (Treatment 1) are shown in **Charts 3.1 and 3.2**. Nitrate and sulfate remained essentially constant over the 271-day incubation period, but DO decreased with time. Perchlorate was below detection initially so the three replicate microcosms were spiked on day 34 to an average of 67µg/L. After spiking, perchlorate remained elevated with no evidence of anaerobic biodegradation. The analytical results show a temporary increase in perchlorate on Day 118. However, this increase was also observed in the killed-ambient microcosms suggesting a temporary analytical problem.

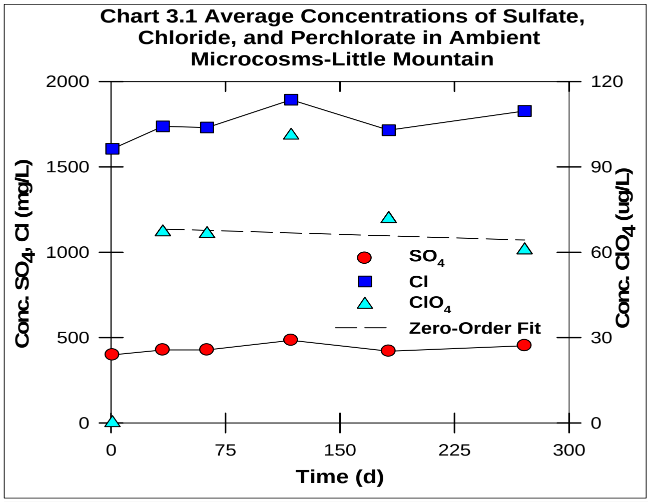


Chart 3.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms-Little Mountain

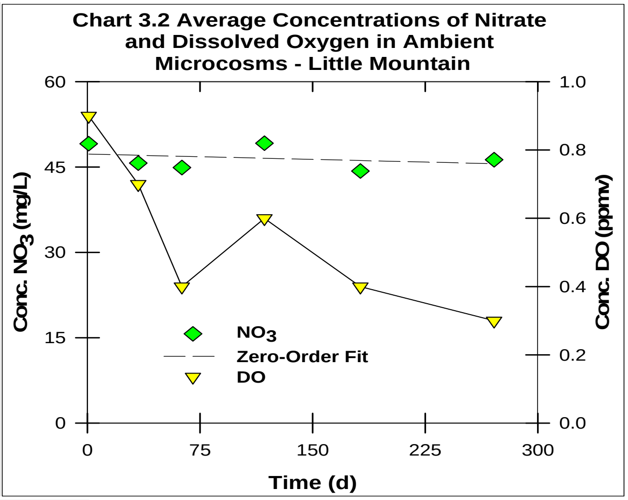


Chart 3.2 Average Concentrations of Nitrate and Dissolved Oxygen in Ambient Microcosms - Little Mountain

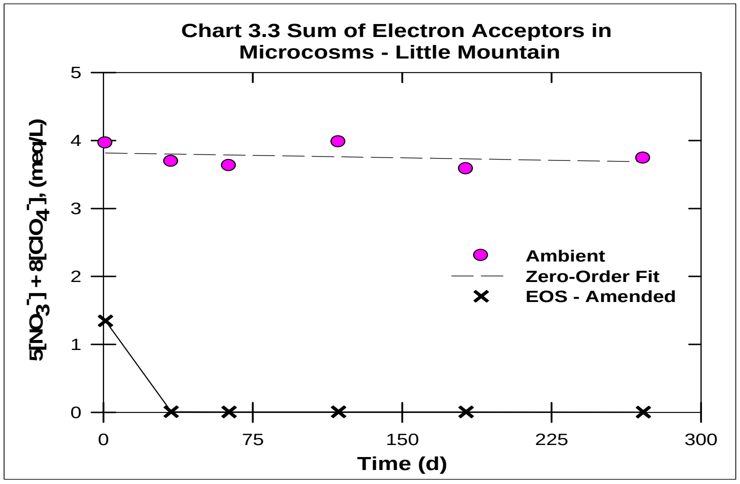


Chart 3.3 Sum of Electron Acceptors in Microcosms - Little Mountain

Chart 3.3 shows change in sum of electron acceptors with time for ambient and EOS-amended microcosms. There was not much change observed in sum of electron acceptors in ambient microcosms, since there was no evidence of perchlorate and nitrate degradation. The sum of electron acceptors decreased with time in EOS-amended microcosms as the concentration of the electron acceptors, nitrate and perchlorate, decreased with time.

The data were fit to the regression equations described in Section 2.8. The straight dashed line for perchlorate (**Chart 3.1**) represents a linear regression fit to the data that indicates zero-order kinetics (Eq. 2). The data point for perchlorate concentration on Day 118 was not included while fitting the regression line as it is an outlier (due to analytical problem). Similarly, the straight line in **Chart 3.2** represents a linear regression of the nitrate data. The regression line show a good fit to the zero-order kinetic model used in Eq. 2 for the sum of electron acceptors (**Chart 3.3**). The degradation/removal rate constants for perchlorate, nitrate and sum of electron acceptors in ambient microcosms are shown in **Table 3.4**.

Table 3.4
Rate Constants from the Ambient Treatment Microcosms
LMTA, Hill AFB

	Order	**k**	**R^2**
Perchlorate	Zero	<0.01 mg L^{-1} y^{-1}	0.157
Nitrate	Zero	2.26 mg L^{-1} y^{-1}	0.089
Sum of Electron Acceptors	Zero	0.18 meq $L^{-1}y^{-1}$	0.086

3.5 Summary

In summary, the field and microcosm results indicate very limited potential for anaerobic biodegradation of perchlorate in the downgradient portion of the LMTA OU-A plume. While microorganisms capable of perchlorate biodegradation are present at the site, there was no evidence of perchlorate biodegradation in the ambient condition microcosms, either at low or high starting concentrations. The absence of perchlorate biodegradation is presumably due to the low levels of BOD and high levels of nitrate present in groundwater in this area. This site is not likely to be a good candidate to demonstrate the potential for MNA of perchlorate in groundwater.

4.0 Field and Laboratory Results – Alliant Techsystems, Inc., Elkton, MD

This section presents results from the field and laboratory studies conducted at the TCE/Perchlorate Area SWMU, Alliant Techsystems, Inc. (formerly ATK Tactical Systems Company LLC) site in Elkton, MD. The site is referred to as "ATK Elkton."

4.1 Background Information

Solutions-IES contacted Mr. William Lucas, Environmental Engineer, at the facility about the conditions at the ATK Elkton site. Solutions-IES was working on another part of the site under a separate ESTCP-funded contract. Mr. Lucas provided additional information regarding groundwater investigations across the site prepared by other consultants. Some elements of the information that was provided were used in devising and describing a scope-of-work for this current project. Mr. Lucas provided information about the history and site conditions, as well as guidance regarding operational issues at the ATK Elkton site. In addition to the anecdotal information provided by Mr. Lucas, Solutions-IES used three reports prepared by Arcadis Geraghty & Miller (AGM) as primary sources of information about the site. The information is paraphrased below.

4.1.1 Location and Layout

The ATK Elkton facility has been conducting environmental investigations at their 600-acre facility since 1984. As part of the 1984 Hazardous and Solid Waste Amendments (HSWA) of the RCRA, the US EPA identified various Solid Waste Management Units (SWMUs) at the facility. The majority of the environmental assessment and remediation work at the site has been performed by Arcadis Geraghty & Miller (AGM), including the delineation of the area designated as the "TCE Area SWMU" in the southeast portion of the site. A site map with previous sampling locations from AGM is provided as **Figure 4.1.**

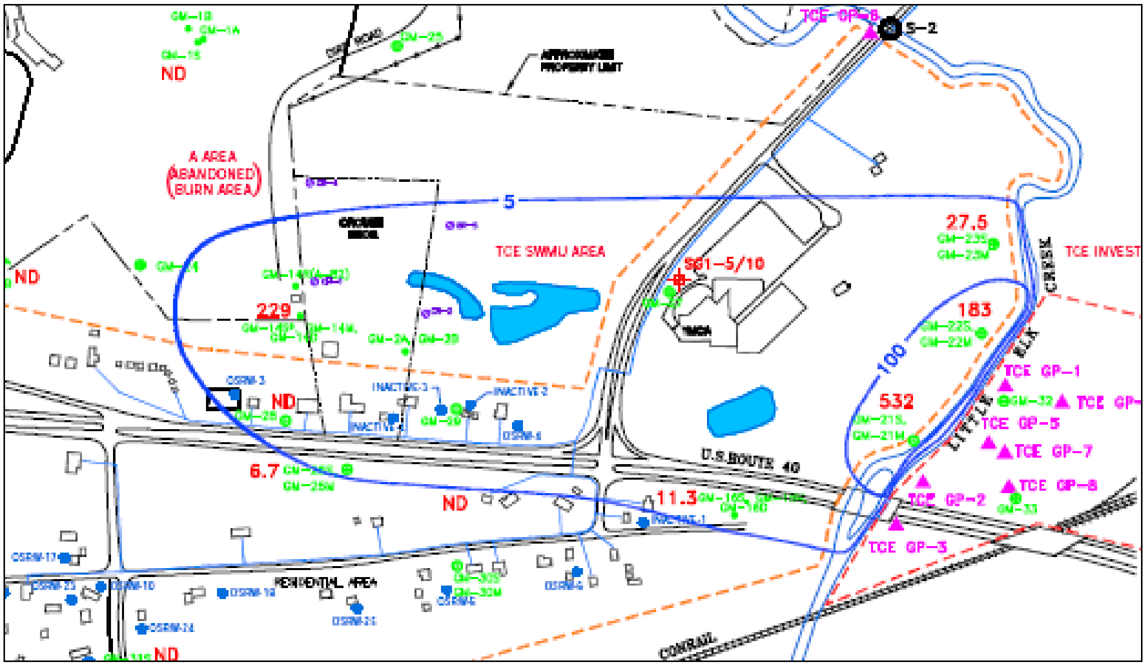


Figure 4.1 TCE Groundwater Plume at the TCE/Perchlorate Area SWMU, ATK Elkton

The TCE Area SWMU covers the area including the southern and eastern extent of the main plant area and eastward towards Little Elk Creek (**Figure 4.2**). Recent investigations also identified perchlorate in groundwater and showed that the trichloroethene (TCE) and perchlorate plume extends off site to the east and the south side of U.S. Route 40. For the purpose of this study, groundwater in this portion of the site will be referred to as the TCE/Perchlorate Area SWMU plume.

TCE concentrations found in groundwater on the south side of US Route 40 ultimately led to most of the properties with private wells south of the site being connected to the municipal water supply system in the late 1980s. Additionally, ATK Elkton installed a pump-and-treat system as an interim remedial measure located at the downgradient southeastern site boundary (GM-14M); the system was activated in 1998. The recovery well was replaced in 2002 by GM-14R and continues to operate at approximately 20 gallons per minute.

Three monitoring well pairs, each consisting of a shallow and intermediate depth well, are installed along the western side and within 80 ft of the eastern leg of Little Elk Creek (Figure 4.1). The intermediate depth wells in these clusters were drilled to less than 60 ft because weathered bedrock (saprolite) was encountered at shallower depths. The wells of interest were drilled with hollow stem augers. The shallow depth wells were constructed with 10-feet of 4-inch diameter Sch. 40 PVC well screen (.020 slotted) and the intermediate depth wells were constructed with 15 feet of 4-inch dia. Sch. 40 PVC well screen (.020 slotted). Most historical site data have indicated that the plume is migrating primarily in the intermediate zone of the Potomac Group. The wells of interest for the current study include GM-3B, GM-14M, GM-2B, GM-22S and GM-22M. As shown on Figure 4.2, 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.

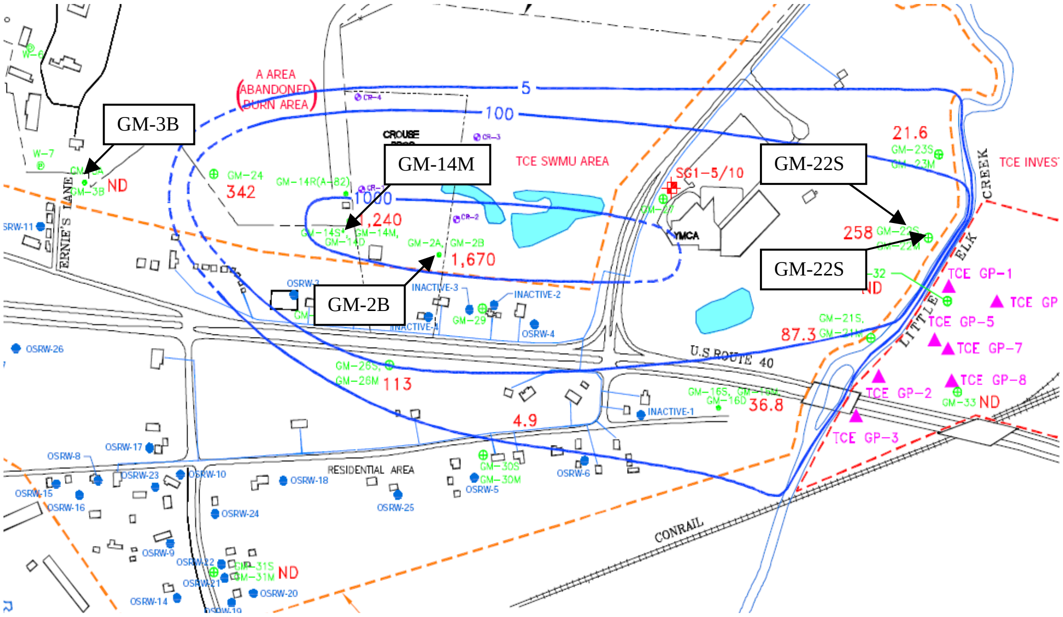


Figure 4.2 Well Locations and the Perchlorate Plume at the TCE/Perchlorate Area SWMU, ATK Elkton

4.1.2 Site Contaminants

The groundwater monitoring event in March 2004 detected elevated concentrations of TCE (1,000 μg/L), 1,1,1-TCA (79 μg/L) and perchlorate (1,240 μg/L) in the presumed source area in the vicinity of GM-14M. Further downgradient, in the vicinity of GM-22M, both the TCE and *cis*-DCE concentrations are higher, reported to be 6,400 and 65 μg/L, respectively. 1,1,1-TCA concentrations were 1,100 μg/L closer to Little Elk Creek where degradation products also appear. By contrast, perchlorate concentrations appear to attenuate as they move toward Little Elk Creek, decreasing from 1,240 μg/L in GM-14M to 258 μg/L in GM-22M, a distance of approximately 2,400 feet.

Table 4.1 summarizes data obtained from an upgradient well (GM-3B), a well in the presumed source area (GM-14M) and one well pair downgradient near the eastern leg of Little Elk Creek (GM-22S and GM-22M). These wells represent groundwater conditions across the area of interest for this project.

Table 4.1
Representative Groundwater Conditions in TCE/Perchlorate Area SWMU
ATK Elkton

	Units	**GM-3B (Upgradient)**	**GM-14M (Source)**	**GM-22M (Downgradient)**	**GM-22S (Downgradient)**
	Date	**March 2004**	**March 2004**	**March 2004**	**March 2004**
Inorganic Anions					
Perchlorate	µg/L	<4	1240	258	183
Chloride	mg/L	NA	NA	NA	NA
Nitrate – N	mg/L	NA	NA	NA	NA
Sulfate	mg/L	NA	NA	NA	NA
Volatile Organic Compounds					
Acetone	µg/L	4.8	66	430	1300
Chloroform	µg/L	<1	<80	17	14
1,1,1-Trichloroethane	µg/L	<1	79	1100	610
1,1-Dichloroethane	µg/L	<1	8.5	39	25
1,1-Dichloroethene	µg/L	<1	110	1200	750
1,2-Dichloroethane	µg/L	<1	<40	<100	<100
Cis/trans-1,2-Dichlorothene	µg/L	<1	34	65	36
Methylene Chloride	µg/L	<2	<80	220	200
Tetrachloroethene	µg/L	<1	<40	<100	<100
Trichloroethene	µg/L	<1	1000	6400	3200
Toluene	µg/L	<1	<40	<100	<100
Dissolved Gases					
Methane	µg/L	NA	NA	NA	NA
Ethene	µg/L	NA	NA	NA	NA
Water Quality					
Total Organic Carbon	mg/L	NA	NA	NA	NA
PH	SU	6.27	4.8	5.0	4.8
Dissolved Oxygen	mg/L	NA	NA	NA	NA
Oxid.-Red. Pot.	mV	83.1	349	327	303

4.1.3 Site Hydrology and Plume Geometry

Borings on and near the ATK Elkton site reveal that bedrock underlying the site is micaceous, feldspar gneiss. The depth to bedrock ranges from about 90 feet to 150 feet below ground surface (bgs) between the ATK plant area and Little Elk Creek to the east. The thickness of the overlying saprolite ranges from 5 to 64 feet. The saprolite is micaceous, silty, and friable, becoming more cohesive and resistant to drilling with depth.

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 and is composed of heterogeneous mixtures of clay, silt, sand and gravel. Alluvium is associated with river and estuary depositional environmental and occurs along Little Elk Creek and its tributaries. Limited data indicate an alluvial thickness of 0 to 40 feet; these beds are extremely variable in their horizontal and vertical extent.

There are three groundwater flow regimes in the vicinity of the ATK Elkton facility: a shallow unconfined water table aquifer, an intermediate Potomac Group aquifer, and a deep saprolite aquifer. Groundwater flow in the shallow unconfined waste-table aquifer is generally influenced by topography and surface-water flow. Groundwater discharge to Little Elk Creek appears to occur in the vicinity of the site.

Groundwater flow in the saprolite is generally to the southeast in accordance with regional flow directions. However, groundwater flow in the Potomac aquifer and saprolite are influenced by pumping of production well W-7 and possibly GM-14. The perchlorate plume geometry is illustrated in **Figure 4.2**. Perchlorate in groundwater has been detected off of the ATK Elkton property all the way to Little Elk Creek. Overall the plume appears to be approximately 3,600 feet long from west to east and 2000 feet wide from north to south at its presumed widest point near Little Elk Creek.

4.2 Biogeochemical Characterization

Based on the data provided by the facility, five monitor wells will be sampled to provide a general characterization of biogeochemical conditions in the aquifer. The wells selected appear to cover the range of biogeochemical conditions at the site including highly contaminated locations, moderately contaminated locations, and uncontaminated background locations. The wells selected at ATK Elkton are identified below and some details about their construction and groundwater geochemistry are provided in **Table 4.2**. The range of contaminants and representative site conditions in GM-3B, GM-14M, GM-22M and GM-22S were provided in **Table 4.1**.

Table 4.2
Summary of Groundwater and Sediment Analytical Results
ATK Elkton

	units	GM-3B	GM-14M	GM-22M	GM-22S	GM-2B	SB-1 (Sed)
Relative Location		Upgradient	Source	Downgradient			
Perchlorate	µg/L	<4	1200	194	243	1260	
Dichloromethane	µg/L		104	930	621	526	
1,1-Dichloroethene	µg/L		3.00		55.0		
trans-1,2-Dichloroethene	µg/L						
Dichloroethane	µg/L		8.00	34.0	24.0	24.0	
cis-1,2-Dichloroethene	µg/L		48.0	74.0	41.0	53.0	
Chloroform	µg/L		2.00	7.00	5.00	5.00	
1,1,1-Trichloroethane	µg/L		86.0	1016	642	615	
Carbon tetrachloride	µg/L					7.00	
Trichloroethene	µg/L	1.00	1270	6310	3530	2410	
Tetrachloroethene	µg/L		3.00	4.00	3.00	10.0	
Vinyl Chloride	µg/L	BQL	BQL	BQL	BQL	BQL	
Chloroethane	µg/L	BQL	BQL	BQL	BQL	BQL	
Chloroemethane	µg/L	BQL	BQL	BQL	BQL	BQL	
Total CVOCs	µg/L	1.00	1530	8370	4820	3650	
Ethane	µg/L	BQL	BQL	BQL	BQL	BQL	
Ethene	µg/L	BQL	BQL	BQL	BQL	BQL	
Methane	µg/L	BQL	BQL	BQL	BQL	BQL	
Total Organic Carbon	mg/L	<1.0	1.05	<1.0	<1.0	<1.0	
Chloride	mg/L	23.8	45.3	65.3	101.4	23.8	
Nitrate	mg/L	10.5	9.90	2.40	2.80	10.5	
Sulfate	mg/L	1.00	8.90	3.20	5.20	1.00	
Phosphate	mg/L	<1.0	<1.0	<1.0	<1.0	<1.0	
Chlorite Dismutase (BioInsite)	pos/neg						--
Chlorite Dismutase (Microbial Insights_)	pos/neg						++
pH	SU	5.49	4.49	4.99	4.77	5.95	
Dissolved Oxygen	mg/L	1.50	2.00	1.50	1.00	4.00	
Oxidation-reduction potential	mV	132	216	212	196	167	

GM-3B	(Background well located ~600 to 800 feet upgradient the suspected source area)
GM-14M	(Source area well located adjacent to recovery well GM-14R)
GM-2B	(Downgradient well ~500 feet from the recovery well GM-14R)
GM-22S	(Downgradient shallow well ~3000 feet from recovery well GM-14R and <100 feet from Little Elk Creek)
GM-22M	(Downgradient well located ~3000 feet from recovery well GM-14R and <100 feet from Little Elk Creek)

4.3 Biochemical Oxygen Demand (BOD) Results

Table 4.3
BOD_6 Results, ATK Elkton

Wells	slope	intercept	R^2	k	Lo
	b	a		2.61(b/a)	1/(2.3*k*a3)
GM-14M	-0.0115	2.21	0.0224	-0.0136	-3
GM-2M	-0.0188	-0.498	0.0345	0.0987	-36

The 6-month BOD test was prepared on groundwater samples from GM-14M and GM-22M. GM-14 M was located in the source area while GM-22M is located downgradient of the source. In ambient groundwater from these wells, the starting nitrate concentrations were less than 10 mg/L, and the perchlorate concentrations were 1.2 and 0.19 mg/L. respectively (**Table 4.2**). The calculated L_o values presented in **Table 4.3** are negative indicating the ultimate BOD of groundwater in this area is below the detection limit of this method. This indicates a lack of bioavailable organic carbon in the groundwater that could be used by microorganisms to create anaerobic conditions favorable for the MNA of perchlorate.

4.4 Microcosm Results

Laboratory microcosms were constructed to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added organic substrates. With the TCE and perchlorate plume extending off to the south and east of US Route 40 and due to the implementation of a pump-and-treat system as an interim remedial measure at the downgradient site of GM-14S, microcosms were constructed with groundwater from monitor well GM-22S and sediment from soil boring SB-1, which was collected immediately adjoining GM-22S.

All the microcosms were tested for the changes in concentration with time of VC, methane, ethene, TCE, *cis*-DCE, DO, nitrate, sulfate, chloride, and perchlorate. For ATK Elkton, all microcosms showed TCE declining or not present along with the absence of *cis*-DCE, VC, methane and ethene except in EOS and carbon-amended microcosms where there occurred a sharp increase in *cis*-DCE and methane.

In Treatments 6 and 5, (i.e., the EOS and carbon-amended microcosms), DO, nitrate, and sulfate were consumed concurrently, indicating a rapid conversion to more optimal conditions for perchlorate degradation. As expected, perchlorate was degraded to below the analytical detection limit within 29 days. Substrate addition also stimulated conversion of TCE to *cis*-DCE. However, there was not further conversion to VC or ethene.

In the high perchlorate microcosms (Treatment 2), nitrate was reduced to below detection, while sulfate, chloride, and DO remained constant with time. The average perchlorate concentration declined from 5,400 µg/L to 1,416 µg/L or a 70% reduction over the one year incubation period. In one of the high perchlorate microcosms, perchlorate was reduced to below the detection limit. In the low and high perchlorate killed microcosms (Treatments 3 and 4), perchlorate, chloride, sulfate, and DO remained constant showing no biodegradation.

Average monitoring results from the low ambient microcosms are presented in **Charts 4.1 and 4.2** below. Nitrate declined first, followed by perchlorate which was reduced to below detection in all the microcosms by Day 121. Any measurable increase in chloride that may have resulted from the degradation of perchlorate was masked by the relatively high background chloride concentration in the microcosms. Sulfate increased somewhat in both the ambient live and ambient killed microcosms suggesting some sulfate release from the aquifer material. **Chart 4.3** shows the decrease in sum of electron acceptors (NO_3 and ClO_4) with time.

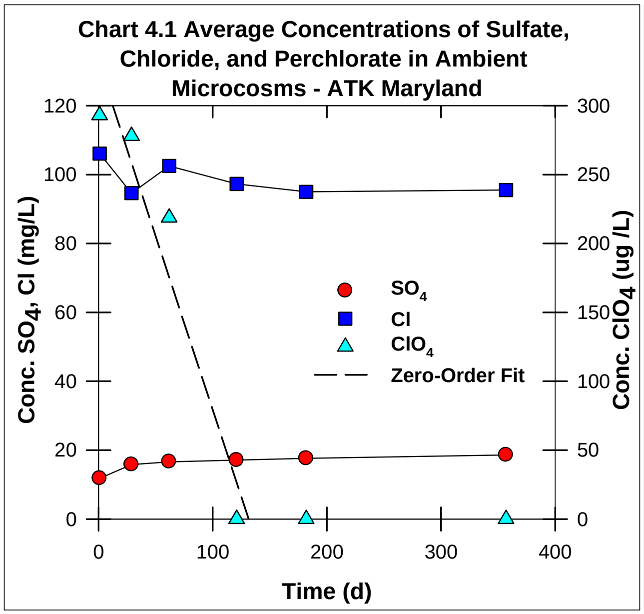


Chart 4.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms - ATK Maryland

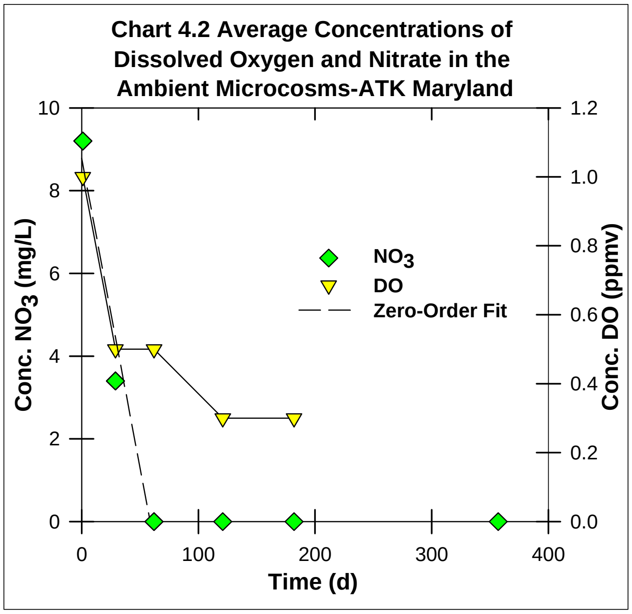


Chart 4.2 Average Concentrations of Dissolved Oxygen and Nitrate in the Ambient Microcosms-ATK Maryland

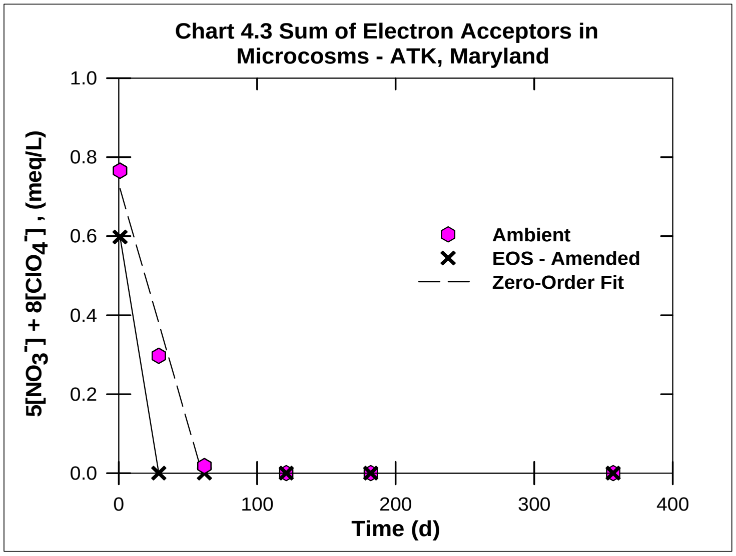


Chart 4.3 Sum of Electron Acceptors in Microcosms - ATK, Maryland

The experimental data were fitted to the kinetic model equations presented in Section 2.8. The results (**Charts 4.1 and 4.2**) indicated that the degradation of perchlorate and nitrate followed zero-order kinetics as the decreases in ClO_4 and NO_3 best fit Eq. 2. The straight line for sum of electron acceptors (**Chart 4.3**) also shows a good fit to the zero-order kinetic model. The degradation/removal rate constants for perchlorate, nitrate and sum of electron acceptors in ambient microcosms are shown in **Table 4.4**.

Table 4.4
Rate Constants from Ambient Treatment Microcosms
ATK Elkton

	Order	k	R^2
Perchlorate	Zero	0.92 mg L^{-1} y^{-1}	0.92
Nitrate	Zero	54.8 mg L^{-1} y^{-1}	0.96
Sum of Electron Acceptors	Zero	3.7 meq L^{-1} y^{-1}	0.96

4.5 Summary

In summary, the field monitoring results suggested that the geochemical conditions in most of the TCE/Perchlorate groundwater plume would not be conducive to anaerobic degradation of perchlorate. Although the CD enzyme assay run on sediment collected near GM-22S was positive indicating the presence of perchlorate-reducing microorganisms, the DO and ORP indicated unfavorable oxidizing conditions and the pH was generally below the range for optimal microbial activity. Nonetheless, perchlorate was eventually degraded under ambient conditions in the microcosms. It appears that the aquifer material collected near Little Elk Creek contained sufficient organic material to support degradation of 9 mg/L of nitrate and 300µg/L perchlorate. This suggests that if there is sufficient contact time, some portion of the perchlorate may be degraded naturally as it discharges to the stream.

5.0 Field and Laboratory Results - NSWC, Indian Head, MD

This section presents results from the field and laboratory studies conducted at Indian Head Division (IHDIV), Naval Surface Warfare Center (NSWC), Indian Head, Charles County, Maryland.

5.1 Background Information

Solutions-IES initially contacted personnel from the IHDIV for information about the Building 1419 site which was known to have historical perchlorate contamination. Mr. Carey Yates provided a report that was used as primary sources of information about the site (Cramer *et al*. 2004). The information is paraphrased below.

5.1.1 Location and Layout

The NSWC is located near Indian Head in Charles County, Maryland, and is approximately 30 miles south of Washington, DC. The Building 1419 site, also referred to as the Hog-out Facility, is located on the southeast side of the facility. The study area is located southeast of Building 1419 and consists of approximately 2 acres of grassy area containing a small drum storage building. The area is bordered to the southeast by Mattawoman Creek which is a large tributary to the Potomac River. Building 1419 is used to clean out or “hog-out” solid propellant containing ammonium perchlorate from various devices that have exceeded their useful life span including rockets and ejection seat motors. The hog-out process and former waste handling methods have impacted the groundwater near Building 1419.

A previous pilot study was conducted by Shaw Environmental, Inc. in this area to evaluate the biostimulation effect of lactate injection on *in situ* biodegradation of perchlorate (Cramer *et al*. 2004). The pilot system employed a recirculation cell design consisting of two small field areas (approximately 12 ft x 12 ft): a test area and a control area. In the test area, groundwater was extracted from the site, amended with lactate and a carbonate/bicarbonate pH buffer solution, and then re-injected into the aquifer. Groundwater was extracted and re-injected without substrate or buffer amendment in the control area. Approximately 20,000 gallons of amendment were recirculated over a 15-week period in 2002. The last sampling event occurred in December 2002. Lactate was shown to be an effective electron donor for stimulating anaerobic perchlorate biodegradation at this site.

As part of the present MNA evaluation, Solutions-IES collected groundwater samples from wells near the control area where lactate substrate was not injected and away from the pilot test area altogether where there was no opportunity for residual affects of the amendment to influence groundwater conditions.

5.1.2 Site Contaminants

Data from previous investigations was provided to Solutions-IES by Carey Yates and Dr. Randall Cramer of the NSWC. The historical data showed that perchlorate had been detected south of Building 1419 in concentrations ranging from 8 to 430 mg/L with an average concentration of approximately 170 mg/L.

Table 5.1 contains data obtained from an upgradient well (MW-1), a well in the presumed source area (MW-4) and a downgradient/crossgradient well (MW-2). These wells represent groundwater conditions in the area of interest for this project. **Figure 5.1** indicates the monitoring well locations, potentiometric surface and direction of groundwater flow at building 1419.

Table 5.1
Well Construction Details and Groundwater Conditions in Selected Wells
NSWC, Indian Head

Well ID	Well Depth (ft)	Screen Interval (ft-btoc)	Perchlorate (mg/L)	pH	Dissolved Oxygen (mg/L)
MW-1	17	7.0 – 17.0	84.7	5.0	1.49
MW-2	17	7.0 – 17.0	1.9	6.8	5.50*
MW-4	17	7.0 – 17.0	181	5.0	1.64

ft-btoc = feet below top of casing.
* = DO meter recalibrated – results may not reflect site conditions.
Data from February 2002.

5.1.3 Site Hydrology and Plume Geometry

The study area is located southeast of Building 1419 and is approximately 300 feet from the Mattawoman Creek. The surficial geology of the area was derived from soil samples collected from 17 Geoprobe borings and six test borings that ranged in depth from 16 to 20 ft bgs (Cramer *et al.* 2004). The top 2 to 4 feet consisted of fill material including organic material, gravel, and silty sand. The underlying 11 to 13 feet consisted of mottled light to olive brown clay to silt. The clay and sand fractions of the silts varied horizontally and vertically. Fine grained sand seams 1 to 2 inches in thickness were seen in many of the boring locations, but these seams were not continuous from boring to boring. At a depth of approximately 15 ft bgs, a 1 to 1.5 feet thick layer of sand and gravel was encountered. This layer was found to be continuous throughout the area. The sand and gravel layer is underlain by a gray clay layer, which extends to a depth of at least 20 ft bgs, the deepest extent of the direct push test borings. These are likely the clays of the Potomac Group.

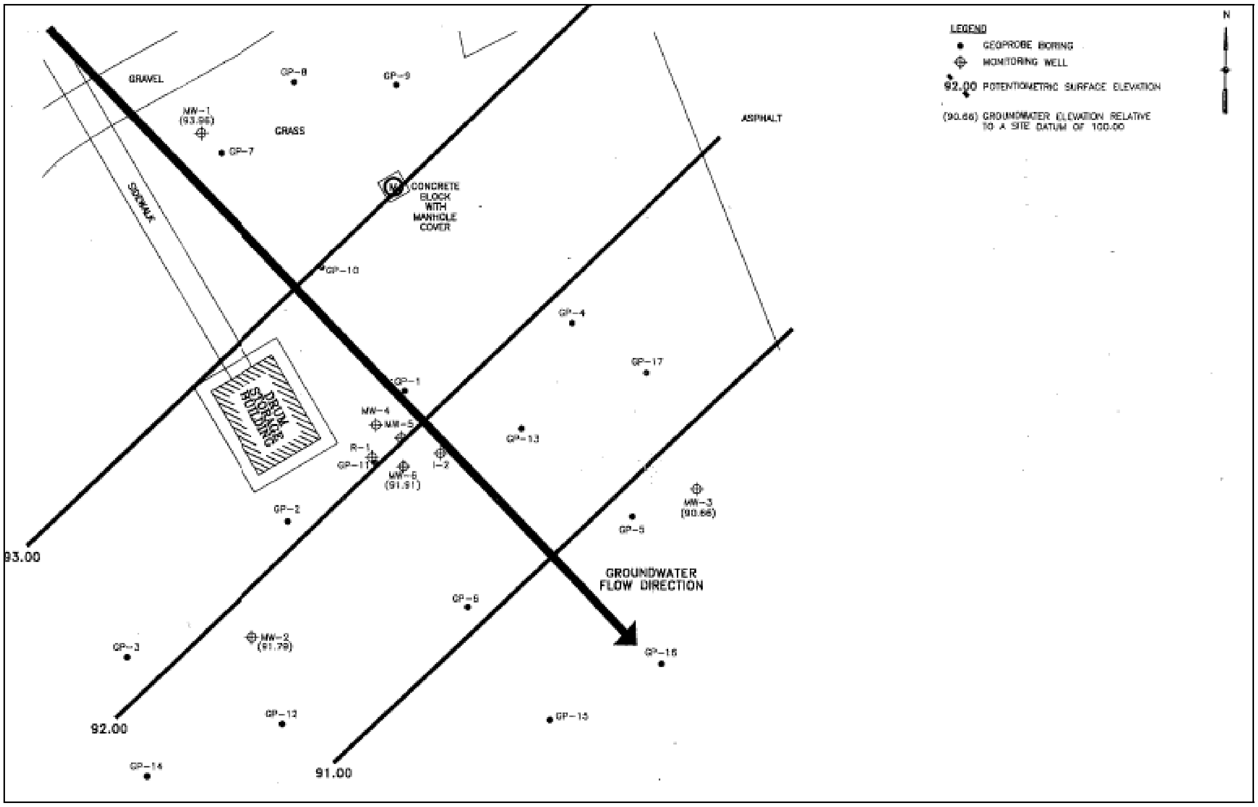


Figure 5.1 Groundwater Potentiometric Surface Map, NSWC, Indian Head

Groundwater elevations measured in the six monitoring wells in the field area indicated a groundwater flow direction to the southeast toward Mattawoman Creek (**Figure 5.1**). The flow direction basically follows the surface topography. Depth to groundwater ranged from approximately 6.5 to 10.25 ft bgs. The average hydraulic gradient, as measured between wells MW-1 and MW-3, was 0.023 ft/ft, indicating a flat topography.

The geometry of the perchlorate plume (**Figure 5.2**) appears to follow the derived groundwater flow direction. However, the plume does not clearly indicate a release source area, nor is it delineated to the northwest or southeast. The plume is at least 200 feet long from northwest to southeast and approximately 55 feet wide from southwest to northeast at its widest point.

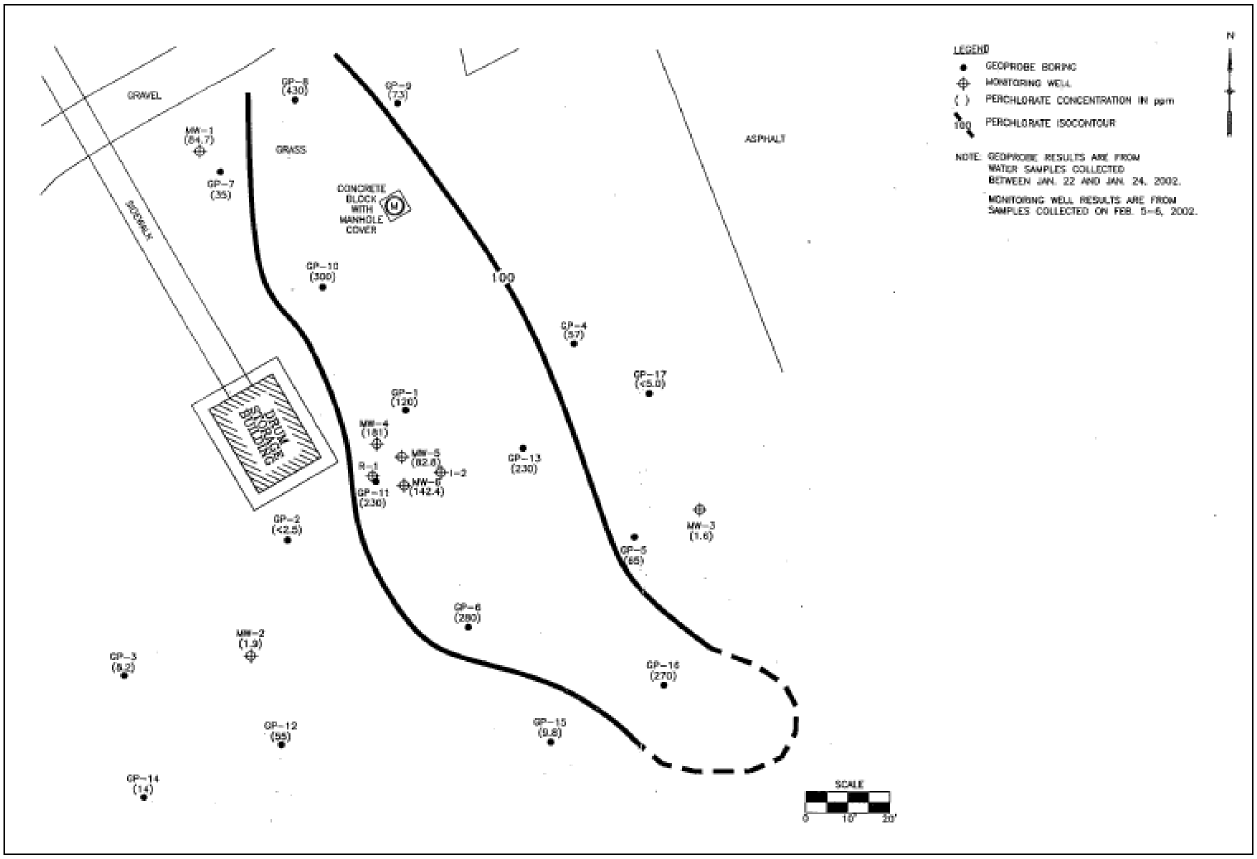


Figure 5.2 Groundwater Perchlorate Distribution, NSWC, Indian Head

5.2 Biogeochemical Characterization

Based on the data provided by the base, three monitor wells were sampled to provide a general characterization of biogeochemical conditions in the aquifer. The wells were selected to cover the range of biogeochemical conditions at the site including highly contaminated locations, moderately contaminated locations, and relatively low contaminated locations. Representative groundwater conditions at the site are summarized in **Table 5.2**.

Table 5.2
Summary of Groundwater and Sediment Analytical Results
NSWC, Indian Head

	units	MW-1	MW-4	MW-2		
Relative Location		Upgradient	Source	Down/crossgradient	SB-MW-2	SB-MW-4
Perchlorate	µg/L	BS	BS	BS	NT	NT
Dichloromethane	µg/L	5.0	13.0	BQL	NT	NT
1,1-Dichloroethene	µg/L	BQL	BQL	BQL	NT	NT
trans-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	NT	NT
Dichloroethane	µg/L	BQL	BQL	BQL	NT	NT
cis-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	NT	NT
Chloroform	µg/L	BQL	BQL	BQL	NT	NT
1,1,1-Trichloroethane	µg/L	BQL	BQL	BQL	NT	NT
Carbon tetrachloride	µg/L	BQL	BQL	BQL	NT	NT
Trichloroethene	µg/L	BQL	BQL	BQL	NT	NT
Tetrachloroethene	µg/L	BQL	BQL	BQL	NT	NT
Vinyl Chloride	µg/L	BQL	BQL	BQL	NT	NT
Chloroethane	µg/L	BQL	BQL	BQL		
Chloromethane	µg/L	BQL	BQL	BQL		
Total CVOCs	µg/L	5.0	13.0	0.0		
Ethane	µg/L	BQL	BQL	BQL	NT	NT
Ethene	µg/L	BQL	BQL	BQL	NT	NT
Methane	µg/L	15.7	80.2	BQL	NT	NT
Total Organic Carbon	mg/L	2.24	2.23	4.36	3500*	240*
Chloride	mg/L	16.1	11.3	1.40	NT	NT
Nitrate	mg/L	113	8.70	2.30	NT	NT
Sulfate	mg/L	38.0	116	64.2	NT	NT
Phosphate	mg/L	BQL	BQL	BQL	NT	NT
Chlorite Dismutase (BioInsite)	pos/neg					
Chlorite Dismutase (Microbial Insights_)	pos/neg	NT	NT	NT	+++	+/-
pH	SU	4.9	5.4	6.9	NT	NT
Dissolved Oxygen	mg/L	1.0	8.0	3.5	NT	NT
Oxidation-reduction potential	mV	113	6.00	>-1000	NT	NT

*filtered sample

5.3 Biological Oxygen Demand (BOD) Results

Biochemical oxygen demand tests were not conducted for the NSWC, Indian Head site.

5.4 Microcosm Results

Laboratory microcosms were constructed to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added organic substrates. The Building 1419 site was previously used to clean out or “hog out” solid propellant containing ammonium perchlorate from various devices and groundwater was known to contain relatively high concentrations of perchlorate. No co-contaminants had been reported. The initial plan included collecting soil samples by hand augering in the grassy area approximately 60 feet southeast of Building 1419. However, a gravel layer was encountered few feet below grade and soil samples could not be obtained. Consequently, microcosms were constructed with groundwater containing suspended sediment slurry collected from the bottom of monitor well MW-2.

All the microcosms were tested for the changes in concentration with time of methane, DO, nitrate, sulfate, chloride, and perchlorate. Since no co-contaminants had been reported, TCE, *cis*-DCE, ethene, and VC were below detection in the groundwater used to prepare the Indian Head microcosms.

In the microcosms treated with EOS and added carbon (i.e., Treatments 6 and 5), sulfate declined to below detection limits with a concurrent increase in methane. At the same time, perchlorate was reduced to below detection limits within 34 days demonstrating that microorganisms capable of perchlorate reduction are present at the site and, with the addition of electron donor, can be stimulated effectively to rapidly degrade perchlorate.

Perchlorate and electron acceptor concentrations remained constant over time in the low perchlorate killed microcosms (Treatment 3), indicating the observed reduction in perchlorate and nitrate in ambient microcosms was due to biological activity. In one of the three high concentration incubations, perchlorate has dropped from 5,200 µg/L to below detection in one year.

Charts 5.1 and 5.2 show average concentrations of sulfate, perchlorate, chloride, DO and nitrate with time in the low perchlorate ambient microcosms (Treatment 1). In two of the three replicates, nitrate decreased to below detection followed by perchlorate within 34 days whereas in third replicate, it took 188 days to completely degrade perchlorate and nitrate. However, there was no evidence of sulfate reduction or a concurrent increase in chloride associated with perchlorate degradation. **Chart 5.3** shows a decrease in sum of electron acceptors (NO_3 and

ClO_4) with time in ambient microcosms compared with the microcosms stimulated with EOS.

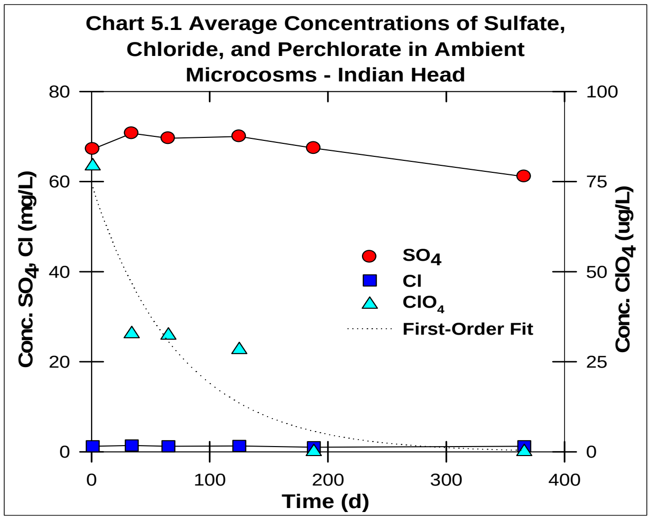


Chart 5.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms - Indian Head

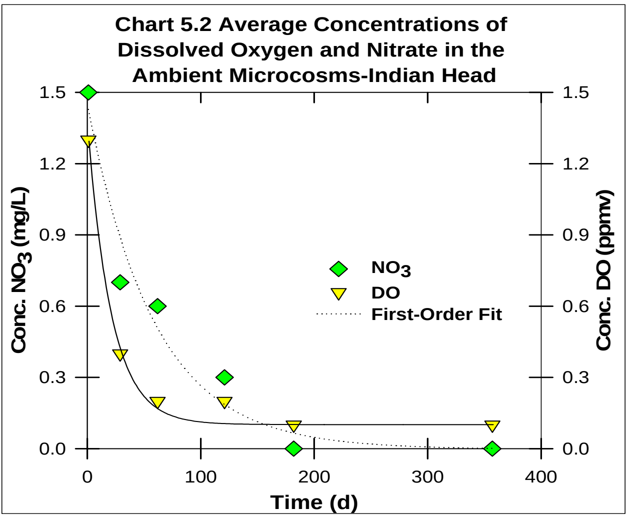


Chart 5.2 Average Concentrations of Dissolved Oxygen and Nitrate in the Ambient Microcosms-Indian Head

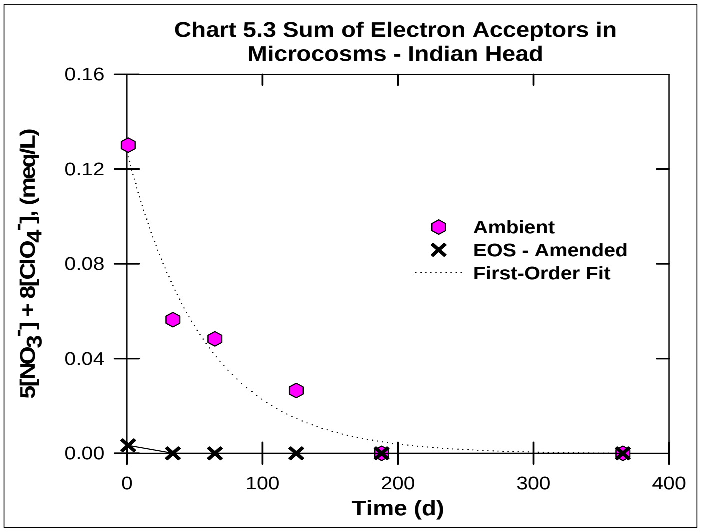


Chart 5.3 Sum of Electron Acceptors in Microcosms - Indian Head

The first order expression, $[C] = [C_0]e^{-kt}$ provides a good fit to the observed decreases in perchlorate (**Chart 5.1**), nitrate (**Chart 5.2**), and sum of electron acceptors (**Chart 5.3**). The degradation/removal rate constants for perchlorate, nitrate and sum of electron acceptors in ambient microcosms are shown in **Table 5.3**.

Table 5.3
Rate Constants from Ambient Treatment Microcosms
NSWC, Indian Head

	Order	k	**R^2**
Perchlorate	First	5.1 y-1	0.89
Nitrate	First	6.2 y-1	0.96
Sum of Electron Acceptors	First	6.2 y-1	0.96

5.5 Summary

The field monitoring results from the Indian Head Building 1419 site suggest the presence of measurable dissolved oxygen in the groundwater, but the ORP measurements vary widely from strongly oxidative to very reducing. The pH also varies across the site with no apparent correlation with distance from the source or proximity to Mattawoman Creek. The CD enzyme assay on sediments from the site, along with the positive results in the biostimulation microcosm treatments, support the presence of perchlorate reducing microorganisms in the aquifer. The TOC was low in groundwater, but elevated in the sediment samples. In the low perchlorate ambient microcosms constructed with a sediment slurry obtained from one well, nitrate and perchlorate were depleted in all the three replicates suggesting potential for natural perchlorate biodegradation to occur. The corresponding killed control microcosms showed no change over time further supporting the potential that natural biological attenuation was the mechanism responsible for the observed changes. Despite the variability of some important field conditions, the observed decrease of perchlorate in the plume from the source toward Mattowoman Creek suggests that there is a good potential for MNA of perchlorate at this site.

6.0 Field and Laboratory Results - Stennis Space Center, MS

This section presents results from the field and laboratory studies conducted at Area H of the John C. Stennis Space Center (SSC), Hancock County, Mississippi.

6.1 Background information

Solutions-IES initially contacted personnel from SSC in September of 2004 about the potential for including SSC in the MNA investigation. Ms. Jenette Gordon was identified as the site contact for Area H and provided three reports prepared by Foster Wheeler Environmental Corporation as primary sources of information about the site**.** A fact sheet prepared by SSC (SSC 2004) provided additional useful information about the site. The information is paraphrased below.

6.1.1 Location and Layout

Area H of the SSC is located approximately 48 miles northeast of New Orleans, LA. Area H, also referred to as Energetic Materials Test Facility (EMTF), includes approximately 200 acres of the northeast quadrant of SSC, and is located at the intersection of Main Line Road and Bombing Range Road (**Figure 6.1**). Explosives testing began at Area H as early as World War II and continued up until 1991 when explosive test activities were halted. The site is still inactive and is controlled by the National Aeronautics and Space Administration (NASA). Most of the site is covered with grass, some small plants, and young trees.

Eight monitoring wells were installed in the vicinity of Area H (**Figure 6.2**). Most of these wells were installed in a portion of Area H-known as “ground zero area” in the upper water bearing zone (WBZ-1). Perchlorate was not detected in monitoring wells installed in the lower water bearing zone (WBZ-2). The wells of interest for the current study include 30-06MW located upgradient of the perchlorate plume and 30-02MW, 30-05MW, 30-13MW, and 30-15MW located within the perchlorate plume. The wells of interest were drilled with hollow stem augers or installed using direct-push technology by others as part of previous assessments for SSC unrelated to the current project.

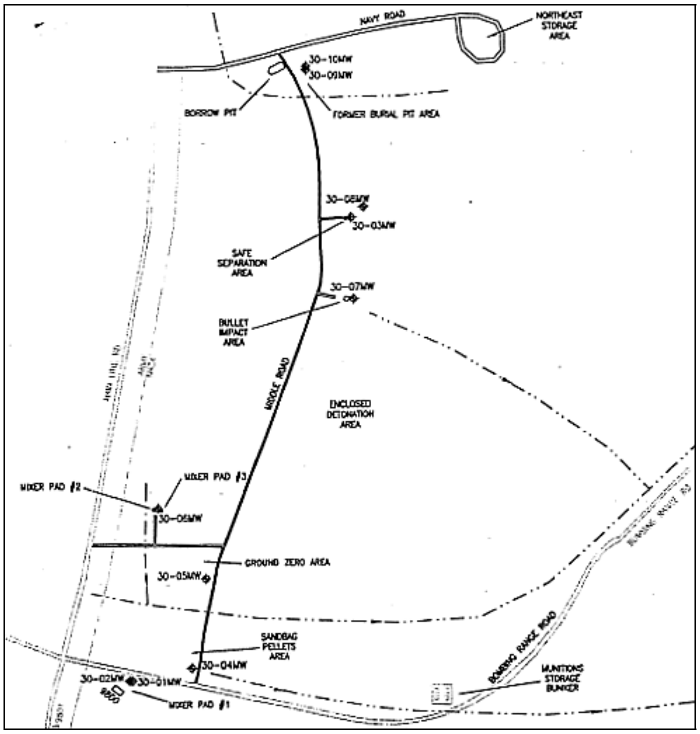


Figure 6.1 Location and Layout of Area H, Stennis Space Center

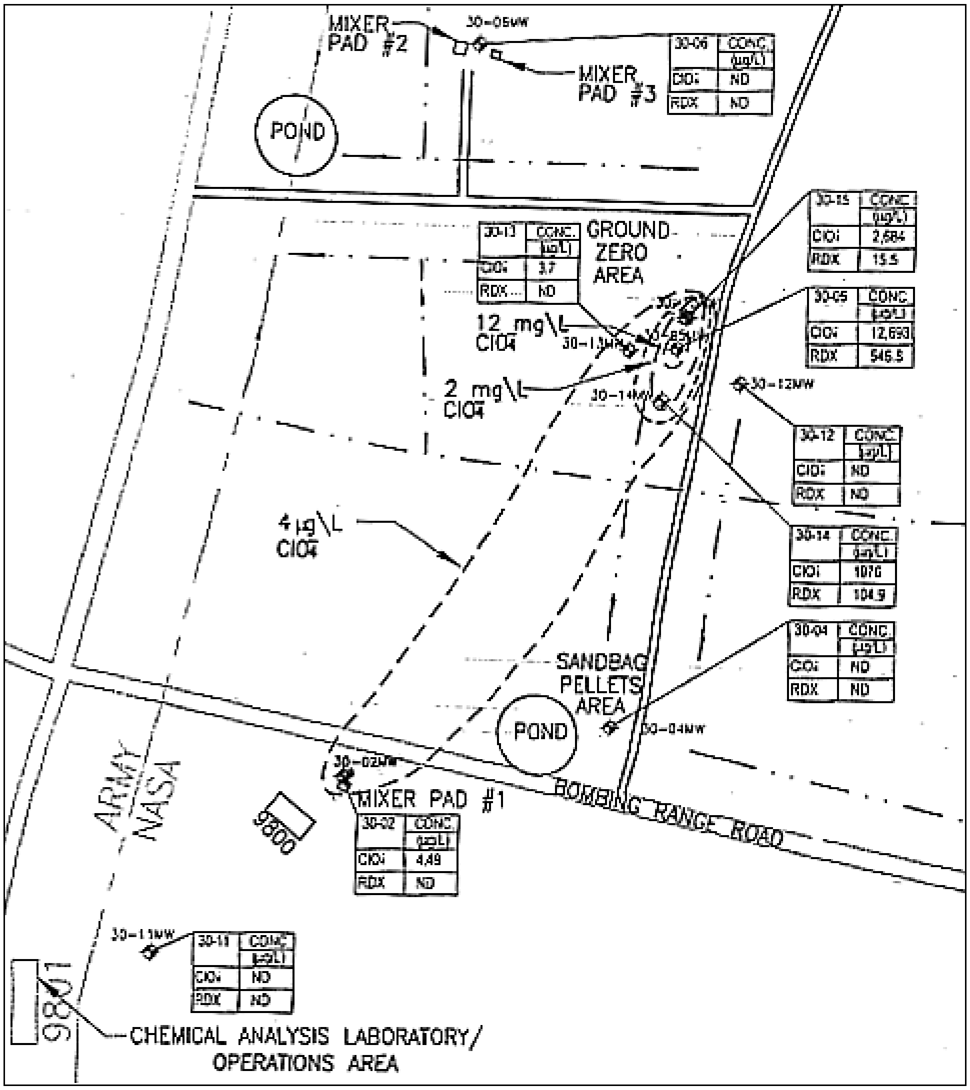


Figure 6.2 Location of Monitoring Wells in Area H, Stennis Space Center

6.1.2 Site Contaminants

Perchlorate has been detected at Area H in concentrations ranging from 3.7 to 12,693 µg/L. Previous investigations showed that various explosive compounds such as 2,6-dinitrotoluene (2,6-DNT) and cyclonite (RDX) have also been detected in the vicinity of Area H along with low concentrations of volatile and semi-volatile organics compounds. Concentrations of perchlorate (12,693 µg/L) and RDX (546 µg/L) tend to decrease as they move from the “ground zero area” toward “mixer pad #1” to concentrations of approximately 4.49 µg/L and non-detect, respectively (Figure 6.2). **Table 6.1** summarizes data obtained from an upgradient well (30-06MW), a well in the presumed source area (30-05MW) and a downgradient well near “mixer pad # 1” (30-02MW). These wells represent groundwater conditions across the area of interest for this project.

Table 6.1
Representative Groundwater Conditions in Area H
Stennis Space Center

	Units	30-06MW	30-05MW	30-02MW
		(Upgradient)	(Source)	(Downgradient)
	Date	April & May 2000	April & May 2000	April & May 2000
Explosives				
Perchlorate	µg/L	0.7 u	12,693	4.49
RDX	µg/L	65.7 u	546.8	65.7 u
2,6-DNT	µg/L	4.3 u	13.4	4.3 u
Inorganic Anions				
Chloride (total)	mg/L	4.64	17.4	13.2
Nitrate & Nitrite	mg/L	0.16 u	0.18	0.157 u
Sulfate (total)	mg/L	0.31	21.6	1.41
Iron (dissolved)	mg/L	1.73	3.52	0.008
Manganese (dissolved)	mg/L	0.02	0.05	1.37
Semi – Volatile and Volatile Organic Compounds				
bis (2-Ethylhexyl) phthalate	µg/L	10 u	150	10 u
1,1,2-Trichlorotrifluoroethane	µg/L	15 u	15 u	155
Additional				
TDS	mg/L	71.	127.	38.

6.1.3 Site Hydrology and Plume Geometry

Borings advanced in Area H indicate the presence of a clay or silty stratum from land surface to a depth of approximately 10 feet below land surface. This stratum is generally dark brown and moist, and contains various amounts of sand. The water table is usually encountered in this stratum. A sand or silty sand is usually encountered after the clay/silty stratum, and is typically 10 to 12 feet in thickness, and referred to as WBZ-1. The monitoring wells of interest were installed into WBZ-1. A second clay stratum ranging from 5 to 25 feet in thickness and then, a second sand stratum (WBZ-2) is typically encountered after WBZ-1. Three monitoring wells were in WBZ-2. Perchlorate was not detected in WBZ-2, and so groundwater conditions in WBZ-2 were not considered for sampling activities at the site. Groundwater flow in WBZ-1 is poorly defined and appears to fluctuate between the northwest, southwest, and southeast. The perchlorate plume geometry is illustrated in **Figure 6.2**. The plume appears to be approximately 740 feet long from northeast to southwest and 124 feet wide from northwest to southeast at its widest point.

6.2 Biogeochemical Characterization

Based on the data provided by the base, five monitor wells were selected to provide characterization of biogeochemical conditions in the aquifer. The wells appear to cover the range of biogeochemical conditions at the site including highly contaminated locations, moderately contaminated locations, and relatively uncontaminated background locations. Representative groundwater conditions at the site are summarized in **Table 6.2**.

Overall, the groundwater appeared slightly oxidative with DO ranging from 0.2 to 1.0 mg/L and ORP between +36 and +119 mV. The pH range from 4.8 to 5.2 was below the optimal range for microbial activity. TOC concentrations in sediment slurry samples from wells 30-02MW and 30-05MW were low, measuring <1 and 1.1 mg/L, respectively. Perchlorate concentrations in samples collected in 2005 were similar to previous measurements. Solutions-IES did not analyze for RDX or 2,6-DNT, but did not find VOCs or semi-VOCs as co-contaminants. The CD enzyme assay was only marginally positive for perchlorate-reducing microorganisms.

Table 6.2 Field Monitoring Results in Area H– January 26, 2005 Stennis Space Center						
	units	30-06MW	30-05MW	30-02MW	30-13MW	30-15MW
Relative Location		Upgradient	Source	Downgradient		
Perchlorate	µg/L	<5	53,600	<5	<5	649
Dichloromethane	µg/L	BQL	BQL	BQL	BQL	BQL
1,1-Dichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
trans-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Dichloroethane	µg/L	BQL	BQL	BQL	BQL	BQL
cis-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Chloroform	µg/L	BQL	BQL	BQL	BQL	BQL
1,1,1-Trichloroethane	µg/L	BQL	BQL	BQL	BQL	BQL
Carbon tetrachloride	µg/L	BQL	14	BQL	BQL	BQL
Trichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Tetrachloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Vinyl Chloride	µg/L					
Chloroethane	µg/L					
Chloromethane	µg/L					
Total CVOCS	µg/L	0	14	0	0	0
Ethane	µg/L	NT	NT	NT	NT	NT
Ethene	µg/L	NT	NT	NT	NT	NT
Methane	µg/L	NT	NT	NT	NT	NT
Total Organic Carbon	mg/L	<1.0	1.08	<1.0	1.9	1.81
Chloride	mg/L	4.6	20.6	7.1	8.5	9.2
Nitrate	mg/L	BQL	1.3	BQL	BQL	BQL
Sulfate	mg/L	1.8	9.5	1.1	1.4	10.8
Phosphate	mg/L	BQL	BQL	BQL	BQL	BQL
Chlorate Dismutase (BioInsite)	pos/neg	NT	positive	Negative	NT	NT
Chlorite Dismutase (Microbial Insights)	pos/neg	NT	+	+-	NT	NT
pH	SU	5.08	4.79	5.2	5.23	5.1
Dissolved Oxygen	mg/L	1	0.2	0.5	1	1

6.3 Biological Oxygen Demand (BOD) Results

The 6-month BOD test was prepared on groundwater samples from 30-02MW and 30-05MW. Monitor well 30-05MW was located in the source area while 30-02MW is located downgradient of the source. In ambient groundwater from these wells, the starting nitrate concentrations were less than 1.3 mg/L. However, perchlorate concentrations were very different in these two wells: 53.6 mg/L in the source and below detection at the downgradient loction (**Table 6.2**). The ultimate BOD (L_o) in the source area well 30-02MW is negative indicating the groundwater BOD in this area was below the detection limit. This also suggests a lack of available organic carbon in the groundwater that could be used by microorganisms to create anaerobic conditions favorable for the MNA of perchlorate. However, downgradient, there was some measurable BOD indicating some potential for anaerobic biodegradation of perchlorate.

Table 6.3
BOD$_6$ Results
Stennis Space Center

Wells	slope	intercept	R^2	k	Lo
	b	a		2.61(b/a)	1/(2.3*k*a3)
02-MW	0.00750	1.59	0.834	0.0123	8.8
05-MW	-0.00471	-1.02	0.00590	0.0121	-34

6.4 Microcosm Results

Laboratory microcosms were constructed to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added organic substrates. With the previous investigations defining the perchlorate plume to wells 30-06MW, 30-02MW, 30-05MW, 30-13MW, and 30-15MW coupled with the site access restriction, it was not possible to obtain large amounts of sediment for microcosm construction. Consequently, microcosms were constructed with groundwater containing only suspended sediment collected from the bottom of monitor well 30-02MW.

All the microcosms were tested for the changes in concentration with time of DO, nitrate, sulfate, chloride, and perchlorate. Due to the absence of VOC co-contaminants, VC, methane, ethene, TCE and *cis*-DCE were not examined.

The EOS and added-carbon microcosms (Treatments 6 and 5) showed signs of perchlorate biodegradation with perchlorate and sulfate reducing to below detection in the absence of nitrate (**Charts 6.1 and 6.2**). The removal of alternative electron acceptors was coupled with no measurable changes to the concentration of chloride. This may be attributed to the difference in detection limits between perchlorate (µg/L) and chloride (mg/L).

No changes to the monitored parameters were observed in the high perchlorate ambient microcosms (Treatment 2) and high perchlorate killed microcosms (Treatment 4). Some decrease in DO was noted in both of these treatments, but the amount of scatter associated with the DO results implied some analytical anomalies associated with measuring this parameter.

The low perchlorate killed control microcosms (Treatment 3) showed no significant loss of perchlorate in any of the replicate bottles. In the low perchlorate ambient microcosms (Treatment 1) one of the replicates proceeded to non-detect after 357 days incubation and an average 55% reduction in perchlorate concentration was observed (**Charts 6.3 and 6.4**). **Chart 6.5** shows the decrease in sum of electron acceptors (NO_3 and ClO_4) with time for EOS-amended and ambient microcosms.

Chart 6.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in EOS Microcosms - Stennis Space Center

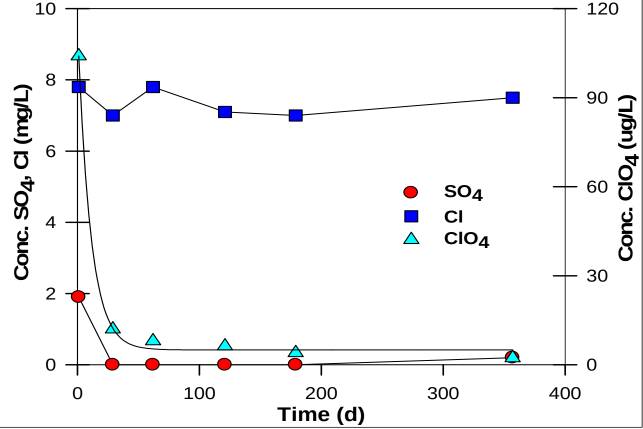


Chart 6.2 Average Concentrations of Nitrate and Dissolved Oxygen in EOS Microcosms- Stennis Space Center

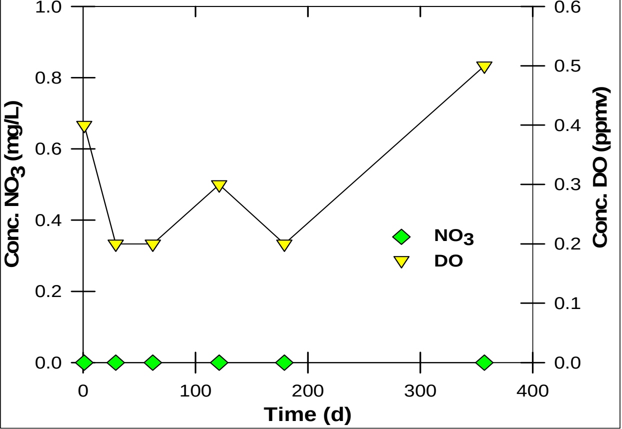


Chart 6.3 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms - Stennis Space Center

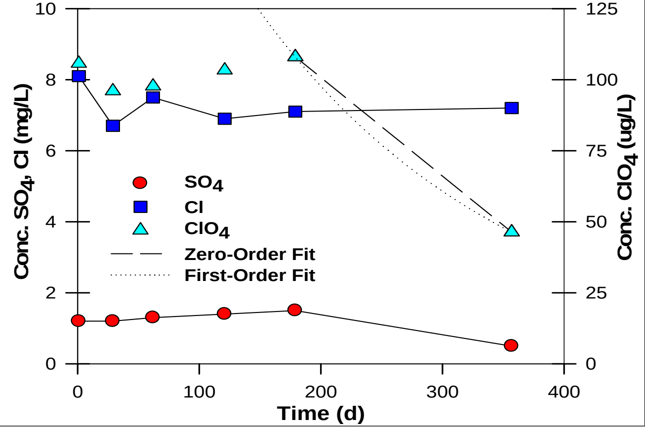


Chart 6.4 Average Concentrations of Nitrate and Dissolved Oxygen in Ambient Microcosms - Stennis Space Center

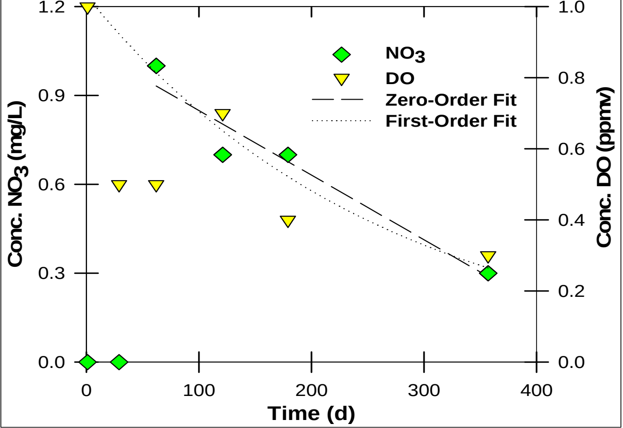
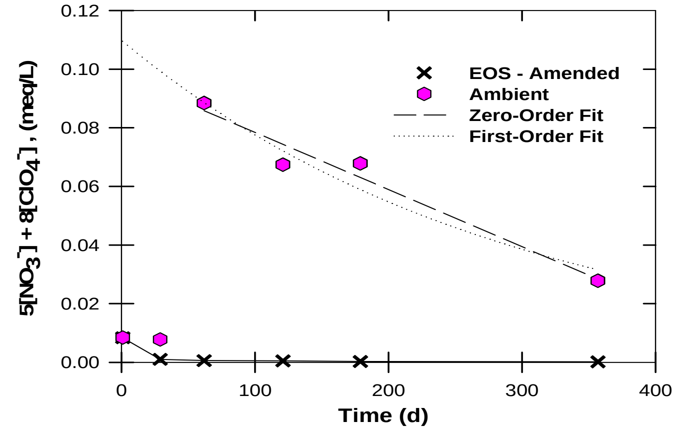


Chart 6.5 Sum of Electron Acceptors in Microcosms - Stennis Space Center



As illustrated in **Chart 6.3**, no perchlorate degradation was observed up to 200 days in the low-perchlorate ambient microcosms, but there was a notable decrease in its concentration thereafter. The zero order equation was fitted to the last two data points for perchlorate to get the degradation rate constant (**Chart 6.3**). Initially there occurred an increase in nitrate concentration from zero to 1.0 mg/L. Nitrate degradation was observed from Day 62 onwards. Thus, the regression line indicating zero-order kinetics was fitted to nitrate data from Day 62 onwards including four data points (**Chart 6.4**). Similarly, the regression line indicating zero-order was fitted to sum of electron acceptors from Day 62 onwards (**Chart 6.5**). The first order expression, $[C] = [C_0]e^{-kt}$) also provides a good fit to the observed decreases in perchlorate (**Chart 6.3**), nitrate (**Chart 6.4**), and sum of electron acceptors (**Chart 6.5**). The degradation/removal rate constants for perchlorate, nitrate and sum of electron acceptors in ambient microcosms are shown in **Table 6.4**.

Table 6.4
Rate Constants from Ambient Treatment Microcosms
Stennis Space Center

	Order	k	R^2
Perchlorate	Zero	0.13 mg L-1 y-1	Not applicable
Nitrate	Zero	0.80 mg L-1 y-1	0.94
Sum of Electron Acceptors	Zero	0.07 meq L-1y-1	0.96
Perchlorate	First	1.75 y-1	1.00
Nitrate	First	1.39 y-1	0.95
Sum of Electron Acceptors	First	1.28 y-1	0.94

6.5 Summary

In summary, the field monitoring results indicate groundwater conditions with limited potential to support natural attenuation via anaerobic biodegradation of perchlorate. Although there are no CVOC co-contaminants, there is evidence of RDX and 2,6-DNT in the groundwater. In laboratory microcosms, perchlorate degradation could be stimulated by adding organic substrate and an average of more than 50% perchlorate was degraded over the one year incubation period. One replicate bottle showed complete degradation of perchlorate in 357 days but no degradation was observed at the higher starting perchlorate concentration. Overall, this site is not a strong candidate for demonstrating the potential for monitored natural attenuation of perchlorate in groundwater.

7.0 Field and Laboratory Results – Redstone Arsenal, AL

This section presents results from the field and laboratory studies conducted at OU-1, Redstone Arsenal (RSA), Alabama.

7.1 Background Information

Solutions-IES initially contacted personnel from RSA to obtain information about areas impacted by perchlorate releases. Mr. Wes Smith was identified as the site contact and he asked Shaw Environmental, Inc. (Shaw) to work with Solution-IES to provide information regarding OU-10. Shaw forwarded information pertinent to the MNA investigation, much of which is paraphrased in the sections below.

7.1.1 Location and Layout

RSA is located approximately 10 miles southwest of Huntsville, AL. OU-10 includes approximately 1979 acres of RSA (**Figure 7.1**), and is located south of Huntsville Spring Branch, and north of the Tennessee River. During the 1940s, Redstone Ordnance Plant (ROP) and subsequently, Redstone Arsenal Rocket Engine (RARE) North Plant were located within the OU-10 area. The ROP was used to produce chemical ammunition, bursters, and chemical bombs. In 1945, the ROP was placed on standby, and munitions production was put on hold. In 1949, rocket research and development began at RSA. Soon thereafter, solid-rocket-motor production began. The degreasing of mechanical parts and equipment was common during production at RARE North Plant, and significant historical releases of chlorinated solvents have occurred as a result of the degreasing operations. Toward the end of the 47-year production history at RARE North Plant, ammonium perchlorate-based solid rocket motors were produced at the RARE North Plant. Solid rocket motor production ceased at RSA in 1996.

Many monitoring wells have been installed in the vicinity of OU-10 in an effort to characterize site conditions and assess contamination documented to exist at RSA (Figure 7.1 & Figure 7.2). Shaw provided a table that summarizes preliminary MNA data collected from 12 monitoring wells located in the vicinity of OU-10. MNA parameters were not collected at other monitoring well locations at OU-10. Some of these monitoring wells were installed into the overburden, others into the interface between the overburden and bedrock, and few into the bedrock. After reviewing the information provided, Solutions-IES identified the wells of interest for the current study to include RS717 (interface), RS966 (overburden), and RS1203 (interface). RS717 is located near one of the source areas, and RS966 and RS1203 are located near ponds located southeast of RSA 96 (**Figure 7.2**).

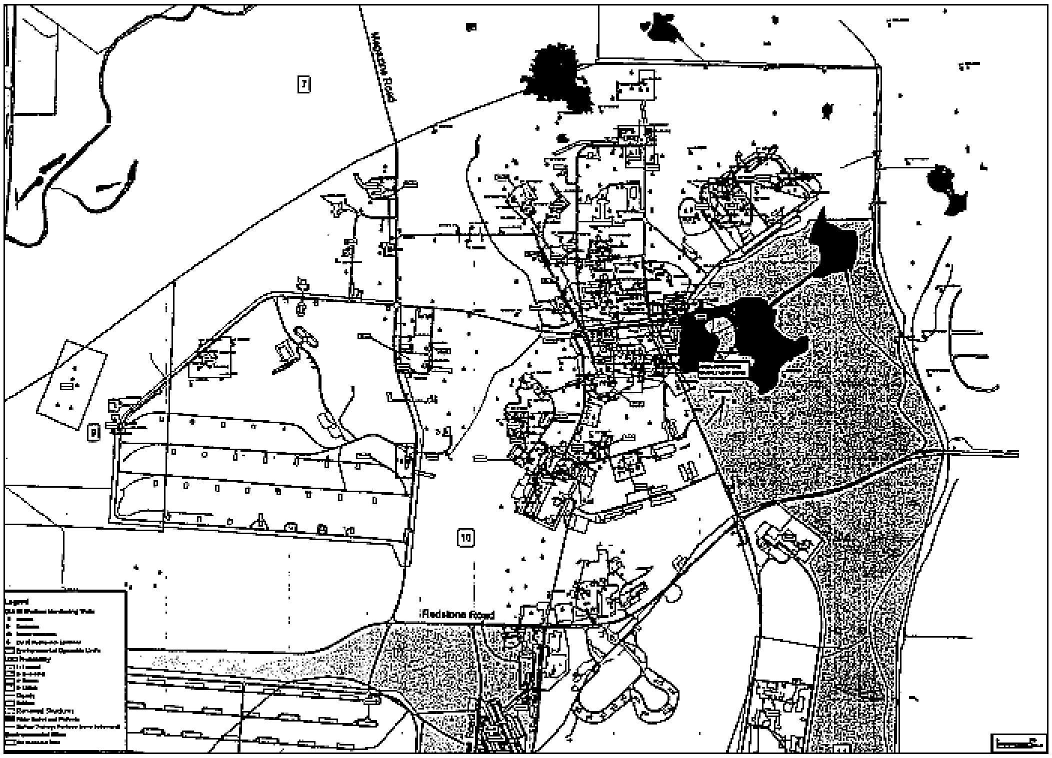


Figure 7.1 Location of OU-10 at Redstone Arsenal

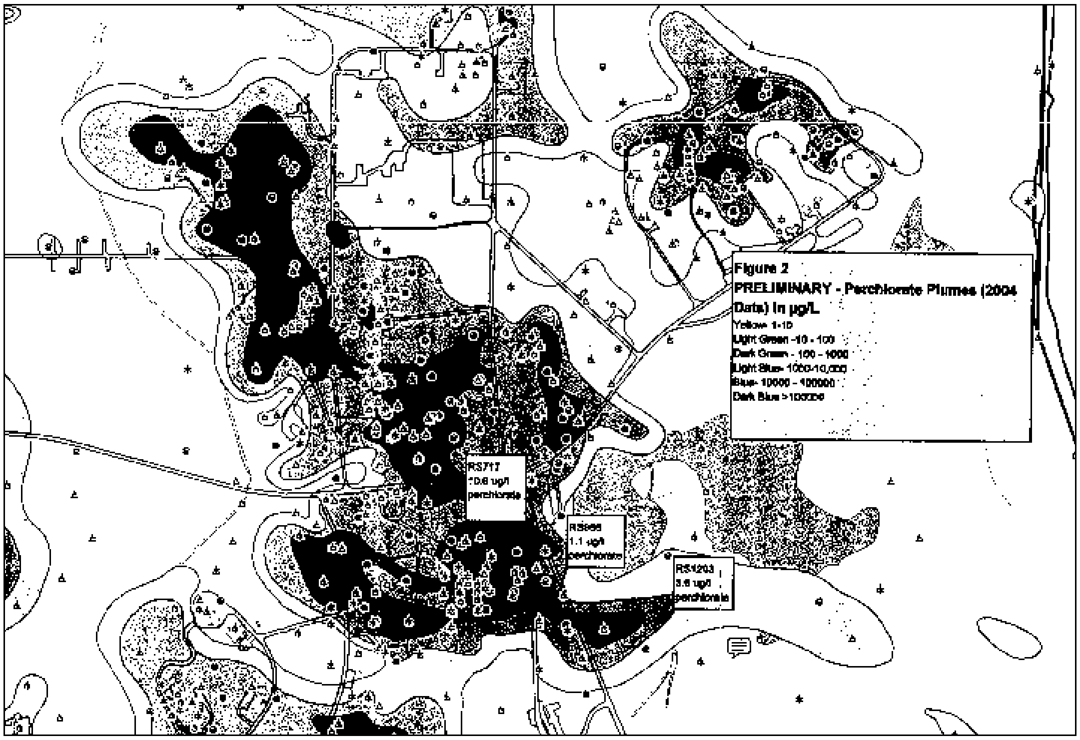


Figure 7.2 Well Locations at OU-10, Redstone Arsenal

7.1.2 Site Contaminants

Previous investigations showed that chlorinated solvents have been released to the groundwater in the vicinity of OU-10. TCE has been documented at concentrations greater than 10,000 μg/L in the source area. As a result of solid-rocket-motor production, perchlorate has been detected in groundwater at concentrations ranging from 1 to greater than 100,000 μg/L in the source areas. Concentrations of perchlorate tend to decrease as they move east away from the ROP/RARE North Plant area toward the pond (**Figure 7.1**). **Table 7.1** summarizes representative recent analytical results of groundwater samples collected from monitoring wells S717, RS966, and RS1203.

Table 7.1
Representative Groundwater Conditions at OU-10
Redstone Arsenal

	Units	RS717	RS966	RS1203
		(source area)	(pond area)	(pond area)
	Date	10/28/2003	11/17/2003	11/18/2003
Explosives				
Perchlorate	μg/L	10.6	1.1	3.6
Trichloroethene	μg/L	3.9	11	11
cis-1,2-Dichloroethene	μg/L	NA	16	170
Inorganic Anions				
Nitrate	mg/L	1.8	BQL	BQL
Sulfate	mg/L	1	BQL	BQL
Ferric Iron	mg/L	0.16	0.27	0.43
Manganese	mg/L	BQL	2.5	0.5

7.1.3 Site Hydrogeology and Plume Geometry

OU-10 is underlain by middle to upper Tuscumbia Limestone with well-developed karst features. OU-10 contains slightly topographically higher areas that form minor groundwater divides within otherwise low-gradient surroundings. Depths to bedrock are highly variable over short lateral distances, due to solutional weathering of the upper bedrock surface.

The lithologic logs from soil and well borings indicate that below the engineered fill are unconsolidated soils consisting of predominantly low to medium plasticity clay with varying amounts of silt and fine- to medium-grained sand. Based on auger refusal, thickness of the residual soils (overburden) ranges from approximately 23 ft to greater than 90 ft, similar to the range of overburden thickness observed throughout OU-10. Chert and limestone fragments found in the clay matrix are residuals from weathering of the cherty limestone bedrock. The amount of residual material increases with depth, and abundant residual chert and limestone fragments are found overlying the limestone bedrock.

Groundwater at RSA occurs in both the unconsolidated overburden and bedrock, primarily as a single, unconfined water table aquifer. Groundwater surfaces mimic topography to some extent in OU-10; however, at RSA-96 topography is subdued, and the natural potentiometric surface is relatively flat.

7.2 Biogeochemical Characterization

Based on the historical data provided by the Shaw on behalf of RSA, three monitor wells were selected to provide a general characterization of biogeochemical conditions in the aquifer. The wells appear to cover the range of biogeochemical conditions at the site including moderately contaminated locations near the presumed source, and locations with minimal perchlorate concentrations in swampy downgradient areas. Groundwater conditions at the site are summarized in **Table 7.2**.

Overall, the groundwater was oxygen-rich in the source area (DO = 5 mg/L) and less oxidative (0.15 to 1.0 mg/L) in the swampy areas downgradient. The ORP correlated with this observation being oxidative (+313 mV) in the source area but strongly reducing in the swamp. The pH varied from 5.4 to 7.8. Concentrations of alternative electron acceptors, nitrate and sulfate, were very low and chloride was also low. The range of perchlorate concentrations and VOCs were similar in the samples collected by Solutions-IES in 2005 compared to those reported by Shaw from 2003. The CD enzyme assay was positive for perchlorate-reducing microorganisms in groundwater from RSA-966. .

Table 7.2
Field Monitoring Results – March 8-9, 2005
Redstone Arsenal

Relative Location	Units	“upgrade. of swamp”	swampy	swampy	
		RS717	RS966	RS1203	RS966-soil
Perchlorate	µg/L	6.40	3.50	16.8	
Dichloromethane	µg/L	BQL	1	BQL	
1,1-Dichloroethene	µg/L	BQL	BQL	BQL	
trans-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	
Dichloroethane	µg/L	BQL	BQL	BQL	
cis-1,2-Dichloroethene	µg/L	BQL	129	71	
Chloroform	µg/L	BQL	BQL	BQL	
1,1,1-Trichloroethane	µg/L	BQL	BQL	BQL	
Carbon tetrachloride	µg/L	BQL	BQL	BQL	
Trichloroethene	µg/L	BQL	179	100	
Tetrachloroethene	µg/L	BQL	BQL	BQL	
Vinyl Chloride	µg/L	BQL	BQL	BQL	
Chloroethane	µg/L	BQL	BQL	BQL	
Chloromethane	µg/L	BQL	BQL	BQL	
Total CVOCs	µg/L	0	309	171	0
Ethane	µg/L	BQL	BQL	BQL	
Ethene	µg/L	BQL	BQL	BQL	
Methane	µg/L	BQL	155	BQL	
Total Organic Carbon	mg/L				
Chloride	mg/L	1.30	2.90	10.7	
Nitrate	mg/L	<0.5	<0.5	<0.5	
Sulfate	mg/L	4.60	4.50	2.40	
Phosphate	mg/L	<1.0	<1.0	<1.0	
	mg/L				
Chlorite Dismutase (BioInsite)	pos/neg				
Chlorite Dismutase (Microbial Insights)	pos/neg		++		
pH	SU	5.42	6.33	7.53	
Dissolved Oxygen	mg/L	5.00	0.15	1.00	
Oxidation-reduction potential	mV	313	-1200	<-800	

7.3 Biochemical Oxygen Demand (BOD) Results

The 6-month BOD test was prepared on groundwater samples from RS1203 and RS966. Both wells are located in swampy areas of the site, downgradient of the source. In ambient groundwater from these wells, there was no measurable nitrate and less than 16 µg/L perchlorate (**Table 7.2**). The ultimate BOD (L_o) values shown in **Table 7.3** indicate the groundwater contains some bioavailable organic carbon that could be used by microorganisms to create anaerobic conditions favorable for the MNA of perchlorate. This might be expected from a “swampy” area. The relatively high BOD values and the low rate constants suggest that microorganisms are present within site matrices that can slowly utilize the dissolved organic carbon. This may explain the absence of perchlorate in this groundwater.

Table 7.3
BOD_6 Results
Redstone Arsenal

Wells	slope	intercept	R^2	k	Lo
	b	a		2.61(b/a)	1/(2.3*k*a3)
RS1203	0.00601	1.57	0.747	0.00997	11
RS966	0.00769	1.61	0.668	0.0125	8.4

7.4 Microcosm Results

All the microcosms were tested for the changes in concentration with time of VC, methane, ethene, TCE, *cis*-DCE, DO, nitrate, sulfate, chloride, and perchlorate.

In the EOS-amended microcosms (**Charts 7.1 and 7.2**), DO, sulfate, and perchlorate declined to below detection within 30 days. The consumption of all available electron acceptors was coupled with a substantial increase in methane from 133 ppm to 350,000 ppm over the one year incubation period. TCE was converted to *cis*-DCE in these incubations followed by subsequent depletion of the *cis*-DCE and production of ethane.

In the carbon-amended microcosm, perchlorate declined to below detection within 30 days accompanied by the reduction in dissolved oxygen and the absence of nitrate suggesting the presence of an active population of perchlorate degraders. TCE was converted to *cis*-DCE followed by subsequent depletion of the *cis*-DCE.

In the high perchlorate microcosms, perchlorate declined by 70-75% reduction over the one year incubation period with perchlorate declining below detection in one replicate. Nitrate was also reduced below detection with a concurrent decrease in the dissolved oxygen. In the high perchlorate killed microcosms, there was no significant change in most electron acceptors.

In the low perchlorate (ambient) microcosms (**Charts 7.3 and 7.4**), perchlorate declined to below the analytical detection limit within 184 days, with somewhat slower perchlorate degradation in one bottle. This was accompanied by a steady decline in nitrate. **Chart 7.5** shows the decrease in sum of electron acceptors (NO_3 and ClO_4) with time for EOS-amended and ambient microcosms. There was no significant loss of perchlorate in the low perchlorate killed microcosms indicating the loss in the ambient microcosms was due to biodegradation.

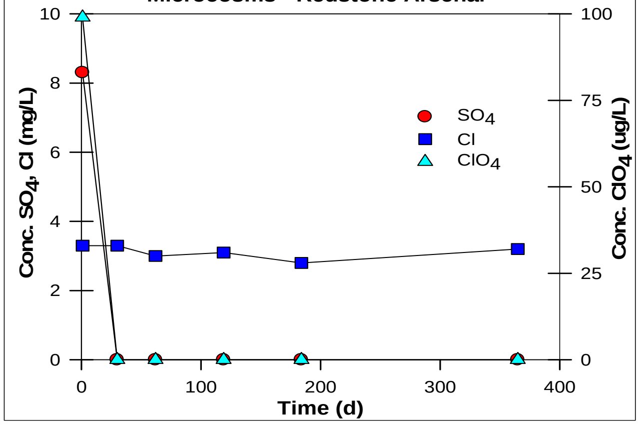


Chart 7.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in EOS Microcosms - Redstone Arsenal

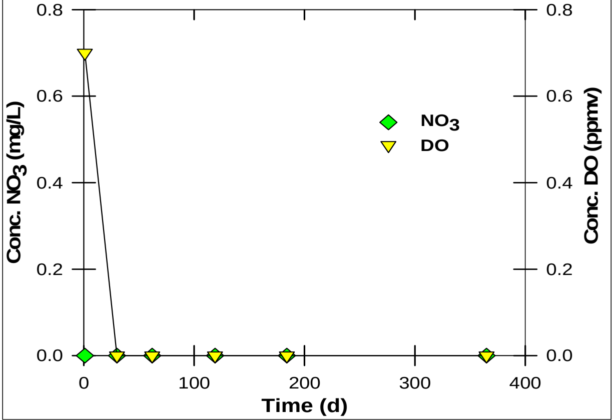


Chart 7.2 Average Concentrations of Nitrate and Dissolved Oxygen in EOS Microcosms- Redstone Arsenal

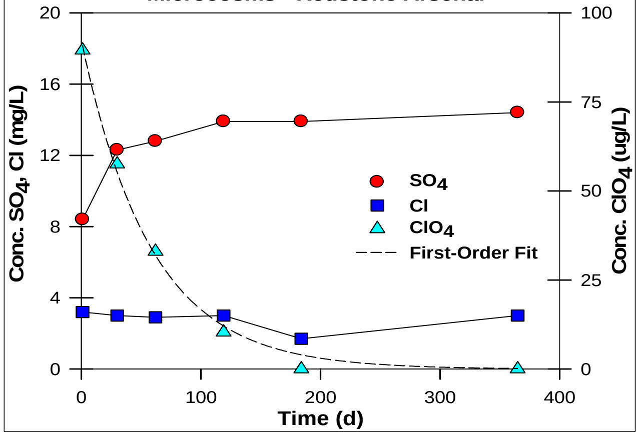


Chart 7.3 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms - Redstone Arsenal

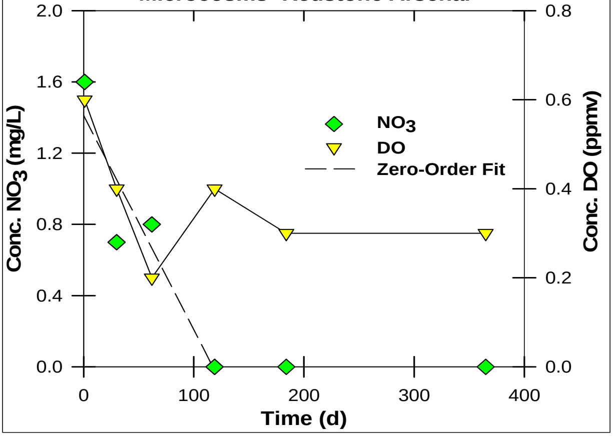
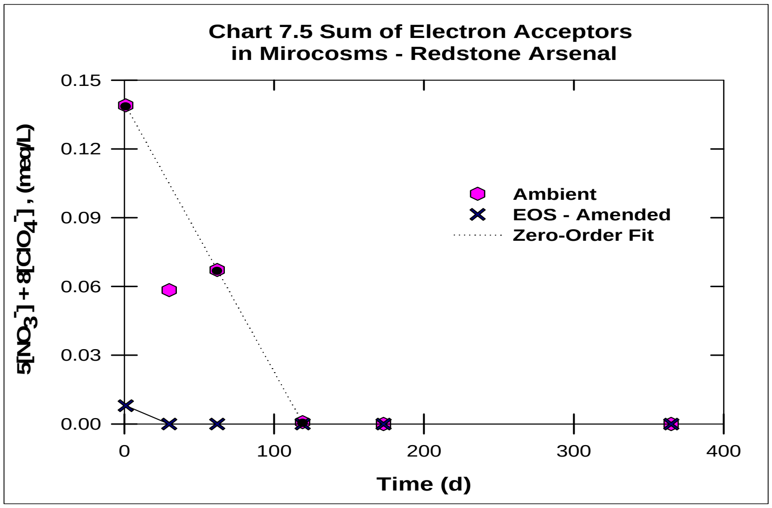


Chart 7.4 Average Concentrations of Nitrate and Dissolved Oxygen in Ambient Microcosms- Redstone Arsenal



The first order expression, $[C] = [C_0]e^{-kt}$ provides a good fit to the observed decrease in perchlorate (**Chart 7.3**). The straight line for nitrate (**Chart 7.4**) and sum of electron acceptors (**Chart 7.5**) show a good fit to the zero-order kinetic model used in Eq. 2. The degradation/removal rate constants for perchlorate, nitrate and sum of electron acceptors in ambient microcosms are shown in **Table 7.4**.

Table 7.4
Rate Constants from Ambient Treatment Microcosms
Redstone Arsenal

	Order	k	R^2
Perchlorate	First	7.3 y^{-1}	0.996
Nitrate	Zero	3.6 mg L^{-1} y^{-1}	0.86
Sum of Electron Acceptors	Zero	0.44 meq L^{-1} y^{-1}	0.999

7.5 Summary

In summary, the field monitoring results indicate good potential for the anaerobic degradation of perchlorate at the RSA site. The plume appears to discharge into a swampy area of the site. Although groundwater from this area is not characterized by elevated TOC, the DO and ORP are reduced in this portion of the site and there is a limited presence of alternative electron acceptors to compete with perchlorate degradation. Concentrations of perchlorate away from the source are very low and the CD enzyme assay suggests the presence of perchlorate reducing microorganisms in the environment.

In the ambient condition microcosms, perchlorate was reduced to below detection in 184 days. The presence of perchlorate-reducing microorganisms was further confirmed by the rapid reduction in perchlorate in substrate amended incubations. The 6-month BOD results show the groundwater contains significant levels of bioavailable natural organic carbon. These results indicate there is a significant potential for MNA of perchlorate at RSA OU-10.

8.0 Field and Laboratory Results – ATK Thiokol, UT

This section presents results from the field and laboratory studies conducted at the Promontory Site, ATK Thiokol, Inc., Box Elder County, Utah.

8.1 Background information

Solutions-IES initially contacted personnel from ATK Thiokol about the potential for including the Promontory site in the MNA investigation. Mr. John Holladay was identified as the site contact for ATK and provided historical information, background and logistical support concerning the site: The information is paraphrased below.

8.1.1 Location and Layout

The Promontory site at ATK Thiokol is located approximately 25 miles west of Brigham City, Box Elder County, Utah. NASA space shuttle rocket motors and other defense and propulsion systems are developed, built, and tested at this location. The wells of interest for the current study include C-6 located on the upgradient fringe of the perchlorate plume, B-4 and C-1 located near the source area, and F-2 and F-3 located downgradient of the source area near Blue Creek (**Figure 8.1**). The wells of interest were drilled by air rotary or cable tool.

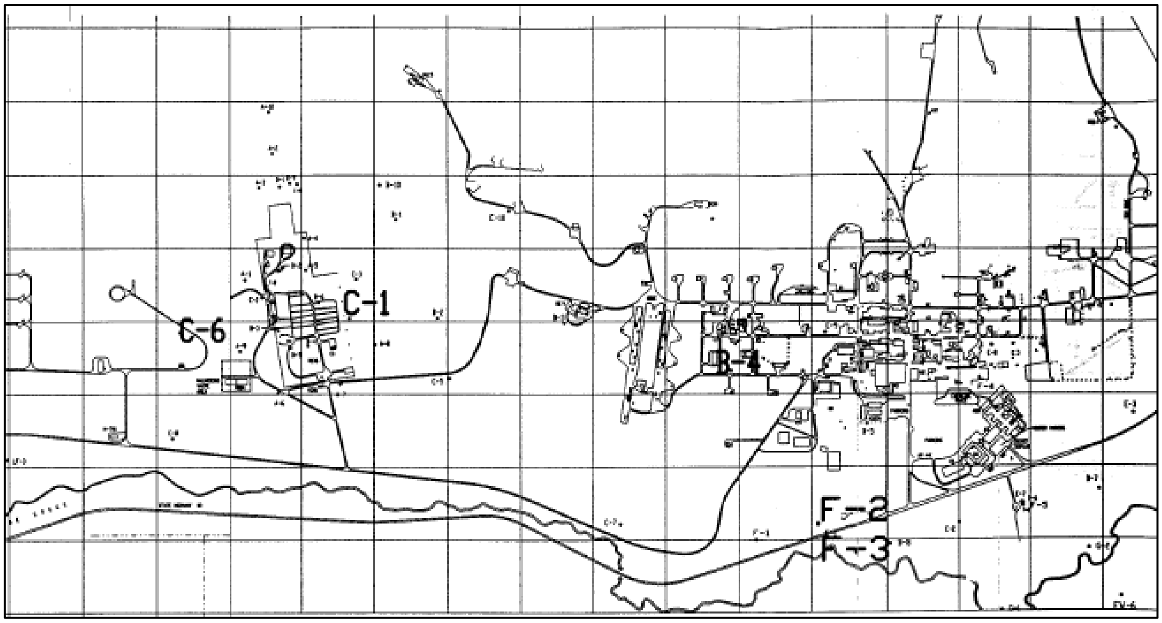


Figure 8.1 Site Layout at ATK Thiokol

8.1.2 Site Contaminants

There are two major sources of perchlorate contamination at ATK Thiokol which include 1) a historic burning ground where waste perchlorate was placed in an impoundment and washed into the subsurface between 1956 and 1988, and 2) a Minuteman washout facility which operated in the 1960s and early 1970s where propellant from waste Minuteman motors was washed out of cases. The washout water from the facility then flowed into three successive impoundments where the perchlorate-laden water entered the subsurface.

Previous investigations showed that chlorinated solvents and perchlorate have been detected in groundwater at the ATK Thiokol facility. The TCE concentration in groundwater ranges from 1 to 5,000 μg/L, and the *cis*-DCE concentration ranges from 1 to 300 μg/L. Perchlorate has also been detected at concentrations ranging from 1 to 50,000 μg/L.

Table 8.1 summarizes the most recent data obtained from an upgradient well (C-6), a well near the presumed source area (C-1) and a downgradient well (F-3) near Blue Creek. These wells represent groundwater conditions across the area of interest for this project (**Figure 8.1**). **Figure 8.2** is representative of historical perchlorate concentration gradients at the ATK Thiokol site.

Table 8.1
Representative Groundwater Conditions
ATK Thiokol

	Units	**C-6 (Upgradient)**	**C-1 (Source)**	**F-3 (Downgradient)**
Perchlorate	μg/L	9.4	4,930	2,260
Trichloroethene	μg/L	6.8	974	149
Cis-1,2-dichloroethene	μg/L	<10	369	<5
Vinyl Chloride	μg/L	<10	<10	<10
Anions				
Sulfate	mg/L	101	74	NT
Nitrate	mg/L	1.9	1.1	NT

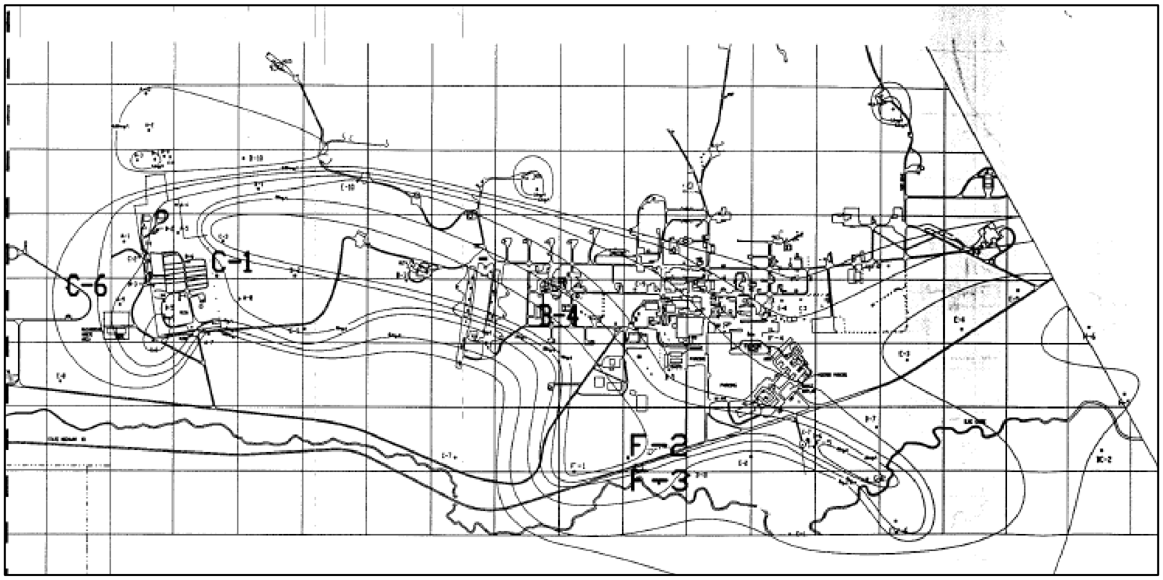


Figure 8.2 Extent of Perchlorate Plume and Well Locations at ATK Thiokol

8.1.3 Site Hydrology and Plume Geometry

The aquifer lithology generally consists of fractured carbonates, with some karst features, and allochthonous thrust in the Mesozoic. There is also some alluvial fan material and some laminated lacustrine deposits in the vicinity of Blue Creek. Based on boring logs provided by ATK Thiokol, shallow soil can consist of various mixtures of sand, silt, clay, and gravel eventually shifting to limestone. Groundwater is generally encountered in the limestone fractures.

Based on the appearance of the perchlorate contamination plume, groundwater generally tends to flow to the east-southeast. The estimated plume dimensions are 22,000 feet by 4,000 feet, and the depth to water ranges from 0 to 250 ft bgs. The perchlorate plume geometry is illustrated in **Figure 8.2**.

8.2 Biogeochemical Characterization

Based on the historical information provided by the base, five monitor wells were chosen to be sampled to provide a current overview of biogeochemical conditions in the aquifer. The wells selected appear to cover the range of biogeochemical conditions at the site including highly contaminated locations, moderately contaminated locations, and relatively uncontaminated background locations. Monitoring data from prior sampling events are summarized in **Table 8.1**.

Table 8.2 summarizes results of groundwater sampling conducted at the site by Solutions-IES personnel in May 2005. Perchlorate concentrations were very high in four wells either in or downgradient of the source. There was also evidence of co-contamination by chlorinated VOCs, particularly TCE, *cis*-DCE, 1,1,1-TCA and dichloromethane. There was < 1.9 mg/L TOC in the groundwater, but there were higher amounts of nitrate (avg. = 17 mg/L) and sulfate (avg. = 140 mg/L). These anions can potentially interfere with natural attenuation of perchlorate. The DO and ORP suggest oxidative, or at best weakly reducing, conditions across the site.

Table 8.2
Field Monitoring Results- April 13-14, 2005
ATK Thiokol

	Units	**C-6**	**C-1**	**F-3**	**B-4**	**B6**
Relative Location		Upgradient	Source	Downgradient		
Perchlorate	µg/L	16	76,000	3,900	84,000	47,000
Dichloromethane	µg/L	BQL	130	11	170	240
1,1-Dichloroethene	µg/L	BQL	BQL	BQL	8	BQL
trans-1,2-Dichloroethene	µg/L	BQL	BQL	3	BQL	3
Dichloroethane	µg/L	BQL	12	BQL	12	10
cis-1,2-Dichloroethene	µg/L	BQL	310	8	18	48
Chloroform	µg/L	BQL	180	BQL	BQL	35
1,1,1-Trichloroethane	µg/L	BQL	410	15	190	300
Carbon tetrachloride	µg/L	BQL	39	BQL	21	BQL
Trichloroethene	µg/L	5	1,100	160	2,000	3,000
Tetrachloroethene	µg/L	BQL	1	BQL	BQL	BQL
Vinyl Chloride	µg/L	BQL	BQL	BQL	BQL	BQL
Chloroethane	µg/L	BQL	BQL	BQL	BQL	BQL
Chloromethane	µg/L	BQL	BQL	BQL	BQL	BQL
Total CVOCs	µg/L					
Ethane	µg/L	BQL	BQL	BQL	BQL	BQL
Ethene	µg/L	BQL	BQL	BQL	BQL	BQL
Methane	µg/L	BQL	BQL	BQL	BQL	BQL
Total Organic Carbon	mg/L	<1.00	<1.00	<1.0	1.9	1.62
Molybdenum	mg/L	0.0068	0.0073	0.018	0.018	NT
Nitrate	mg/L	8	9	4	46	19
Sulfate	mg/L	94	72	190	160	190
Phosphate	mg/L	<10	<10	<10	<10	<10
Chlorite Dismutase (BioInsite)	pos/neg					
Chlorite Dismutase (Microbial Insights_) DNA testing	pos/neg					

Because of site logistics, new soil samples were not collected. Instead, sediment samples were collected by pumping from the bottom of wells F-3 and B-4. TOC concentrations in the sediment samples from these wells were also low, reported at 1.59 mg/L for F-3 and 4.18 mg/L for B-4. The CD enzyme assay was run on the sediment samples and indicated that perchlorate reducing microorganisms were present in sediment material.

8.3 Biological Oxygen Demand (BOD) Results

The 6-month BOD test was conducted on groundwater samples from monitor wells B4 and F3. Both wells are located downgradient of the source. The background nitrate in F3 was 9 mg/L, but the nitrate in B4 was 46 mg/L. The were also significant differences in perchlorated concentrations between these two wells with 3.9 mg/L perchlorate in F3 and 84 mg/L perchlorate in B4 (Table 8.2). The ultimate BOD (L_o) results shown in **Table 8.3** for ATK Thiokol suggest the presence of available dissolved organic carbon in groundwater from B4 and F3. The low rate constants suggest the presence of an active microbial community capable of utilizing the background dissolved organic material in the groundwater, but the slow rate may be responsible for the continuing presence of elevated concentrations of perchlorate downgradient of the source.

Table 8.3
BOD_6 Results
ATK Thiokol

Wells	slope	intercept	R^2	k	Lo
	b	a		2.61(b/a)	1/(2.3*k*a3)
B4	0.00333	1.64	0.413	0.0053	18.6
F3	0.00503	1.53	0.591	0.0086	14.2

8.4 Microcosm Results

Laboratory microcosms were constructed to evaluate the rate and extent of perchlorate biodegradation under ambient conditions and with added organic substrates. However, microcosms were not spiked with additional perchlorate because the ambient levels were already fairly high (2,620 µg/L in ambient Treatment 1).

All the microcosms were tested for the changes in concentration with time of VC, methane, ethene, TCE, *cis*-DCE, DO, nitrate, sulfate, chloride, and perchlorate. TCE was depleted in all live incubations (both substrate amended and ambient). However, substantial levels of *cis*-DCE, VC and ethene were not detected. Large amounts of methane accumulated in the EOS-amended incubations.

In the EOS-amended microcosms (Treatment 6), perchlorate was depleted by Day 30 (starting concentration = 2,550 µg/L) followed by removal of sulfate by Day 64 (**Chart 8.1**). **Chart 8.2** shows that nitrate was absent throughout the incubation period. The degradation of perchlorate may have made some small contribution to the increase in chloride between startup and Day 30, but the increase is more likely attributable to analytical variability since the chloride concentration in all killed and live treatments increased proportionately during the same period.

Under ambient conditions (Treatment 1), the perchlorate declined from 2,620 µg/L to below detection in 30 days (**Chart 8.3**). The sulfate concentration remained relatively constant over the one year incubation period. There was no nitrate at the start and throughout the incubation (**Chart 8.4**). In the corresponding killed microcosms (Treatment 3), there was no loss of perchlorate during the same period indicating the loss in Treatment 1 was likely due to natural biodegradation. **Chart 8.5** shows a very rapid decrease in sum of electron acceptors with time in ambient and EOS-amended microcosms.

Chart 8.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in EOS Microcosms - ATK, Thiokol

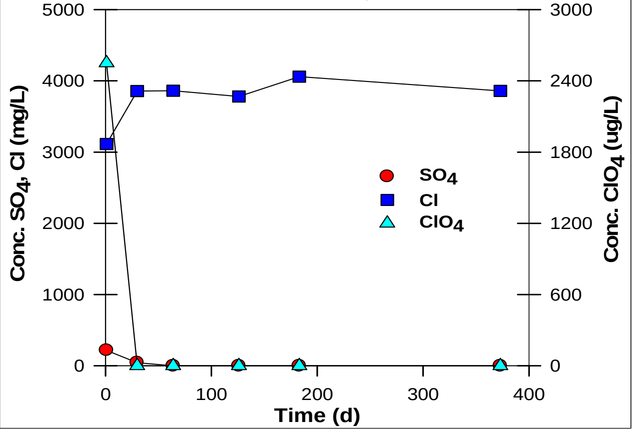
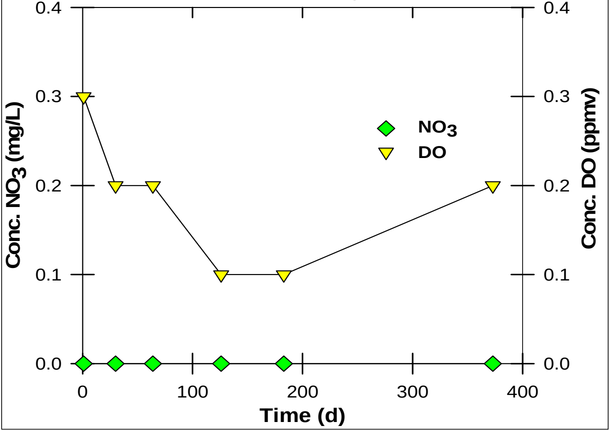


Chart 8.2 Average Concentrations of Nitrate and Dissolved Oxygen in EOS Microcosms - ATK, Thiokol



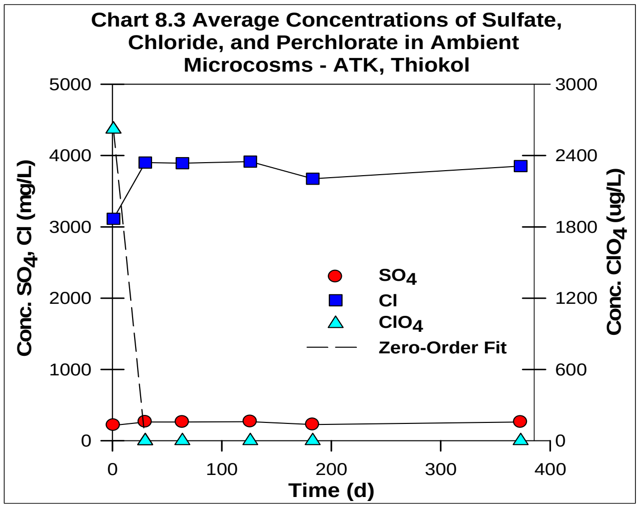


Chart 8.3 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms - ATK, Thiokol

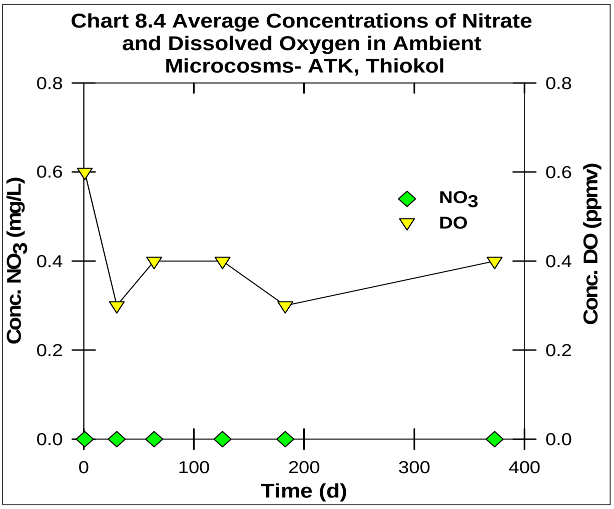


Chart 8.4 Average Concentrations of Nitrate and Dissolved Oxygen in Ambient Microcosms- ATK, Thiokol

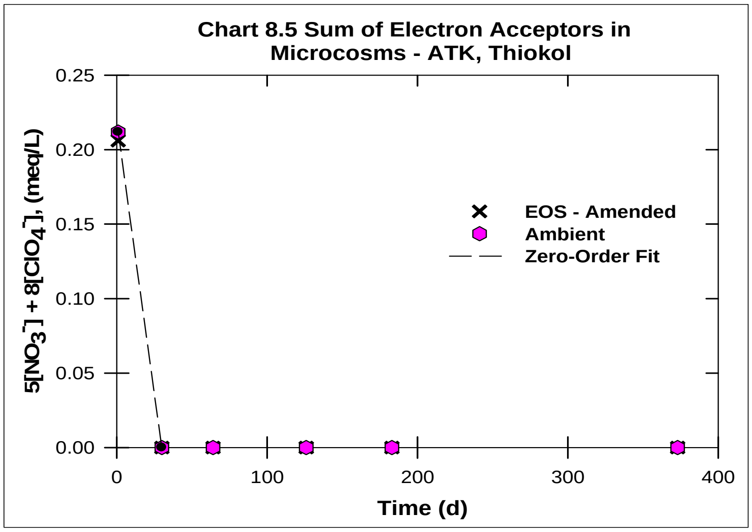


Chart 8.5 Sum of Electron Acceptors in Microcosms - ATK, Thiokol

The perchlorate concentration decreased to below detection within 30 days. Thus, the zero-order equation was fitted to the first two data points for perchlorate to get the degradation rate constant (**Chart 8.3**). Similarly, the zero-order equation was fitted to the first two data points for sum of electron acceptors (**Chart 8.5**). The degradation/removal rate constants for perchlorate and sum of electron acceptors in ambient microcosms are shown in **Table 8.4**.

Table 8.4
Rate Constants from Ambient Treatment Microcosms
ATK Thiokol

	Order	k	R^2
Perchlorate	Zero	33 mg L^{-1} y^{-1}	NA
Sum of Electron Acceptors	Zero	2.7 meq L^{-1} y^{-1}	NA

NA – not applicable

8.5 Summary

In summary, the field monitoring results show that elevated concentrations persist in the source area and several locations downgradient of the source. Nonetheless, the groundwater conditions at the ATK Thiokol may be conducive to the natural attenuation of perchlorate. The pH was in the range for optimal biological activity, and although there is some DO, the ORP suggests that groundwater presents a slightly reducing environment. Nitrate and sulfate are present throughout the groundwater environment, but not elevated uniformly across the site. Although organic carbon levels in the groundwater were very low, the 6-month BOD results indicate that there is sufficient biodegradable material to generate anaerobic conditions.

In the laboratory, the presence of some measurable BOD combined with the low initial nitrate concentrations allowed the indigenous microorganisms readily degraded perchlorate in both the EOS-amended and ambient perchlorate microcosms. Thus, the ATK Thiokol site shows good potential for natural attenuation of perchlorate.

9.0 Field and Laboratory Results – Beale AFB, CA

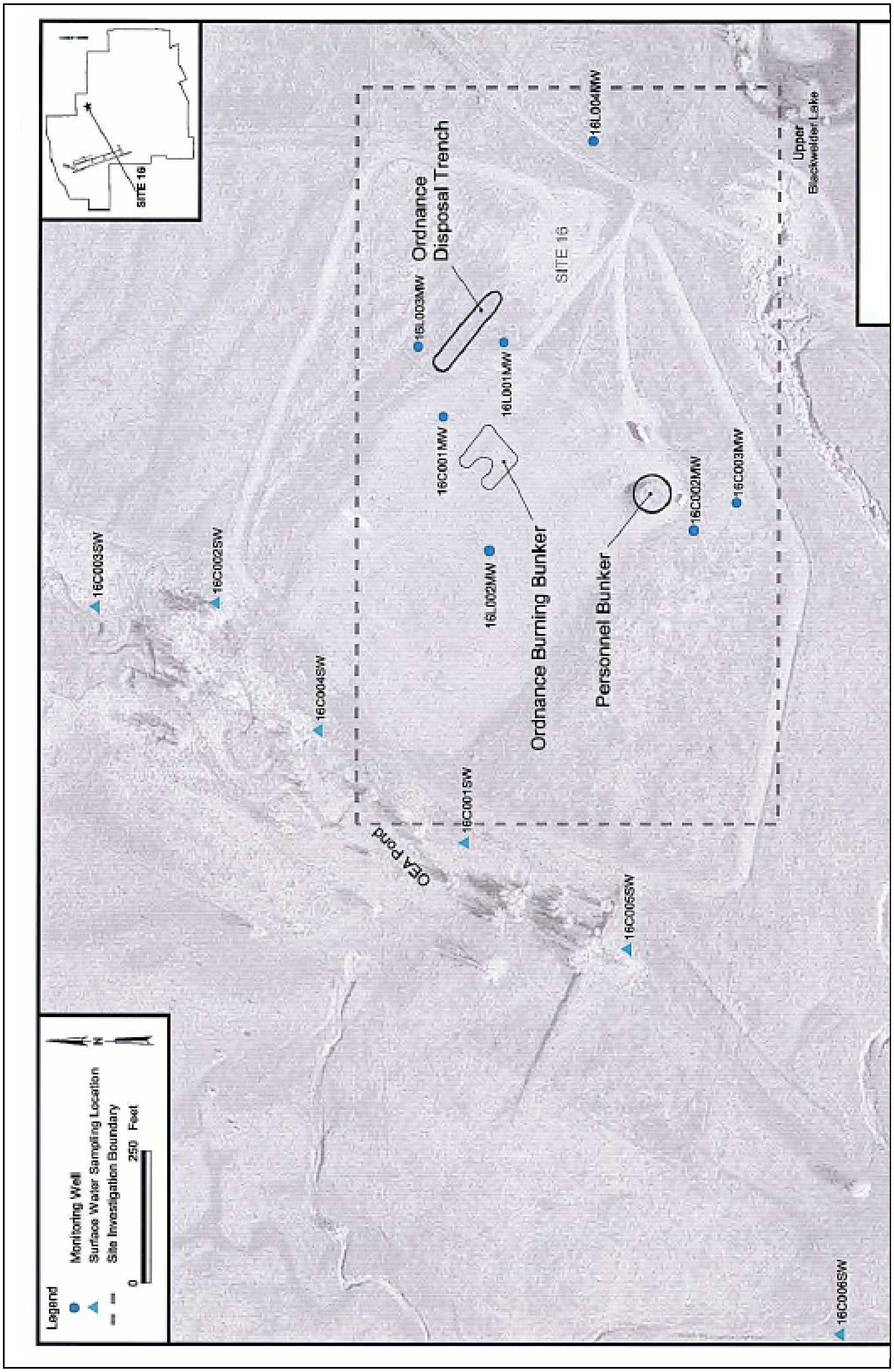
This section presents results from the field and laboratory studies conducted at the Explosive Ordnance Disposal (EOD) Area of Site 16, Beale Air Force Base, California.

9.1 Background Information

Solutions-IES initially contacted personnel from Beale AFB to obtain information related to the potential for MNA of perchlorate. Mr. Mike O'Brien was identified as the contact for Site 16 and he asked Mr. Gerald Vogt of CH2M Hill to work with Solution-IES to provide information regarding Site 16. Because of the large volume of work that has been prepared for numerous sites at Beale AFB, CH2M Hill forwarded information pertinent to the MNA investigation and not necessarily complete documents. Ms. Leslie Royer of CH2M Hill in Sacramento, CA also provided additional information and coordination. The information is paraphrased below.

9.1.1 Location and Layout

Beale AFB is located approximately 45 miles north of Sacramento, CA. Site 16, located within Beale AFB, is a former unlined trench at the Explosives Ordnance Disposal (EOD) Range where burned or exploded ordnance from the open burn/open detonation unit was placed for temporary disposal prior to transport off-site. Open burn activities ceased in 1994. The maximum dimensions of the trench that have been observed are 160 feet long by 30 feet wide by 12 feet deep. The trench is believed to be the primary source of contaminants including perchlorate at the EOD Range. The monitoring wells of interest for the current study include 16L004MW located upgradient of the source (trench) area; 16L001MW located near the source area; and 16C003MW, 16L002MW, and 16L003MW located downgradient of the source area (**Figure 9.1**). The wells of interest were installed using air rotary techniques.


Legend
Monitoring Well
Surface Water Sampling Location
Site Investigation Boundary
0
250 Feet
N
SITE 16
Ordnance Disposal Trench
SITE 16
Ordnance Burning Bunker
Personnel Bunker
Upper Blackwelder Lake
OEA Pond
16L004MW
16L003MW
16L001MW
16C001MW
16L002MW
16C002MW
16C003MW
16C003SW
16C002SW
16C004SW
16C001SW
16C005SW
16C006SW

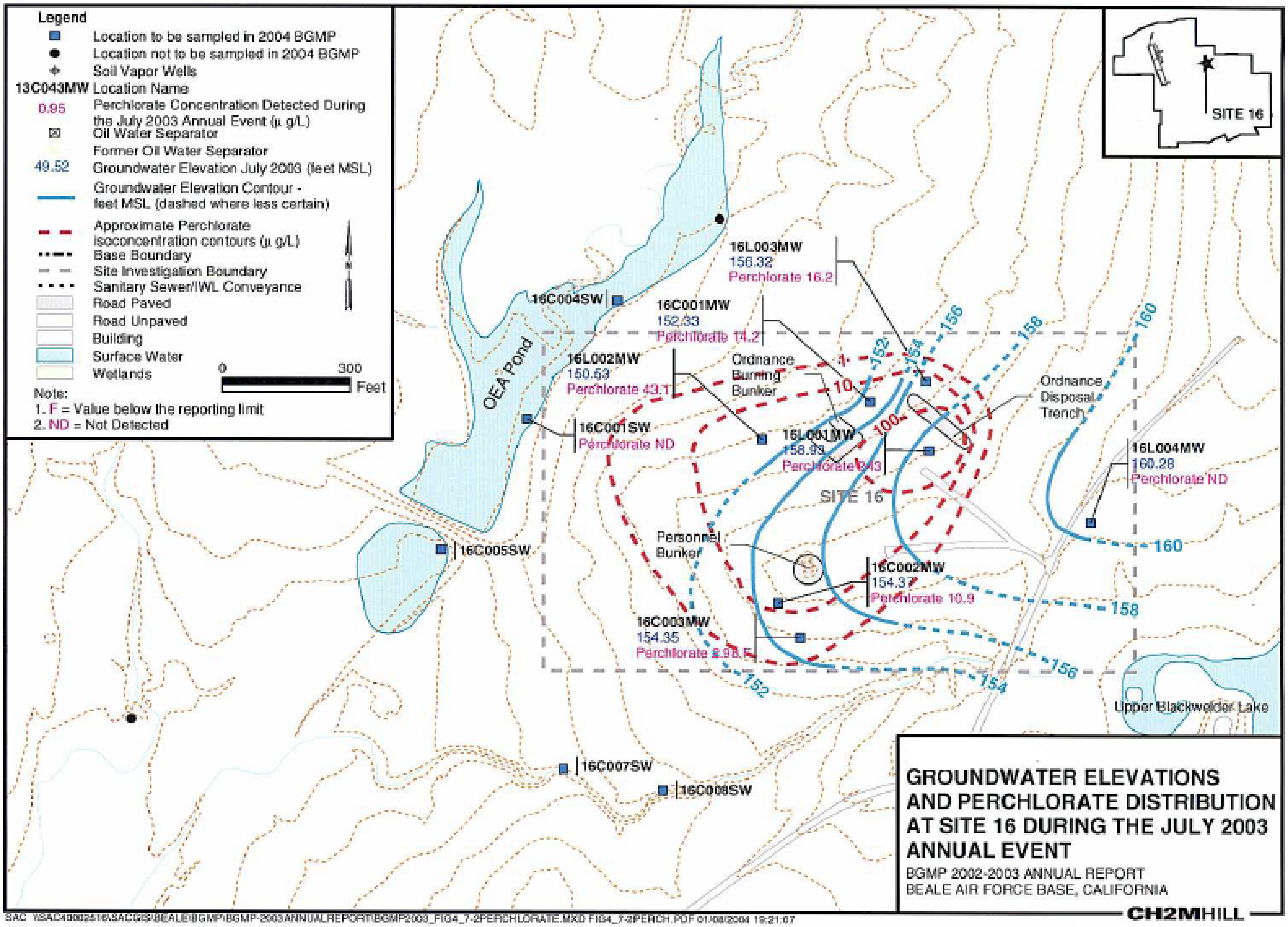


Figure 9.2 Historical Perchlorate Concentrations at Site 16, Beale Air Force Base

9.1.2 Site Contaminants

The trench is believed to be the primary source of contaminants including perchlorate at the EOD Range at Site 16. In 1998 the trench was excavated and the soil was determined to be non-hazardous and used to backfill the trench.

During a January 2001 sampling event, perchlorate analysis was added to the long-term monitoring plan at Site 16. During the April 2001 quarterly sampling event, perchlorate was detected in all the monitoring wells located at Site 16, and so was added to the list of constituents of concern for Site 16. The highest concentrations of perchlorate at Site 16 have been detected in 16L001MW, located near the source area, at concentrations ranging from 120 to 342 µg/L.

Explosives (e.g., RDX, nitrobenzene) have been sporadically detected in groundwater at Site 16 in the past. However, explosives were not detected during the 2002-2003 groundwater sampling events, and explosives may be removed from the monitoring plan in the future if concentrations trends continue.

Table 9.1 summarizes the most recent data obtained from an upgradient well (16L004MW), a well near the presumed source area (16L001MW) and a downgradient well (16L003MW). These wells represent groundwater conditions across the area of interest for this project (Figure 9.2). Figure 9.2 is representative of historical perchlorate concentration gradients at Site 16 during the July 2003 sampling event.

Table 9.1
Representative Groundwater Conditions at Site 16
Beale AFB

	Sample Date	Units	16L004MW	16L001MW	16L003MW
			(Upgradient)	(Source)	(Downgradient)
Perchlorate	Jul-03	µg/L	ND	243	2.98
Anions					
pH	Jul-04	S.U.	7.82	8.1	9.16
Oxidation-Reduction Potential	Feb-03	MVolts	168*	46	-57
Dissolved Oxygen	Feb-03	mg/L	6.42*	6.17	0

9.1.3 Site Hydrology and Plume Geometry

The aquifer lithology generally consists of fractured metavolcanic basement rock overlain by thin surficial deposits of unconsolidated sediment. The bedrock consists of metamorphosed igneous and sedimentary rocks and intrusive igneous rocks. The surficial deposits at the site consist primarily of silt and clay with a thin layer of sand and gravel. Although groundwater flow at Site 16 is primarily through fractures in the metavolcanic basement fractures, some groundwater also flows through the surficial deposits. The most recent groundwater contours at Site 16 indicate that groundwater flow is predominately to the west-northwest (**Figure 9.2**). However, the appearance of the perchlorate contamination plume suggests that there is also a southwest flow component. The estimated plume dimensions are 900 feet by 600 feet, and the depth to water ranges from 10 to 20 feet bgs. The perchlorate plume geometry is illustrated in **Figure 9.2**.

9.2 Biogeochemical Characterization

Based on the historical information provided by the CH2M Hill representatives, five monitor wells were chosen to be sampled to provide a current overview of biogeochemical conditions in the aquifer. The wells selected appear to cover the range of biogeochemical conditions at the site including the more highly contaminated locations, moderately contaminated locations, and relatively uncontaminated background locations. Monitoring data from prior sampling events are summarized in **Table 9.2**.

Table 9.2 summarizes results of groundwater sampling conducted at the site by Solutions-IES personnel in May 2005. Perchlorate concentrations were highest in the source area, but dropped by two orders of magnitude at the furthest downgradient location. No VOC co-contaminants were detected in any of the five wells. TOC was below detection in the groundwater, but there were higher amounts of nitrate (avg. = 14.5 mg/L) and sulfate (avg. = 23.7 mg/L) detected. These anions can interfere with natural perchlorate degradation. The DO and ORP suggest oxidative conditions across the site.

Because of site logistics, new soil samples were not collected. Instead, sediment samples were collected by pumping from the bottom of 16L003MW. TOC concentrations in the sediment samples from these wells were also low, reported at1.59 mg/L for F-3 and 4.18 mg/L for B-4. The CD enzyme assay was run on the groundwater samples from in the source area and downgradient and were moderately positive for the presence of perchlorate reducing microorganisms. The pH range was neutral, except for 16L003MW.

Table 9.2
Field Monitoring Results – May 18, 2005
Beale AFB

	units	16L004	16L001	16L003	16L002	16C003
Relative Location		Upgradient	Source	Downgradient		
Perchlorate	µg/L	ND	174	22.0	44.0	3.00
Dichloromethane	µg/L	BQL	BQL	BQL	BQL	BQL
1,1-Dichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
trans-1,2-Dichloroethene	µg/L	ND	ND	ND	ND	ND
Dichloroethane	µg/L	ND	ND	ND	ND	ND
cis-1,2-Dichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Chloroform	µg/L	BQL	BQL	BQL	BQL	BQL
1,1,1-Trichloroethane	µg/L	BQL	BQL	BQL	BQL	BQL
Carbon tetrachloride	µg/L	BQL	BQL	BQL	BQL	BQL
Trichloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Tetrachloroethene	µg/L	BQL	BQL	BQL	BQL	BQL
Vinyl Chloride	µg/L	BQL	BQL	BQL	BQL	BQL
Chloroethane	µg/L	BQL	BQL	BQL	BQL	BQL
Chloromethane	µg/L	BQL	BQL	BQL	BQL	BQL
Total CVOCs	µg/L					
Ethane	µg/L	BQL	BQL	BQL	BQL	BQL
Ethene	µg/L	BQL	BQL	BQL	BQL	BQL
Methane	µg/L	BQL	BQL	BQL	BQL	BQL
Total Organic Carbon	mg/L		<1	<1	<1	<1
Molybdenum	mg/L	<0.010	<0.010		<0.010	<0.010
Nitrate	mg/L	19.6	13.4	11.4	14.4	13.9
Sulfate	mg/L	13.4	13.1	44.0	9.40	38.6
Phosphate	mg/L	<1.0	<1.0	<1.0	<1.0	<1.0
Chlorite Dismutase (BioInsite)	pos/neg					
Chlorite Dismutase (Microbial Insights_) DNA testing	pos/neg		+++	++		
pH	SU	7.38	7.47	9.44	6.85	7.91

9.3 Biological Oxygen Demand (BOD) Results

The 6-month BOD test was prepared on groundwater samples from monitor wells 16 L001 and 16 L003. Monitor well 16 L001 is located in the source area and 16 L003 is downgradient. The background nitrate was 13.4 and 11.4 mg/L in each well, respectively. There was also an abundance of dissolved oxygen. The concentrations of perchlorate were 0.174 mg/L in 16 L001 and 0.022 mg/L in 16 L003 (Table 9.2). As presented in Table 9.3, the ultimate BOD (L_o) results for Beale AFB suggest the presence of measurable bioavailable organic carbon in groundwater.

Table 9.3
BOD_6 Results
Beale AFB

Wells	slope	intercept	R^2	k	Lo
	b	a		2.61(b/a)	1(2.3*k*a3)
L001	0.0125	1.58	0.364	0.0206	5.3
L003	1.40E-02	1.51	9.00E-04	0.0242	5.3

9.4 Microcosm Results

Laboratory microcosms were constructed to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added organic substrates. Maximum perchlorate concentrations occurred in a former unlined trench at the EOD Range. Due to site access restrictions and difficult drilling conditions (fractured rock), it was not possible to obtain large amounts of sediment for microcosm construction. Consequently, the microcosms were constructed with groundwater / suspended sediment slurry obtained from the bottom of monitor well 16L003MW.

Because there were no detectable VOC co-contaminants in groundwater, the microcosms were only monitored for the changes in concentration with time of DO, nitrate, sulfate, perchlorate, and chloride. In the EOS-amended microcosms (Treatment 6) (**Charts 9.1 and 9.2**), DO, nitrate and sulfate were reduced rapidly to below detection limit within 30 days. However, perchlorate declined much more slowly with 25 µg/L of perchlorate present in the one of the EOS-amended bottles even after 371 days whereas in other two bottles, it was reduced to below detection after 200 days. The slow degradation rates suggest that the population density of perchlorate-degrading may have been low to start in the sediment slurry. Alternatively, the pH 9.4 measured in 16L003MW may not be conducive for growth of the required microorganisms. The carbon-amended microcosm in Treatment 5 showed the same trend with exception of slow reduction of sulfate.

There was no change in perchlorate concentrations in the ambient low perchlorate condition microcosms (Treatment 1) even after 371 days of incubation (**Chart 9.3**), indicating very limited potential for intrinsic biodegradation of perchlorate in groundwater near 16L003MW. Also there was no reduction observed in the sulfate and nitrate concentrations **(Charts 9.3 and 9.4)**. Results were similar in the corresponding killed microcosms (Treatment 3) further supporting the interpretation that the prevailing groundwater conditions are not conducive to natural attenuation. Results were similar in both the high perchlorate (Treatment 2) and killed high perchlorate (Treatment 4) microcosms.

Table 9.4
Rate Constants from Ambient Treatment Microcosms
Beale AFB

	Order	k	R^2
Perchlorate	Zero	<0.01 mg $L^{-1}y^{-1}$	0.07
Nitrate	Zero	0.91 mg $L^{-1}y^{-1}$	0.475
Sum of Electron Acceptors	Zero	0.07 meq $L^{-1}y^{-1}$	0.447

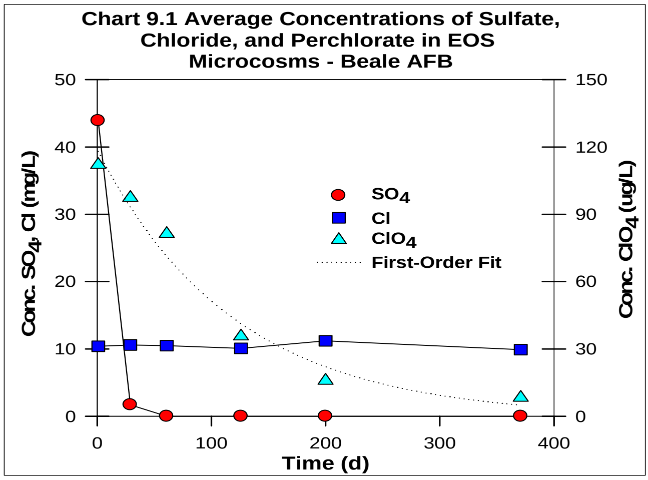


Chart 9.1 Average Concentrations of Sulfate, Chloride, and Perchlorate in EOS Microcosms - Beale AFB

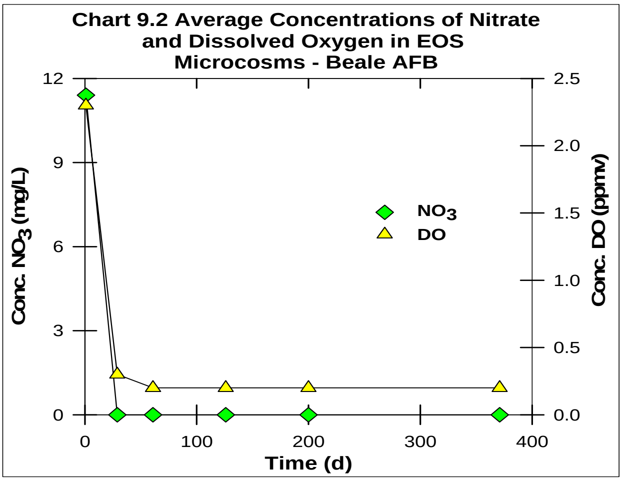


Chart 9.2 Average Concentrations of Nitrate and Dissolved Oxygen in EOS Microcosms - Beale AFB

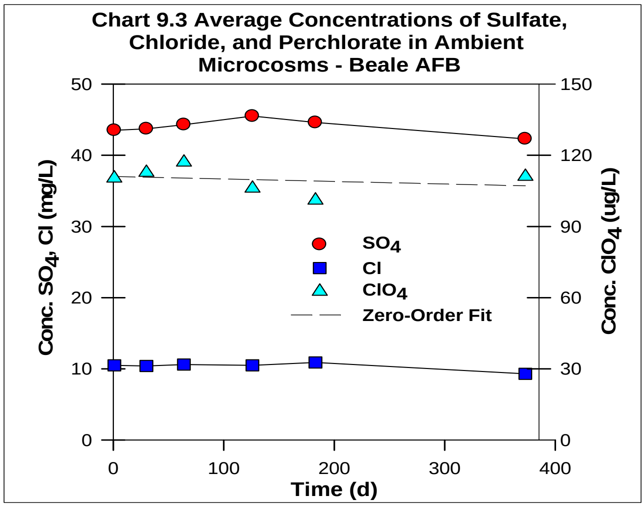


Chart 9.3 Average Concentrations of Sulfate, Chloride, and Perchlorate in Ambient Microcosms - Beale AFB

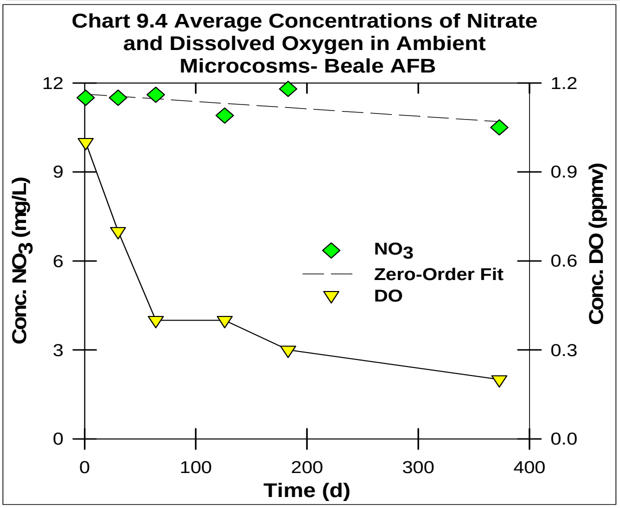


Chart 9.4 Average Concentrations of Nitrate and Dissolved Oxygen in Ambient Microcosms- Beale AFB

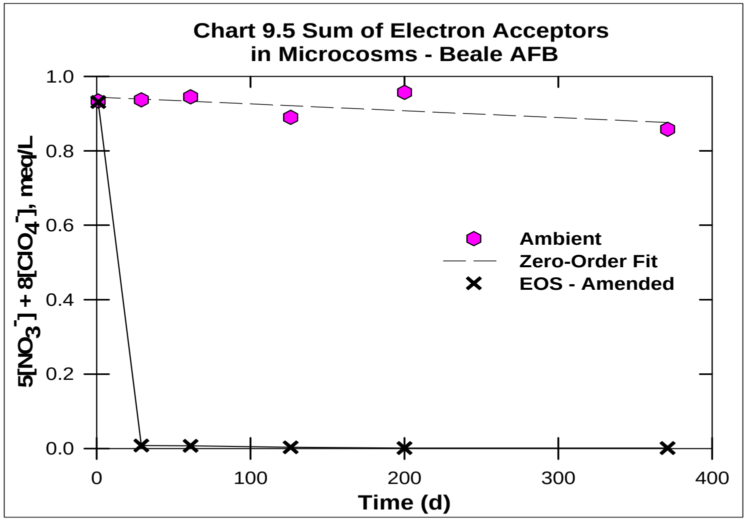


Chart 9.5 Sum of Electron Acceptors in Microcosms - Beale AFB

Chart 9.5 showed rapid decrease in sum of electron acceptors with time in EOS-amended microcosms due to the rapid depletion of nitrate. Conversely, there was very slight change observed in sum of electron acceptors with time in ambient microcosms which reflects the lack of degradation of perchlorate and nitrate in ambient microcosms.

The straight line for perchlorate (**Chart 9.3**) represents a linear regression fit to the data that indicates zero-order kinetics (Eq. 2). Similarly, the straight line in **Chart 9.4** represents a linear regression of the nitrate data. The regression line show a good fit to zero-order kinetic model used in Eq. 2 for the sum of electron acceptors (**Chart 9.5**). The degradation/removal rate constants for perchlorate, nitrate and sum of electron acceptors in ambient microcosms are shown in **Table 9.4**.

Table 9.4
Rate Constants from Ambient Treatment Microcosms
Beale AFB

	Order	k	R^2
Perchlorate	Zero	<0.01 mg L^{-1} y^{-1}	0.07
Nitrate	Zero	0.91 mg L^{-1} y^{-1}	0.475
Sum of Electron Acceptors	Zero	0.07 meq L^{-1} y^{-1}	0.447

9.5 Summary

In summary, the field results indicate limited potential for anaerobic biodegradation of perchlorate at the Beale AFB site. Although the perchlorate concentrations decrease away from the source, conditions conducive to a biological mechanism to explain this change are not present. The groundwater is oxidative and contains little usable dissolved organic carbon. Although the CD enzyme assay was positive, even the response to added carbon substrate was slow. The presence of nitrate across the site also does not favor intrinsic attenuation of the perchlorate. The microcosm studies further support the lack of capability of natural attenuation at this site.

10.0 Conclusions and Recommendations

A thorough site screening process was performed from which seven sites in five states were identified for additional field and laboratory studies. At each site, several wells were sampled to define geochemical conditions within the aquifer and evaluate the potential for MNA of perchlorate. The intent was to compare ambient site conditions and test representative site matrices in controlled laboratory studies with two objectives:

1) Establish a set of conditions that could be used to predict the potential for natural attenuation of perchlorate to occur.
2) Use the information to select two sites for a field demonstration of monitored natural attenuation of perchlorate.

The suite of parameters tested was based on the assumption that the anaerobic biodegradation of perchlorate would occur under conditions similar to those shown to be optimal for anaerobic reductive dechlorination of CVOCs. These include:

1) Low DO (anaerobic conditions) and low ORP (a reducing environment);
2) Elevated concentrations of indigenous dissolved organic carbon;
3) Low concentrations of competing electron acceptors, particularly nitrate; and
4) Neutral pH and presence of a contaminant degrading microbial population.

The results from each site were discussed in the preceding sections. To evaluate the importance and impact of the individual parameters, the results have been placed in three groups:

1) Perchlorate biodegradation and biologically important measurements
2) Electron acceptors and oxidation-reduction conditions
3) Background organic carbon

10.1 Perchlorate Biodegradation and Biologically Important Measurements

The biologically important measurements obtained from each site are summarized in **Table 10.1**. The data are taken from tables presented earlier in this report (i.e., Tables 3.2, 4.2, 5.2, 6.2, 7.2, 8.2 and 9.2), but focus only on groundwater measurements from the “source area” wells and “downgradient” wells at each site. Measurements from wells located “upgradient” of the source were not included in the ranges shown in **Table 10.1**.

TABLE 10.1
Summary of Perchlorate Degradation Characteristics in Source Area and Downgradient Wells

Project Site	pH (S.U.)	CD Enzyme (+/-) (Matrix)	Perchlorate Conc. (µg/L)		Perchlorate Degradation Rate	
			Source	Down-gradient	Zero Order (mg/L/yr)	1st Order (1/yr)
Little Mountain Test Annex	6.3 to 7.5	+++ (sediment)	34	<10	<0.01	--
ATK Elkton	4.5 to 5.0	++ Sediment	1,200	194	0.92	--
NSWC, Indian Head	5.4 to 6.9	+++ (sediment)	181	1.9	--	5.1
Stennis Space Center	4.8 to 5.2	+ (groundwater)	53,600	<5	0.13	1.75
Redstone Arsenal	5.4 to 7.5	++ (groundwater)	6.4	3.5 to 16.8		7.3
ATK Thiokol	7.2 to 7.4	NM	7,600	3,900	33	--
Beale AFB	6.8 to 7.4	++ (groundwater)	174	22	<0.01	--

At all locations, the perchlorate concentration decreased between the source and the downgradient well that was tested. However, the differences were not as pronounced at Little Mountatin Test Annex or Redstone Arsenal. The extent of the disappearance depended to some extent on the plume geometry and the distance between the source and downgradient wells that were sampled. At most of the locations, based on historical site-specific information, it is likely that higher residual concentrations of perchlorate could be found in other wells. The pH at all the sites except ATK Elkton and Stennis Space Center was generally favorable to microbial activity. Perchlorate-reducing microorganisms are not believed to be as sensitive to ranges of pH as are Dehalococcoides-like microorganisms that are needed for dehalorespiration of aliphatic chlorinated hydrocarbons.

The CD enzyme test was run on either sediment or groundwater from wells on six of the seven sites. As discussed in Section 2.2, perchlorate-reducing microorganisms are thought to be widespread in the environment. The results of this study showed that regardless of the background conditions, there was evidence of microbial communities at each locale that were genetically capable of perchlorate reduction.

The microcosm studies tested the capacity of each site to support natural attenuation of perchlorate as well as the potential for biostimulation to enhance biodegradation. In all sites, the addition of electron donor, either as known concentrations of lactate and acetate, or in a complex commercially available vegetable oil-based product (EOS®), quickly stimulated perchlorate degradation. This further supports the conclusion that capable microorganisms are present at each site.

Under conditions of natural attenuation, results varied widely. A degradation rate was calculated for each site and fitted to one of two kinetic models. Zero-order kinetics implies that the rate of degradation is independent of the perchlorate concentration; first-order kinetics implies that the rate is dependent on the perchlorate concentration. The degradation rates were zero-order at two of the seven sites (ATK Elkton and ATK Thiokol), 1st order at two sites (NSWC Indian Head and Redstone Arsenal) and could be fitted to both models at one site (Stennis Space Center). At two sites (LMTA and Beale AFB), apparent zero-order biodegradation rates were less than 0.01 mg/L per year indicating no measureable perchlorate degradation. When measurable, zero order rates ranged from 0.13 mg/L/yr at Stennis Space Center to 33 mg/L/yr at ATK Thiokol. The first order rates ranged from 1.75 yr^{-1} at Stennis Space Center to 5.1 yr^{-1} at NSWC Indian Head. Although microcosms can be used as an effective tool to determine the biodegradation potentials, they are not always representative of degradation rates under field conditions (Azadpour-Keeley *et al.* 2001b).

10.2 Electron Acceptors and Oxidation-Reduction Conditions

Some perchlorate-reducing microorganisms are strict anaerobes and some are facultative anaerobes. This affords the population with the ability to withstand a range of oxidation-reduction conditions. Perchlorate is used directly in the metabolism of these organisms, with a sequence of enzymes responsible for the breakdown of the anion to chloride and oxygen. Some of these enzymes are very similar to enzymes used by denitrifying microorganisms under anaerobic conditions. The presence of nitrate has been shown to interfere with perchlorate degradation. Sulfate is not reported to have the same impact. **Table 10.2** shows a summary of the electron acceptor and oxidation-reduction conditions at the seven sites. The data are taken from tables presented earlier in this report (i.e., Tables 3.2, 4.2, 5.2, 6.2, 7.2, 8.2 and 9.2), but focus only on groundwater measurements from the "source area" wells and "downgradient" wells at each site. Measurements from wells located "upgradient" of the source were not included in the ranges shown in **Table 10.2**.

The groundwater in the perchlorate plumes at ATK Elkton and Stennis Space Center are most oxidative. At the other sites, redox conditions vary widely, but tend to be more reducing, especially in the downgradient portions of the site. Nitrate is highest at ATK Thiokol, but not much greater than 10 mg/L at the other sites. The sulfate concentrations varied widely, presumably due to background geochemical conditions at each site.

TABLE 10.2
Summary of Electron Acceptors and Oxidation-Reduction Conditions in Source Area and Downgradient Wells

Project Site	Dissolved Oxygen	Oxidation-Reduction Potential	Nitrate	Sulfate
	mg/L	mV	mg/L	mg/L
Little Mountain Test Annex	0.1 to 0.2	-9 to -129	<.5 to 45	5 to 410
ATK Elkton	1.0 to 4.0	+167 to +212	2.8 to 9.9	5.2 to 8.9
NSWC, Indian Head	3.5 to 8.0	+6 to very neg	2.3 to 8.7	64.2 to 116
Stennis Space Center	0.2 to 1.0	+36 to +119	BQL to 1.3	1.1 to 9.5
Redstone Arsenal	0.15 to 5.0	+313 to very neg	<0.5	2.4 to 4.6
ATK Thiokol	1.5 to 2.5	+20 to -12.7	9 to 46	72 to 190
Beale AFB	3.5 to 0.35	+28 to +6.7	11.4 to 13.9	9.4 to 44.0

10.3 Background Organic Carbon

As shown in the microcosm work, the presence of organic carbon can promote biodegradation of perchlorate by providing a readily metabolizable source of carbon for microbial growth and energy. The degradation of the organic carbon is mediated by electron transfer with the electron acceptors present in the environment. The TOC measurements in the groundwater from each site give an indication of the amount of background carbon that may be readily available. The 6-month BOD test was devised to provide additional information about the availability of background carbon to indigenous microorganisms. This is shown by the ultimate BOD. The BOD test also gives an indication of the rate at which indigenous microorganisms can consume oxygen using the background organic carbon as electron donor.

TABLE 10.3
Summary of Organic Carbon Measurements in Downgradient Wells

Project Site	Total Organic Carbon (mg/L)	Ultimate BOD_6 (mg O_2/L)
Little Mountain Test Annex	1 – 2	9.0 – 9.3
ATK Elkton	<1.0	BDL
NSWC, Indian Head	4.4	Not measured
Stennis Space Center	<1 – 1.9	8.8
Redstone Arsenal	Not measured	8.4 – 11
ATK Thiokol	<1.0 – 1.9	14 – 19
Beale AFB	<1.0	5.3

10.4 Sites for Further Study

Results of the field and treatability studies were used to help select sites for detailed field demonstrations. The data show the difficulty in predicting the potential for the MNA of perchlorate to occur. Consequently, the selection of two sites for further study is not an “absolute science”. One of the most important pieces of evidence was the observed disappearance of perchlorate along the axis of the plume. At most locations evaluated, perchlorate appeared to attenuate. However, at LMTA and Beale AFB, the declines in perchlorate concentration with distance were not large enough to warrant further study; these locations were also eliminated from further consideration based on site conditions, lab performance, hydrogeological or site access conditions. Redstone Arsenal was also eliminated because of difficulty defining the plume geometry and complex karst hydrogeology which greatly increased the difficulty in accurately characterizing groundwater flow paths.

Based solely on perchlorate attenuation along the length of the plume, the plumes ATK Elkton, ATK Thiokol and Stennis Space Center remained promising sites to consider. Results from the microcosm studies from Stennis Space Center showed some potential for natural attenuation, but the geochemical conditions throughout the plume weighed against selecting this site for the field demonstration, so it was eliminated.

The site conditions at ATK Thiokol were generally favorable for demonstration MNA of perchlorate. There is TOC, a measurable rate of degradation in the microcosm studies, a low DO, mostly reducing environment and a neutral pH. The slightly elevated nitrate concentrations and presence of co-contaminants would be a concern in this plume. Also, the depth to groundwater and logistics of working at this site increased the cost for the demonstration dramatically, thus removing it from further consideration.

The two sites selected for detailed field demonstrations are both located in Maryland: ATK Elkton and NSWC Indian Head. The conditions at these locations are summarized as follows:

- Throughout most of the plume at ATK Elkton, groundwater is oxidative with low levels of organic carbon and a low pH. However, in the downgradient portion of the plume near Little Elk Creek, microcosm studies showed relatively rapid biodegradation of perchlorate suggesting the potential for MNA within the riparian buffer of this stream.

- The preliminary field data from NSWC Indian Head suggested very little difference in the perchlorate concentrations in the three wells that were tested, but additional data not used in this study suggested that higher concentrations of perchlorate were present in close to the source. There is a large decrease in perchlorate concentration from the source to the downgradient portion of the plume. Nitrate concentrations are low and there is some TOC in the groundwater. Laboratory microcosms showed evidence for reasonably rapid biodegradation of perchlorate.

11.0 References

American Public Health Association, American Water Works Association, Water Environment Federation, 1999. Standard Methods for the Examination of Water and Wastewater. Method 5210-Biochemical Oxygen Demand.

Azadpour-Keeley, A., J.W. Keeley, H.H.Russell and G.W. Sewell. 2001a. Monitored natural attenuation of contaminants in the subsurface: Processes. *Ground Water Monitoring Review*, Spring 2001: pp 97-107.

Azadpour-Keeley, A., J.W. Keeley, H.H.Russell and G.W. Sewell. 2001b. Monitored natural attenuation of contaminants in the subsurface: Applications. *Ground Water Monitoring Review*, Summer 2001: pp 136-143.

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. and P.B. Bedient, 1986. Transport of Dissolved Hydrocarbons Influenced by Reaeration and Oxygen Limited Biodegradation: 1. Theoretical Development. *Water Resources Research* 22(13): 1973-1982.

Borden, R.C. and P.B. Bedient, 1987. *In Situ* Measurement of Adsorption and Biotransformation at a Hazardous Waste Site. *Water Resources Bulletin* 23(4): 629-636.

Borden, R.C., P.B. Bedient, M.D. Lee, C.H. Ward, and J.T. Wilson, 1986. Transport of Dissolved Hydrocarbons Influenced by Re-aeration and Oxygen Limited Biodegradation: 2. Field Application. *Water Resources Research* 22(13): 1983-1990.

Borden, R.C., M.D. Lee, J.M. Thomas, P.D. Bedient, and C.H. Ward, 1989. *In Situ* Measurement and Numerical Simulation of Oxygen Limited Biotransformation. *Ground Water Monitoring Review*, Winter, pp. 83-91.

Borden, R.C., C.A. Gomez and M.T. Becker, 1995. Geochemical Indicators of Intrinsic Bioremediation. *Ground Water* 33(2):180-189.

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

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

Borin, M. and E. Bigon, 2002. Abatement of NO3-N Concentration in Agricultural Waters by Narrow Buffer Strips. Environ. Poll. 117: 165-168.

CPEO, 2006. http://www.ewg.org/issues/perchlorate/20061004/release.php. Center for Public Environmental Oversight, October 4, 2006.

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., 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.

Cramer, R.J, C. Yates, P Hatzinger and J. Diebold. 2004. Field Demonstration of In Situ Perchlorate Bioremediation at Building 1419. NOSSA-TR-2004-001, January 22, 2004.

Fennessy, M.S. and J.K., Cronk, 1997. The Effectiveness and Restoration of Potential Riparian Ecotones for the Management of Nonpoint Source Pollution, Particularly Nitrate. *Crit. Rev. Environ. Sci. Tech.* 27(4): 285-317.

Heaton, T.H.E., 1986. Isotopic Studies of Nitrogen Pollution in the Hydrosphere and Atmosphere: A Review. *Chemical Geology* 59: 87-102.

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

Hunt, M.J., R.C. Borden, and M.A. Barlaz, 1998. Determining Anaerobic BTEX Decay Rates in a Contaminated Aquifer. *J. Hydrologic Engineering*. October 1998, p 285-293.

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

Jackson, W.A., 2003. Distribution, Degradation, and Uptake of Perchlorate (PC) in Contaminated Stream Sediments. Presented at: *In Situ* and On-Site Bioremediation, the Seventh International Symposium, Orlando, FL, June 2003.

Johnston, J.J., R.C. Borden, and M.A. Barlaz, 1996. Anaerobic Biodegradation of Hazardous Organics in Groundwater Down Gradient of a Sanitary Landfill. *J. Contaminant Hydrology* 23(4): 263-283.

Kao, C.M. and R.C. Borden, 1997. Site Specific Variability in BTEX Biodegradation under Denitrifying Conditions, *Ground Water* 35(2): 305-311.

Kolhatkar, R., T. Kuder, P. Allen, and J.T. Wilson, 2002. Use of Compound-Specific Stable Carbon Isotope Analyses to Demonstrate Anaerobic Biodegradation of MTBE in Groundwater at a Gasoline Release Site. *Environ. Sci. Tech.* 36(23): 5139-5146.

Lee, M.D., R.C. Borden, J.T. Wilson, M. Thomas, P.B. Bedient, and C.H. Ward, 1988. Biorestoration of Organic Contaminated Aquifers. *CRC Critical Reviews in Environmental Control* 18(1): 29-89.

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

Martin, T.L., N.K. Kaushik, J.T. Trevors, and H.R. Whitely, 1999. Review: Denitrification in Temperate Climate Riparian Zones. *Water, Air and Soil Pollution* 111: 171-186.

MassDEP 2006. http://www.mass.gov/dep/toxics/pchlorqa.pdf

O'Connor, S.M., and J.D. Coates, 2002. Universal Immunoprobe for (Per)Chlorate-Reducing Bacteria. *Appl. Environ. Microbiol.* 68 (6): 3108-3113.

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.

Schoonover, J.E. and K.W.J. Williard, 2003. Ground Water Nitrate Reduction in Giant Cane and Forest Riparian Buffer Zones. *J. Amer. Water Res. Assoc.* 39(2): 347-354.

Stennis Space Center, 2004. Site Clean Up Program, Fact Sheet No. 10. NASA Stennis Space Center, August 2004.

Thomas, H.A., Jr., 1950. Graphical Determination of BOD Curve Constants. *Water & Sewage Works*, 97:123.

U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM). Perchlorate in Drinking Water. http://chppm-www.apgea.army.mil//documents/FACT/31-003-0502.pdf

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

USEPA 2004. http://www.epa.gov/fedfac/pdf/releases_04_29_04-with-datesDB.pdf.

USEPA OSWER Directive 9200.4-17, 1997

Weidemeier, 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.

Wu, J., R.F. Unz, H. Zhang and B.E. Logan, 2001. Persistence of Perchlorate and the Relative Numbers of Perchlorate- and Chlorate-Respiring Microorganisms in Natural Waters, Soils and Wastewater. *Bioremediation Journal* 5 (2): 119-130.

12.0 Points of Contact

POINT OF CONTACT	ORGANIZATION	ROLE IN PROJECT
M. Tony Lieberman	Solutions-IES, Inc. 1101 Nowell Rd. Raleigh, NC 27607 919-873-1060 (phone) 919-873-1074 (fax) tlieberman@solutions-ies.com	Lead Principal Investigator
Dr. Robert C. Borden, P.E.	North Carolina State University Dept. of Civil, Construction and Environmental Engineering Campus Box 7908 208 Mann Hall Stinson St. Raleigh, NC 27695-7908 919-515-1625 (phone) 919-515-7908 (fax) rcborden@eos.ncsu.edu	Co-Principal Investigator
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Signature and Date:

M. Tony Lieberman

April 19, 2007

M. Tony Lieberman
Solutions-IES, Inc.

Date

APPENDIX A

SITE SELECTION QUESTIONNAIRE

QUESTIONNAIRE FOR ESTCP PERCHLORATE MNA PROJECT
ER-0428

With support from the DoD’s Environmental Security Technology Certification Program (ESTCP), Solutions-IES is evaluating the potential for Monitored Natural Attenuation (MNA) of perchlorate in groundwater. As part of this project, we will conduct preliminary screening studies at 8 sites and then extensive field evaluations at 2 sites. All costs by Solutions-IES and other outside contractors will be covered by ESTCP.

If you would like your site to be considered for this project, please complete the attached form and return is to us at any one of the following addresses

By Mail: Tony Lieberman, Project Manager
Solutions-IES, Inc.
3722 Benson Drive
Raleigh, NC 27609

By Fax: 919-873-1074

By e-mail: tlieberman@solutions-ies.com

You should be able to complete this questionnaire in 15 minutes. If you don’t know the answer to a question, insert a question mark and move on. Please provide your response within two weeks of receiving this questionnaire. Thank you for participating in this project!

I. Site Information

Name:

Regulatory Oversight Agency:

Location:

Brief Description of Site:

Are major site characterization and monitoring reports available for our use in this project upon our request? ___ Yes ____ No

Does facility have environmental monitoring data available via the internet? ___ Yes ____ No
(If so, provide website or FTP address).

II. Site Manager Contact Information

Name:

Title:

Phone:

Fax:

E-mail:

Mailing Address:

III. Description of Contaminant Source Area(s)

Please provide a brief description of the source area including any information you have on the source of the release (i.e. tank farm, drums, impoundment, etc), estimated date of release, source area size, or other information. Feel free to include qualitative information or even your ‘best guess’ about these items.

IV. Description of Contaminant Plume

Please provide a brief description of the contaminant plume. Feel free to include qualitative information or even your ‘best guess’ about these items.

Maximum Plume Length (ft):

Maximum Plume Width (ft):

Depth to Groundwater (ft):

Maximum Depth of Contamination (ft):

Aquifer Thickness (ft):

Hydraulic Conductivity (ft/d): (Based on ______ field measurements or _______ estimated)

Hydraulic Gradient (ft/ft):

Seepage Velocity (ft/d):

General Description of Aquifer Lithology:

V. Contaminants Present

Please provide a brief description of the primary contaminants present. Include information on perchlorate concentrations, chlorinated solvents, and any other significant groundwater contaminants. Please include maximum contaminant concentrations and units. If it is easier, attach a spreadsheet with recent monitoring data.

VI. Monitored Natural Attenuation Results

Do you believe there is any potential for natural attenuation of perchlorate or chlorinated solvents at the site? If so, please explain why you suspect natural attenuation is occurring at this site.

Natural attenuation parameters that would be of interest are provided in the following table. Please complete the table with available information or provide an attached spreadsheet with relevant data.

Natural Attenuation Parameters	**Range**	**Units**	**Date Collected**	**Source of Data**		
				Actual Data from Plume	**Actual Data from Another Area of the Site**	**Estimate**
Dissolved Oxygen						
Nitrate						
Iron Total						
Iron (Fe $^{+2}$) Dissolved						
Manganese – Total						
Manganese - Dissolved						
Sulfate						
Sulfide						
Methane						
Ethene/Ethane						
ORP (Redox)						
pH						
Total Org. Carbon (TOC)						
Temperature						
Carbon Dioxide						
Alkalinity						
Hydrogen						
BOD						

V. Receptors/Risk

MNA is normally only considered at low to moderate risk sites. On a qualitative scale, is this a high, medium or low risk site?

______ High ______ Medium ______ Low

VI. Remediation Alternatives

What remediation alternatives are being considered for this contaminant plume or have been implemented to date?

VII. Other Information

Please attach any other information you think might be relevant in this evaluation.

APPENDIX B

SIX MONTH BOD MEASUREMENT PROTOCOL

APPENDIX B – Six Month BOD Measurement Protocol

1.0 Modified Winkler Titration Method for Dissolved Oxygen

The following reagents will be purchased or prepared for the titration method:

Purchased Solutions

- Alkaline azide reagent
- Manganese sulfate solution, Fisher.
- Potassium biiodate stock solution, 0.15N, Fisher.
- Potassium iodide solution, 10% by weight, Fisher.
- Sodium thiosulfate stock solution, 0.0375 N, Fisher.
- Starch indicator solution, Fisher.

Prepared Solutions

- Sodium thiosulfate standard titrant, 0.0075 N: Dilute 200 ml (or an appropriate volume) of stock solution (6.6) to 1 liter. Standardize according to the following directions. Prepare weekly.
- Sulfuric acid, concentrated.
- Sulfuric acid, 10%: Carefully add 50 ml of concentrated sulfuric acid to 460 ml of water.

Standardization of sodium thiosulfate:

The sodium thiosulfate will be standardized to provide a measurable volume of titrant based on the expected concentration of dissolved oxygen. To standardize of 0.0075N sodium thiosulfate, add 10 ml of 10% KI and 10 ml of 10% H_2SO_4 to 100 ml of water, followed by 4 ml of potassium iodated working standard. Place the solution in the dark for 5 minutes and then titrate with sodium hyposulfite standard tartan to a pale straw color. Add 1-2 ml of starch solution and continue the titration drop wise until the blue color disappears. The standardization of sodium thiosulfate will be run in duplicate. The volume of titrant necessary is expected to be 20 ml.
If the titrant (sodium thiosulfate) volume is greater than 20 ml, it is too weak, and the following equation will be used to calculate the volume of 0.0375 N sodium thiosulfate needed to adjust and increase the concentration of the titrant to 0.0075 N: (titrant-20) x 200/20. The calculated value derived from this equation is the volume of stock sodium thiosulfate that needs to be added to, and per, one liter of titrant (0.0075 N sodium thiosulfate).

If the titrant (sodium thiosulfate) volume is less than 20 ml, it is too strong. The following equation will be used to calculate the volume of water needed to adjust and decrease the concentration of the titrant to 0.0072 N: (20-titrant) x 1000/20. The calculated value derived from this equation is the volume of water that needs to be added to, and per, one liter of titrant (0.0075 N sodium thiosulfate). After adjusting the concentration of the titrant, standardize the solution again. Repeat procedures as necessary.

2.0 Dissolved Oxygen Sample Analysis

Obtain 15 sixty ml serum bottles and corresponding rubber stoppers for each well sample to be analyzed and 15 sixty ml serum bottles and corresponding rubber stoppers for a deionized (DI) water control. Per well sample and DI control, divide the serum bottles into 5 groups of 3 bottles and label accordingly: date, sampling area, well name, and sampling time. The sampling intervals are 1 day, 7 days, 21 days, 2 months, and 6 months after preparation. Acquire one hypodermic needle head for each stopper and an additional hypodermic needle head for each group of 3 bottles along with one 5 ml syringe for each well sample and DI control to be analyzed. Place one hypodermic needle head through each stopper to allow air to pass when sealing the serum bottles. Pour sample water into 1 gallon bottle until half full; shake up and down 25 times. Pour sample water into the 1 day group of serum bottles, filling bottles completely. Seal each bottle with a stopper leaving the hypodermic needle head in place. Repeat the filling procedure until all groups of bottles are full, shaking the 1 gallon bottle up and down 25 times between each group of serum bottles. Once all bottles are sealed, shake the 1 gallon bottle up and down 25 times then fill the 5 ml syringe. Using the hypodermic needle head already in the serum bottle stopper as an air valve, inject each bottle with sample water until no headspace remains, switching needle heads as necessary. Repeat entire procedure for each well sample and DI control to be analyzed.

Each of samples will be analyzed in triplicate at 1day, 7 days, 21 days, 2 months, and 6 months for DO concentration using the following procedure:

> Inject 0.4 ml of the manganese sulfate solution through rubber stopper using disposable plastic syringe, followed by 0.4 ml of the alkaline iodide-azide solution into the appropriate serum bottle. Mix the solution well by repeated inversion of the bottle. When the precipitate settles and the upper 1/3 of the bottle is clear, mix again by repeated inversion. After a second settling period and when the upper 1/3 of the serum bottle free is free of precipitate, add 0.4 ml of concentrated sulfuric acid to the serum bottle. Mix the solution by repeated inversion. Occasionally, a dark brown or black precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if the precipitate is particularly persistent, adding a few more drops of H_2SO_4 will affect dissolution.
>
> Transfer the bottle contents to a 150- or 200-mL beaker and titrate with 0.0075 N thiosulfate solution to a pale straw color. Add 1 to 2 ml of starch indicator and continue the titration to the first disappearance of the blue color. Record the volume (ml) of the titrant and the volume of the BOD bottle.

3.0 Calculations

The DO concentration (mg/L) will be read directly from the burette if the corresponding BOD serum bottle volume is 60.8 ml as proposed, or else the DO concentration is the burette reading times 60.8 divided by the BOD bottle volume. The volume of titrant and the BOD bottle volume will be recorded.

4.0 Quality Assurance/Quality Control

Before DO is measured on test samples, the concentration of DO will be measured for two deionized (DI) water samples for quality control using the following procedure:

> For each duplicate sample, fill 1 L bottle half full with DI water. Let each of the bottles reach room temperature, shaking the bottles periodically.

The DO concentration of the duplicate DI water samples will be determined as discussed in the previous section, and the results will be compared to the concentration to published values of oxygen concentration at room temperature. If the measured DO concentration of the DI water samples does not fall within 0.2 mg/L of published values, the sample titrations will not be performed until the problem is resolved.