ESTCP
Cost and Performance Report

(ER-200428)

Monitored Natural Attenuation of Perchlorate in Groundwater

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ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT
Project: ER-200428

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ACRONYMS AND ABBREVIATIONS

bgs	below ground surface
CD	chlorite dismutase (enzyme)
cld	chlorite dismutase
CVOC	chlorinated volatile organic compound
DO	dissolved oxygen
DoD	Department of Defense
DPRB	dissimilatory perchlorate-reducing bacteria
EOS®	Emulsified (Edible) Oil Substrate
ESTCP	Environmental Security Technology Certification Program
IRZ	In Situ Reactive Zone
ITRC	Interstate Technology & Regulatory Council
MBT	molecular biological tool
MDE	Maryland Department of the Environment
MNA	monitored natural attenuation
NPV	net present value
NSWC	Naval Surface Warfare Center
ORP	oxidation-reduction potential
P&T	pump-and-treat
pcrA	perchlorate reductase
RAO	remedial action objective
SCM	site conceptual model
Shaw	Shaw Environmental, Inc.
SWMU	Solid Waste Management Unit
TBC	to be considered
TCE	trichloroethene
TOC	total organic carbon
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound

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1.0 EXECUTIVE SUMMARY

Solutions-IES identified and tested the processes and methods needed to obtain lines of evidence to support monitored natural attenuation (MNA) as a remedy for perchlorate contaminated groundwater. The information and observations were compiled in a guidance document, which was then applied to two field demonstration sites in Maryland for validation. The first site was located on the Naval Surface Warfare Center (NSWC), Indian Head, MD, and the second at a manufacturing facility in Maryland. The work was funded by the ESTCP Project ER-200428.

The goals of this project were to provide Department of Defense (DoD) managers and industry professionals with the tools needed to demonstrate to regulatory agencies that MNA can be an effective remedy for managing the environmental impacts of perchlorate contaminated groundwater. To assess the demonstration sites, the project used the tiered approach developed and described in the Perchlorate MNA Protocol (ESTCP, 2008) prepared during this project. The Protocol guides the end user through the process of developing multiple lines of evidence to support perchlorate MNA. It includes the following steps:

- Tier 1 - Plume stability and geometry
- Tier 2 - Biogeochemical parameters and biological indicators
- Tier 3 - Biodegradation rates

At the Indian Head site, trends in groundwater flow, biogeochemical parameters, microbial populations, and perchlorate concentrations indicated that perchlorate attenuates mostly as a result of nonbiological mechanisms near the presumed source and areas downgradient from the source but prior to discharge to Mattawoman Creek, a large tributary of the Potomac River. As contaminated groundwater moves away from the source area toward the discharge zone along the creek bank, perchlorate was shown to biologically degrade in the intertidal, organic-rich Littoral Zone. Low oxidation-reduction potential (ORP), elevated total organic carbon (TOC), reduced competition with nitrate, pH>5.5 and the presence of perchlorate-reducing bacteria provided conditions conducive to biodegradation. Biodegradation rates were calculated by several methods and were generally reproducible, providing supporting lines of evidence for natural bioattenuation.

At the Maryland manufacturing site, the perchlorate in a commingled trichloroethene (TCE)/perchlorate plume on the east side of the manufacturing facility has attenuated slowly over time. There is some evidence that perchlorate has decreased in several source area wells, but TCE appears to have remained largely unchanged for over 3400 ft from the source. The apparent decrease in perchlorate is likely a result of the combination of abiotic attenuation processes, an ongoing pump-and-treat system in the area, and enhanced anaerobic reductive dechlorination from a bioremediation pilot study conducted years ago. There is little change in perchlorate in the mid-plume area, but as the plume approaches its end at Little Elk Creek, the intermediate and shallow aquifers merge and contaminated groundwater migrates vertically until it discharges to the creek. The conditions within the riparian buffer alongside the creek are not optimal for biodegradation of perchlorate, but are nonetheless more conducive to biodegradation than the areas downgradient of the source and throughout the mid-plume. Consequently, sufficient biodegradation of perchlorate was observed to keep it from entering the creek, while TCE was transformed minimally throughout the same area and was reported both in and just

beyond the creek. Perchlorate biodegradation rates were calculated, but bioattenuation time frames were measured in decades.

MNA of perchlorate is often less costly than engineered passive and active remediation systems. As shown at the manufacturing site, changes in mass flux across the site can be competitive with pump-and-treat, whose effectiveness is limited by the pumping radius of influence and changes to contaminant loading. The laboratory and field demonstrations performed as part of this project demonstrated the potential for using MNA as a groundwater remedy for perchlorate. The site conditions favorable to perchlorate biodegradation were defined and tested in the field to confirm their usefulness in MNA evaluations. The key favorable factors include mildly to strongly reducing conditions (ORP<+100 mV), the absence of strongly acidic groundwater (pH>5.5), relatively low nitrate concentrations, and the presence of TOC to supply electrons for perchlorate reduction (TOC>4 to 6 mg/L). MNA of perchlorate can be protective of human health and the environment and should be considered during a remedial alternatives evaluation as a potential remedy for remediating perchlorate contamination in groundwater.

2.0 INTRODUCTION

This Cost and Performance Report summarizes two demonstrations of perchlorate MNA. The work was funded by ESTCP Project No. ER-200428. The demonstrations evaluated the effectiveness of MNA as a technology for remediating and managing perchlorate contaminated groundwater. The demonstrations were conducted near Building 1419 at Indian Head NSWC in Indian Head, MD (Indian Head Site), and at the TCE/Perchlorate Solid Waste Management Unit (SWMU) field site at a manufacturing facility in Maryland. These sites were selected from a list of 120 DoD or DoD-related sites that were contacted by Solutions-IES. Samples from seven sites were subjected to laboratory testing and microcosm studies to estimate potential bioactivity on perchlorate.

While planning for the demonstrations, Solutions-IES prepared a Protocol for perchlorate MNA based on the lessons learned during preliminary field work completed at the demonstration sites (ESTCP, 2008). Both demonstrations were implemented following the tiered approach described in the Protocol to develop multiple lines of evidence related to perchlorate MNA. Separate technical reports were prepared for each site (ESTCP, 2010a, 2010b). The designs, concepts, results, discussions, and conclusions provided in these project reports are used without further citation in this Cost and Performance report to provide the reader a summary of the performance of the technology at each site and to provide the basis of the cost comparisons.

2.1 BACKGROUND

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

As contaminants emerge and are considered during a review of remedial strategies, MNA can be evaluated as an alternative if there is a thorough understanding of how MNA can be applied successfully. Specifically, groundwater contamination by perchlorate (ClO_4^-) has become a major environmental issue for DoD. In many cases, perchlorate has entered groundwater through the release and/or disposal of ammonium perchlorate, a strong oxidant that is used extensively in solid rocket fuel, munitions, and pyrotechnics. Perchlorate is highly soluble in water, sorbs poorly to mineral surfaces and can persist for decades under aerobic conditions. Treatment technologies applied to perchlorate contamination often include groundwater extraction with ion exchange or aboveground bioreactors to remove the contaminant (ITRC, 2005). The cost associated with these technologies can be very expensive compared to MNA, even when considering the long-term monitoring often required by MNA.

The potential for use of MNA is evident since a variety of studies have shown that microorganisms from a wide variety of sources (Coates and Pollock, 2003; Coates et al., 1999; Logan, 2001; Gingras and Batista, 2002) can utilize perchlorate as an electron acceptor and

anaerobically biodegrade perchlorate when organic carbon is available (Logan, 1998; Hunter, 2002; Zhang et al., 2002; Waller et al., 2004; Hatzinger, 2005).

The biodegradation pathway of perchlorate is illustrated in Figure 1. Perchlorate biodegradation can occur under strict anaerobic conditions as well as facultative anaerobic conditions. The breakdown of perchlorate to chlorate and then to chlorite is governed by perchlorate reductase enzymes. Final breakdown of chlorite to chloride and oxygen is controlled by the chlorite dismutase (CD) enzyme. In addition, some facultative anaerobic microorganisms are capable of both aerobic respiration under low oxygen tension and anaerobic respiration when oxygen is not present. This metabolic versatility suggests that environments exist that can support a variety of perchlorate-reducing microbial populations. This combination would presumably increase the potential that MNA can occur.

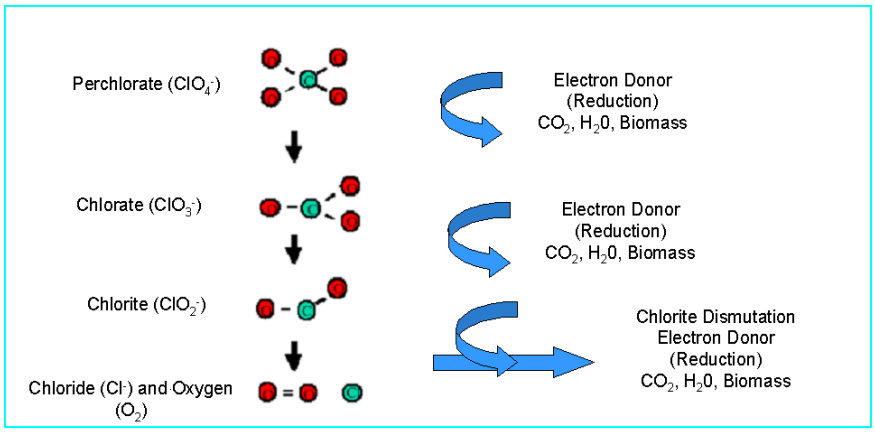

Figure 1. Perchlorate biodegradation pathway.

The key to perchlorate MNA is to establish the appropriate lines of evidence to support MNA during early phases of the remedial evaluation. Solutions-IES used the Protocol to guide this process at both demonstration sites to evaluate use of perchlorate MNA as a remedial alternative.

2.2 PROJECT OBJECTIVES

The overall goal of this project was to evaluate the potential for MNA of perchlorate and identify conditions for use of MNA as a remedial technology, more specifically:

- Demonstrate to regulatory agencies through field study that perchlorate MNA can be an effective method for managing impacts of perchlorate released to the environment
- Provide DoD managers with the tools needed to evaluate whether MNA may be appropriate for management of perchlorate–impacted groundwater on their site(s).

With this information, regulators and site owners can evaluate MNA along with other alternatives as a remediation strategy for groundwater impacted by perchlorate.

2.3 REGULATORY DRIVERS

Sampling performed by USEPA in 2004 revealed that over 11 million people in the United States had greater than 4 µg/L in their drinking water (Stroo et al., 2009). It appears that the primary exposure to perchlorate in the United States is through consumption of food (USFDA, 2007). This is a significant concern because high levels of perchlorate interfere with iodide uptake by the thyroid (NRC, 2005).

As of 2009, USEPA has not established a maximum contaminant level for perchlorate in drinking water (USEPA, 2009). However, in January 2006, the USEPA issued "Assessment Guidance for Perchlorate" identifying 24.5 µg/L as the recommended "to be considered" (TBC) value and preliminary remediation goal for perchlorate (USEPA, 2006). Since then several states have identified advisory levels that range in concentration from 1 µg/L to 18 µg/L (Hatzinger, 2005). Massachusetts promulgated the first state drinking water standard in 2006, at 2 µg/L (MADEP, 2006), and California has established a drinking water standard of 6 µg/L (CDHS, 2006). In 2008, Maryland adopted 2.6 µg/L as the drinking water standard (Maryland Department of the Environment [MDE], 2008).

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3.0 TECHNOLOGY DESCRIPTION

3.1 MONITORED NATURAL ATTENUATION

An integral component of any MNA remedy for groundwater is a clear understanding of the hydrogeologic conditions present in the site area. A site conceptual model (SCM) should be formulated and then calibrated against local data. Physical conditions of the aquifer, groundwater flow characteristics (e.g., flow velocity, dilution, and dispersion), and contaminant concentration data must be obtained and evaluated. It is also important to understand the interactions between contaminant and background geochemistry, including major aquifer anions and cations along with organic or anthropogenic sources of carbon. Finally, for MNA to be accepted, the practitioner must demonstrate biological activity on the contaminant to an extent that can affect the desired reduction in concentration.

USEPA and others have developed protocols and guidance documents for implementing MNA for specific contaminants. Published methods for evaluating MNA of petroleum hydrocarbons (Wiedemeier et al., 1995; USEPA, 1999) and chlorinated solvents (USEPA, 1998) have been in use for many years. These documents describe systematic steps for delineating contaminant plumes, describing trends in contaminant fate and transport, monitoring site geochemistry, testing site biology and even scoring the site for its potential to support natural attenuation (USEPA, 1998). Prior to current work, MNA of perchlorate had not been systematically tested in the field. To address this need, Solutions-IES developed an MNA Protocol for perchlorate (ESTCP, 2008) that used a tiered approach.

- Tier 1 - Plume stability and geometry
- Tier 2 - Geochemical parameters and biological indicators
- Tier 3 - Biodegradation rates

This tiered approach was then applied to evaluate MNA of perchlorate at each demonstration site.

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

3.2.1 Cleanup Objectives

The objective of all remediation approaches is to return groundwater to its beneficial uses whenever practicable. MNA is an appropriate remediation method when its use is protective of human health and the environment and it is capable of achieving site-specific remediation objectives within a time frame that is reasonable compared to other alternatives. If cleanup objectives are out of alignment with risks, use of MNA as a stand-alone technology may not be appropriate.

3.2.2 Advantages and Limitations of MNA

Natural attenuation is a combination of physical, chemical, and biological processes. Because perchlorate is an inorganic salt, it is very soluble and mobile in groundwater. It is subject to greater dilution than many organic contaminants. High solubility is both an advantage and

disadvantage. Flushing and dilution can reduce concentrations rapidly, but solubility can result in extended plumes with low concentrations that are difficult to capture and expensive to treat. As paraphrased from Wiedemeier et al. (1998), primary advantages of using MNA to remediate contaminants of concern in groundwater, including perchlorate, are:

- Reduced potential for cross-media transfer of contaminants commonly associated with ex situ treatment (i.e., no active remediation equipment)
- Reduced risk of human exposure to contaminants, contaminated media, and other hazards
- Destruction of contaminants via natural attenuation processes
- Less disturbance to site operations and ecological receptors
- No artificial or secondary impact to groundwater geochemistry and biology
- Applicability to all or a portion of a site depending on site characteristics and goals
- Usefulness in combination with other technologies
- Lower capital costs with low, if any, maintenance costs.

The limitations of MNA include:

- Potentially longer life cycles to reach remediation goals compared to active remediation measures at the site
- Need for more detailed site characterization to demonstrate attenuation, which may mean more complex and costly up-front investigation
- May require institutional controls to ensure long-term protection
- Long-term performance monitoring generally more expensive and for a longer time period
- Potential for continued contaminant migration, and/or cross-media transfer of contaminants
- May require a re-evaluation of MNA over time because of changing site conditions
- Public acceptance possibly more difficult and costly to obtain.

Although perchlorate remains an emerging contaminant of concern, sufficient methods are in place to obtain reliable data that can be used to evaluate the potential for MNA of perchlorate in groundwater. The cost drivers related to the advantages and disadvantages of perchlorate MNA specific to the Indian Head and Elkton site demonstrations are described in greater detail in Section 6.0.

4.0 INDIAN HEAD DEMONSTRATION SITE

4.1 PERFORMANCE OBJECTIVES

The Indian Head site was selected as one of the two sites for testing the potential for MNA of perchlorate in groundwater based on site conditions, microcosm studies, site logistics, and cost considerations. The SCM suggested that perchlorate-contaminated groundwater from the source near Building 1419, the former "hog-out" facility, was migrating approximately 300 to 400 ft toward Mattawoman Creek, a large tidally influenced creek that is a tributary of the Potomac River. Just prior to reaching the creek, perchlorate-laden groundwater migrates upward through highly organic sediments of the intertidal Littoral Zone where conditions are suitable for the anaerobic biodegradation. Wetlands and similar organic-rich environments at groundwater/surface interfaces have been shown to be important zones for anaerobic biodegradation and, therefore, the reduction of chlorinated volatile organic compounds (CVOCs) and other compounds (Lorah et al., 1997; Lorah and Olsen, 1999).

The objectives of the technical demonstration the Indian Head site were to:

- Further develop and evaluate lines of evidence established during the site selection process for their applicability to MNA in the field
- Evaluate the use of various biological indicators of perchlorate biodegradation
- Compare biodegradation rates established in microcosm studies with biodegradation rates in the field
- Evaluate the cost-effectiveness of MNA of perchlorate at the Indian Head site
- Validate the approach identified in the Protocol.

4.2 SITE BACKGROUND

4.2.1 Location and Current Conditions

The Town of Indian Head, MD, and the NSWC are located approximately 30 miles south of Washington, DC, on a narrow peninsula (neck) of land bounded to the north by the Potomac River and to the south by Mattawoman Creek (Figure 2). Both the Potomac River and Mattawoman Creek are tidal estuaries of the Chesapeake Bay estuary system. The surficial (water table) aquifer consists of more recent saturated alluvial soil resting on top of the Patapsco clay that is encountered at approximately 16 ft below ground surface (bgs). The surficial aquifer is unconfined and varies in its position seasonally in response to precipitation and evapo-transpiration. The water table surface generally slopes similar to the land surface topography, with the effect that upland areas generally serve as groundwater recharge areas and low areas generally serve as groundwater discharge areas. The demonstration area consists of approximately 2 acres extending from a former perchlorate clean-out or "hog-out" building (Building 1419) to Mattawoman Creek.

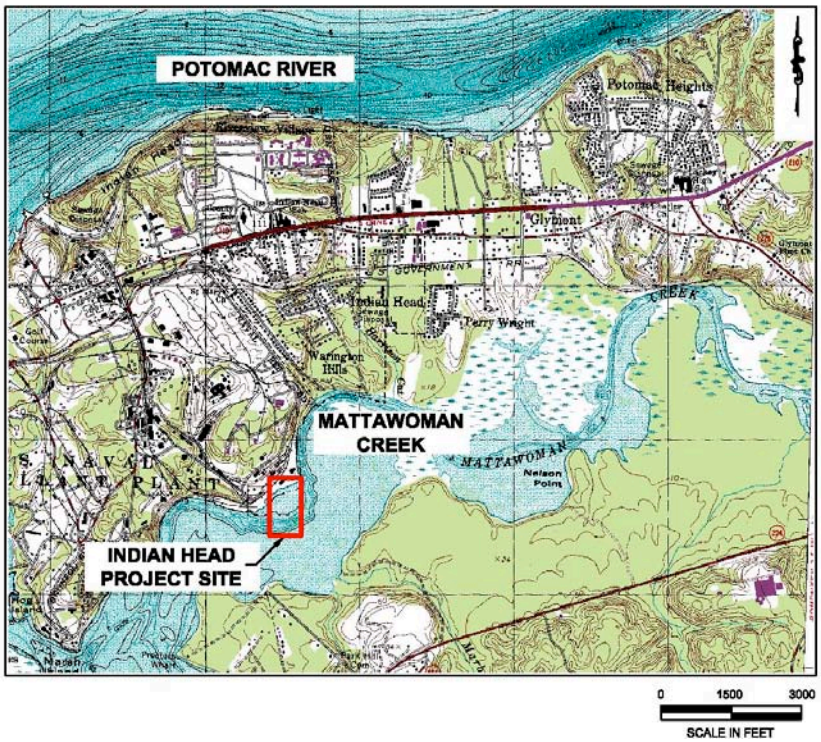

Figure 2. Map showing the Indian Head Project Site and vicinity at the Naval Surface Warfare Center, Indian Head, MD.
(Image from U.S. Geological Survey, 7.5 Minute Topographic Map, Indian Head, MD-VA, 1966, Photorevised 1978; Bathymetry added 1982)

4.2.2 Previous Remediation Studies

In 2001, ESTCP funded an independent study at the same location to demonstrate and validate the use of passive flux meters to determine groundwater and perchlorate fluxes at the Indian Head site (ESTCP, 2006). The study showed that perchlorate flux did not change over time from 2002 through 2005, suggesting the presence of a persistent source of perchlorate since no perchlorate-contaminated hog-out wastewater had been discharged since 1996. Measurements of vertical perchlorate flux suggested the possibility of a vadose zone source that would continuously release perchlorate to the aquifer by recharge induced by rainfall. This phenomenon could be used to explain high temporal variability of perchlorate concentrations in wells located 180 and 125 ft downgradient from the presumed source area near Building 1419.

In 2002, Shaw Environmental, Inc. (Shaw) conducted an enhanced in situ bioremediation pilot study (Cramer et al., 2004; Hoponick, 2006) at the Building 1419 site. In the Test Plot amended with >100 mg/L lactate and buffer, the results demonstrated that:

- "Naturally occurring perchlorate-degrading bacteria are present in the groundwater underlying [the Bldg. 1419 site]
- These organisms can be stimulated to degrade perchlorate from more than 50 mg/L to below detection using lactate as a food source

- The pH of the aquifer must be buffered to achieve optimal perchlorate biodegradation"
- Lactate lasted just about one month in the aquifer after its injection was stopped.

4.2.3 Pre-Demonstration Testing

Prior to initiating the current field demonstration, several tasks were completed to assess the current groundwater conditions.

4.2.3.1 Task 1: Groundwater and Soil Sampling

In February 2005, Solutions-IES collected groundwater samples from existing monitor wells MW-1, MW-2, and MW-4, used previously to monitor the Shaw pilot test, and saturated soil samples from immediately adjacent to MW-2 and MW-4. These samples were analyzed for TOC, a complete suite of biogeochemical parameters, and presence of the CD enzyme. From these results, Solutions-IES concluded that:

- The long-term impact from the Shaw lactate injection would not likely complicate the perchlorate MNA technical demonstration as there was little indication of residual TOC in groundwater in proximity of the pilot test treatment cell.
- In general across the site, perchlorate concentrations in groundwater remain elevated.
- A strong positive indication (+++) of CD was reported from soil collected near MW-2; a more variable indication (+/-) was reported from sediments in the vicinity of MW-4.

4.2.3.2 Task 2: Laboratory Studies

Solutions-IES created 250-mL microcosm bottles using sediment and groundwater obtained from the vicinity of MW-2 to test three conditions: (1) natural attenuation of perchlorate (ambient conditions) starting at relatively low concentrations (i.e., ~100 to 200 µg/L); (2) natural attenuation of perchlorate starting at relatively high concentrations (i.e., ~5,000 µg/L); and, (3) for comparison, enhanced attenuation in the presence of added simple and complex electron donors, i.e., lactate and Emulsified (Edible) Oil Substrate (EOS®)[1] solutions, respectively. The treatments testing natural attenuation received no amendments unless perchlorate had to be added to achieve the desired starting concentration.

The Treatability Report (ESTCP, 2007) indicated that perchlorate declined slowly but measurably over the 1-year incubation period in unamended microcosms with both high and low starting concentrations. In the presence of EOS®, the concentration of perchlorate quickly decreased below detection indicating that bacteria with perchlorate-reducing capacity were present in the environment and could be readily stimulated to achieve high rates of biodegradation. The first-order biodegradation rate for low perchlorate starting concentration

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

without donor amendment was calculated to be 0.01/d (3.7/yr). In the killed control microcosms, the concentrations of perchlorate and other electron acceptors (nitrate and sulfate) remained constant over time further supporting the conclusion that the observed reduction in perchlorate in ambient microcosms was due to biological activity and the site was a good candidate for demonstrating the potential for perchlorate MNA.

4.3 DEMONSTRATION APPROACH

4.3.1 Additional Site Characterization and Performance Monitoring

Analytical methods are available to monitor the concentration of perchlorate in the environment with high sensitivity and selectivity; geochemical tests can indicate whether ambient conditions are conducive to perchlorate biodegradation; and molecular biological tools (MBTs) are available to monitor the activity and sustainability of perchlorate-reducing bacterial populations. With some minor exceptions, the tiers outlined in the Protocol were followed to help the planning and selection of tasks to address specific challenges. An additional 35 monitor wells and 10 piezometers were installed across the site and into Mattawoman Creek to characterize the site and facilitate data collection.

4.3.2 Site Hydrogeology and Plume Configuration

Figure 4 shows the monitor well network across the project site from Building 1419 to Mattawoman Creek. The four geomorphological zones are identified from the land surface into the creek. The SCM hypothesized that perchlorate entered the water table aquifer near the former “hog-out” building, and has moved advectively with groundwater to the south toward the creek. Along the flow path, it has been subjected primarily to dispersion and dilution. Sorption to the aquifer matrix is minimal because of its high solubility and poor sorption characteristics. In addition, the underlying Patapsco clay restricts downward movement of dissolved perchlorate so that most of the remaining perchlorate mass moves horizontally with groundwater flow towards Mattawoman Creek. The plume is at least 400 ft wide along the creek bank, and dispersion of the plume has resulted in similar perchlorate concentrations being observed throughout the thickness of the surficial aquifer. The perchlorate concentrations reported across the site in April 2008 are also shown on Figure 3.

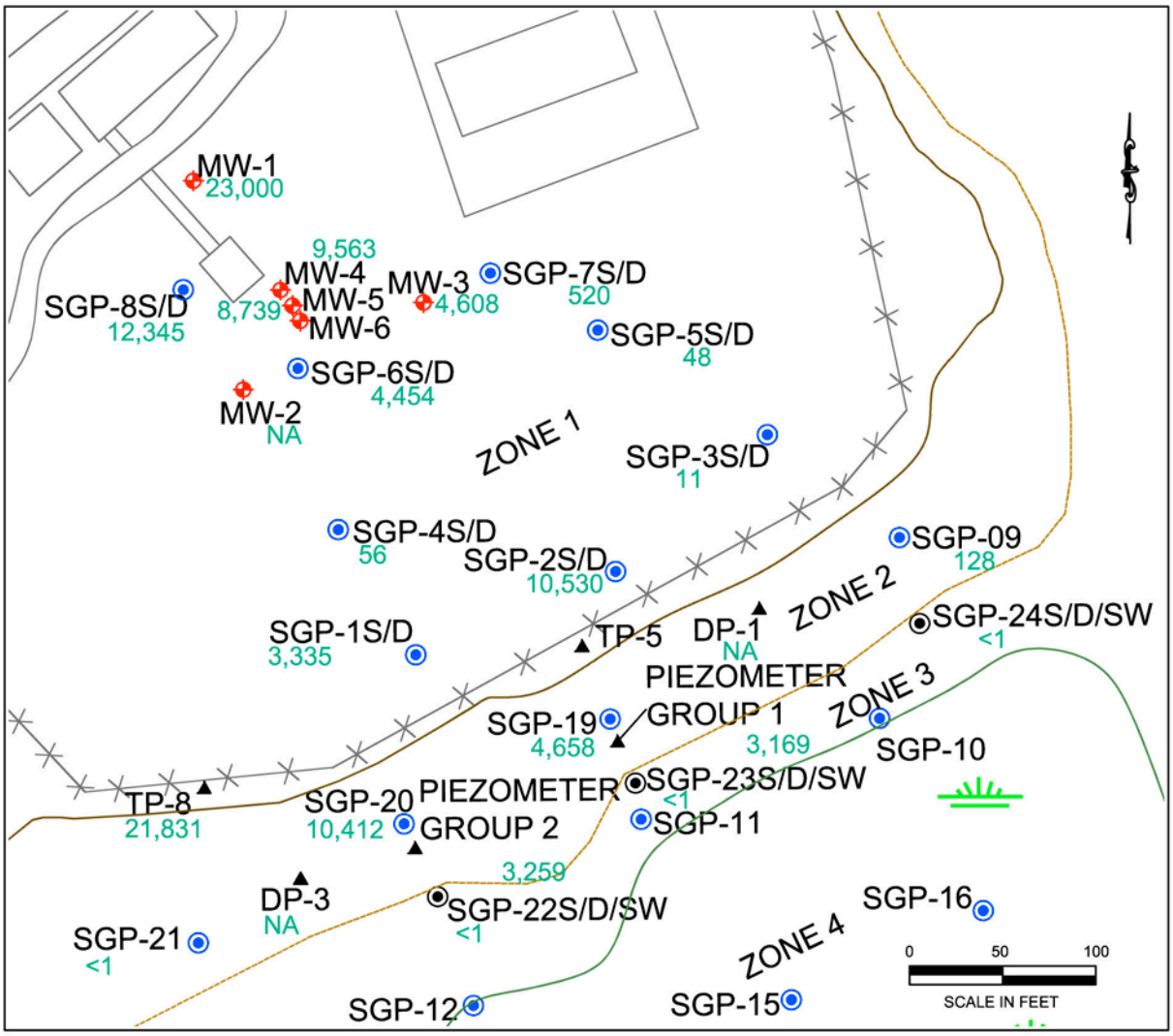

Figure 3. Perchlorate concentration map at the Indian Head Project Site (April 2008)**.**

The land area south of Building 1419 is referred to as Land Zone 1. Cramer et al. (2004) described fill soils beneath Land Zone 1 as having been previously placed in various areas of the site. The fill was described as gravel and silty sand containing some organic matter and debris. Thickness ranged from <1 ft to approximately 4 ft. Underlying the fill is 13 to 16 ft of silty sandy-sandy silt containing thin (1 to 2 inches thick) discontinuous sand lenses. The units vary both horizontally and vertically and rest on 12- to 18-inches of coarse alluvial sand and gravel. The coarse alluvium also appears to be variable in thickness and location.

Solutions-IES identified similar subsurface conditions also further south of the Shaw pilot test, but the coarse alluvium was not identified in two borings located closer to Mattawoman Creek. At these locations, the basal portion of the alluvium consists of fine-grained sand without the gravel, resting on dark gray clay, which extends to a depth of at least 24 ft bgs. The clay encountered beneath the alluvium in the land borings appears to be extensive and was reported at other locations across the NSWC.

Zones 2 through 4 are located within Mattawoman Creek. Zone 2, the Littoral Zone, is defined as the region that is above the low-water mark and below the high-water mark, i.e., exposed to air at low tide and submerged at high tide (Figure 4). Zone 3, the Subtidal Channel, is a relatively narrow channel-like depression that parallels the creek bank at the edge of the Littoral Zone, and Zone 4 (the Subtidal Shallows) is an expanse of accreted sediment located south of the Subtidal Channel along an inside meander of Mattawoman Creek. Zone 4 is submerged with 6 to 18 inches of water at low tide. The monitoring well/ piezometer network was sampled up to five times during the 38-month performance monitoring period.

Figure 4. Appearance of Littoral Zone in winter and summer at the Indian Head Project Site.

4.4 INDIAN HEAD PERFORMANCE ASSESSMENT

The Tier 1 and Tier 2 evaluations are summarized together as they are both derived from contaminant and biogeochemical information collected during performance monitoring. The Tier 3 evaluation includes specialized laboratory testing and the installation, data collection, and analysis of in situ columns designed to derive biodegradation rates, so it is summarized separately.

4.4.1 Tier 1 and 2 Evaluations

The performance monitoring data are presented in tables in the Indian Head Technical Report (ESTCP, 2010a). Figure 5 illustrates selected groundwater parameters beneath the four zones as groundwater moves toward the discharge area along the creek bank. As illustrated by the figure, elevated perchlorate concentrations are present in the groundwater beneath the land surface and partly beneath the Littoral Zone (dark red color). However, the perchlorate concentration decreases rapidly (orange) as it moves vertically through the Littoral Zone and into the Subtidal Channel (yellow).

4.4.1.1 Zone 1 (Land)

The pH of the groundwater beneath the Land Zone is acidic and below optimal for the growth of many bacteria, although populations of 10^4 to 10^5 eubacteria/mL were measured in both the shallow and deep portions of the surficial aquifer. Generally positive ORPs were measured throughout and only low concentrations of methane were detected, suggesting somewhat oxidative conditions with limited bioavailable TOC. Based on these biogeochemical conditions, residual elevated perchlorate concentrations throughout the vertical groundwater profile beneath the Land Zone would not be unexpected. However, in several wells located in the upgradient portion of the plume near the source area, a statistically significant decrease in the perchlorate concentration with time was measured. Estimated time to reach the cleanup standard of 24.5 µg/L was also calculated using the best fit linear regression and varied from 11 to 27 years. Much of these declines could be attributed to flushing of highly soluble perchlorate out of the aquifer by incoming groundwater, but some contribution by biodegradation remains possible, despite the less than optimal conditions.

4.4.1.2 Zone 2 (Littoral – Intertidal)

The Littoral Zone is subject to tidal cycles, is heavily vegetated with grasses in the spring and summer, and subject to plant deposition and decay in the fall and winter. This zone is also subject to mixing of surface water with groundwater. Pore water within the deeper Littoral Zone sediment is more characteristic of groundwater beneath the land, whereas shallow pore water within the Littoral Zone is a mixture of groundwater and surface water.

Biogeochemical conditions in the deeper pore water are also similar to those in groundwater beneath the land. Perchlorate is still present at concentrations similar to that measured in wells along the shoreline as suggested by the dark red color in Figure 5. The pH of the water collected in the deeper portions of the Littoral Zone is also generally lower than optimal for bacterial growth, but there are high populations of bacteria ($>10^6$ eubacteria/mL) nonetheless. The positive ORP and absence of methane production suggest generally oxidative conditions. These are conditions that do not favor perchlorate-reducing bioactivity and are corroborated by the relative absence of reportable concentrations of perchlorate reductase (*pcrA*) gene copies in 67% of the locations tested.

However, pore water in the shallow sediment would be expected to be influenced by the cyclical growth, death and decay of plant matter resulting in deposition of organic carbon and formation of the muck layer that was observed. The data from the nutrient-rich Littoral Zone showed this

relationship as there is increased TOC, a drop in ORP to a more favorable range (i.e., ORP<50 mV) for dissimilatory perchlorate-reducing bacteria (DPRB) and methanogenesis to occur, and a pH closer to pH 6. Even higher populations of eubacteria (>10^7 eubacteria/mL) were enumerated with up to 19,000 *pcrA* gene copies reported in the shallow sediment. Perchlorate mass flux decreased from 10 mg/d/linear ft as groundwater moves laterally from beneath the Land Zone to beneath the Littoral Zone to less than 0.0002 mg/d/linear ft as groundwater moves vertically just below the mud bottom of the creek. As a result, perchlorate concentrations in the shallow groundwater beneath the Littoral Zone are nondetect.

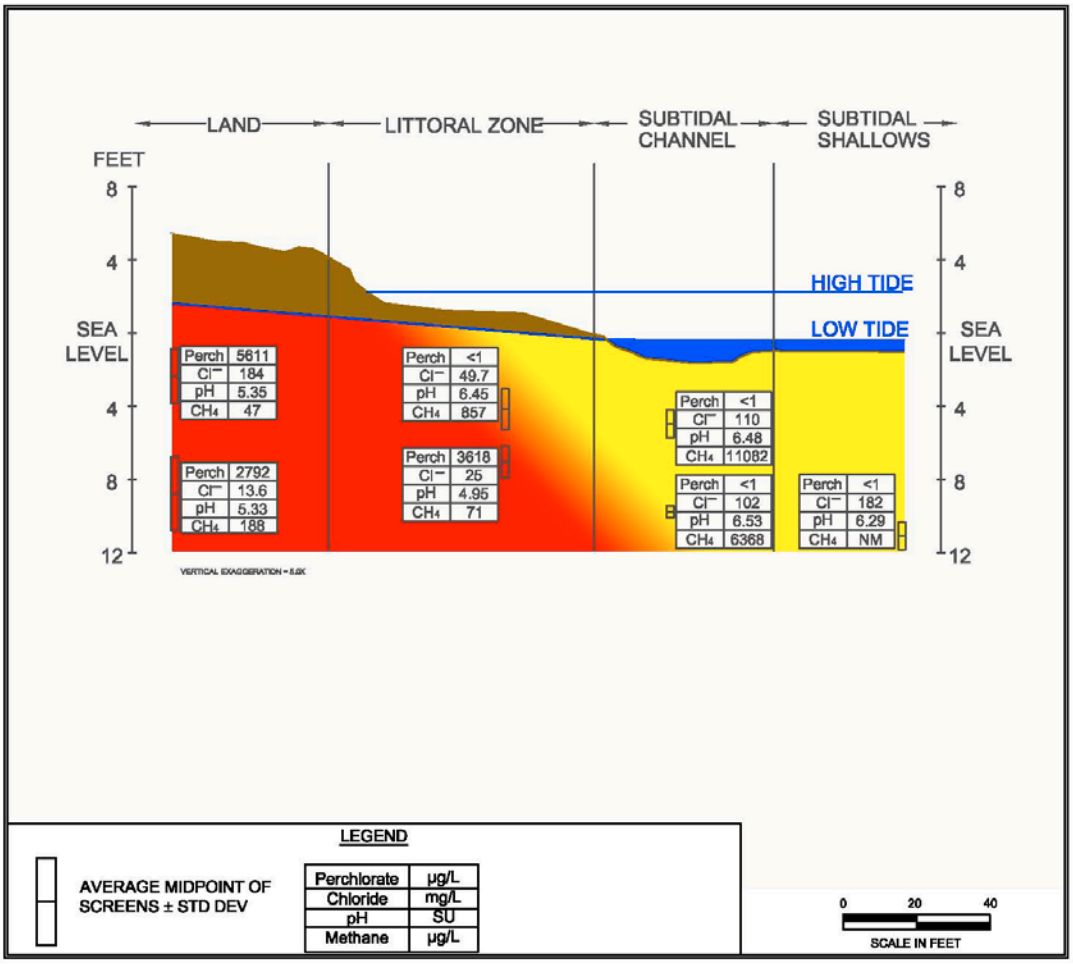

Figure 5. Geochemical changes in groundwater and sediment pore water beneath the four geomorphological zones at Indian Head Project Site.

4.4.1.3 <u>Zone 3 (Subtidal Channel) and Zone 4 (Subtidal Shallows)</u>

Regulatory agencies require that contaminant plumes are stable or shrinking before MNA can be employed as the primary groundwater remediation technology. The data show no evidence of an increase in perchlorate concentrations over time in the deep wells in the Littoral Zone and further downgradient migration of perchlorate in groundwater beyond the Littoral Zone is limited by the organic rich sediments beneath the creek. The conditions observed in the shallow and deep sediment beneath the Subtidal Channel and Subtidal Shallows are conducive for the

biodegradation of perchlorate. The perchlorate concentration was less than 1 µg/L in monitoring points within the Subtidal Channel indicating perchlorate was not migrating underneath or into the Subtidal Channel. DPRB, as enumerated by quantitative polymerase chain reaction count of the number of copies of the *pcrA*, are present in this nutrient-rich environment and would be expected to degrade any residual perchlorate that might migrate via discharging groundwater beyond the Littoral Zone. In this project, perchlorate was reduced to below detectable levels in every sample with greater than 10^2 *pcrA* copies/mL.

The Tier 2 evaluation showed that groundwater conditions are conducive to perchlorate biodegradation beginning in the nutrient-rich shallow groundwater beneath the Littoral Zone and continuing out into Mattawoman Creek. However, because of the complex hydrogeology and the complicating potential contribution of the mixing and dilution to the observed perchlorate attenuation, additional steps were taken to provide direct evidence of perchlorate-reducing bioactivity. The Tier 3 evaluation describes additional lines of evidence obtained from studies designed to obtain biodegradation rate measurements

4.4.2 Tier 3 Evaluation

Macrocosm and in situ column studies were designed for the Tier 3 evaluation. The set-up details and results are provided in the Technical Report (ESTCP, 2010a). The first-order biodegradation rates ranged from 0.12 to 0.63/day (Table 1). The rates and corresponding half-lives generated in macrocosms, in situ columns, and piezometers are similar. This supports the use of these tests for estimating biodegradation in the natural environment. The results also support the information obtained in Tier 1 and 2 as additional lines of evidence for the natural attenuation of perchlorate. The findings, when considered together, support the SCM and could be used to form the basis of a recommendation that perchlorate MNA is potentially an acceptable remedy for this site.

Table 1. Summary of first-order biodegradation rates in perchlorate plume matrices from the Indian Head Site.

Test	Rate Constant (per day)	Half-Life (days)
Macrocosms	0.12	5.8
In situ columns	0.12 to 0.63	5.8 to 1.1
Piezometers	0.27	2.6

4.5 INDIAN HEAD COST ASSESSMENT

The total cost of the Indian Head test demonstration was approximately $509,100 (ESTCP, 2010a). Primary cost elements included:

- Technical Demonstration Plan, White Papers/Design: ~$51,300 (10%)
- Additional Characterization: ~$103,600 (20%)
- Performance Monitoring & Data Acquisition for Tiers 1 & 2: ~$209,300 (41%)
- Tier 1 and 2 Data Evaluation: ~$14,900 (3%)
- Tier 3 Data Acquisition and Evaluation: ~$60,000 (12%)
- Technical Reporting: ~$70,000 (14%)

Large portions of the demonstration costs were associated with performance monitoring and site characterization, which included the installation of 35 additional monitoring wells and piezometers in the Littoral Zone, Subtidal Channel and Subtidal Shallows in Mattawoman Creek in order to evaluate the complex hydrogeology. The Tier 3 evaluation also cost more in comparison to other elements of the demonstration because of the complexity of installation and data collection from the in situ columns in the Littoral Zone and construction of and additional monitoring of the macrocosms. Project costs not directly related to the individual technical demonstrations such as project management and technical transfer, site screening and treatability study, and protocol development are not included in the cost summary.

5.0 MARYLAND MANUFACTURING FACILITY DEMONSTRATION SITE

5.1 PERFORMANCE OBJECTIVES

The goal at this site was to show that the tiered approach could be used effectively at a second, different site to demonstrate the potential for natural attenuation of perchlorate. The demonstration objectives were the same as those for the Indian Head project (see Section 4.1), but the SCM for this location was slightly different. At the Maryland manufacturing site it was hypothesized that perchlorate-contaminated groundwater migrates primarily through an intermediate aquifer (from 20 to 70 ft bgs) from the presumed source area almost 3400 ft prior to discharge to Little Elk Creek. As the contaminated groundwater moves toward the creek, the deeper intermediate aquifer thins and merges with the shallow aquifer, which passes beneath a wooded riparian buffer just prior to discharge into the creek. The data suggested that conditions close to the discharge area were sufficient to naturally attenuate perchlorate, but TCE commingled with perchlorate was reported both in and just beyond the creek without complete removal. This indicated that conditions were probably suboptimal for anaerobic reductive dechlorination of CVOCs.

5.2 SITE BACKGROUND

5.2.1 Location and Current Conditions

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

Recent investigations have identified perchlorate in groundwater and showed that the commingled TCE and perchlorate plume extending eastward from the manufacturing area goes off site to the east under Elkton Road and all the way to Little Elk Creek beyond the neighboring YMCA property, and to the south side of U.S. Route 40. The horizontal extent of the TCE and perchlorate in groundwater is shown in Figure 6. In the absence of a defined source, this entire plume is considered to be a SWMU and is called the TCE/Perchlorate SWMU.

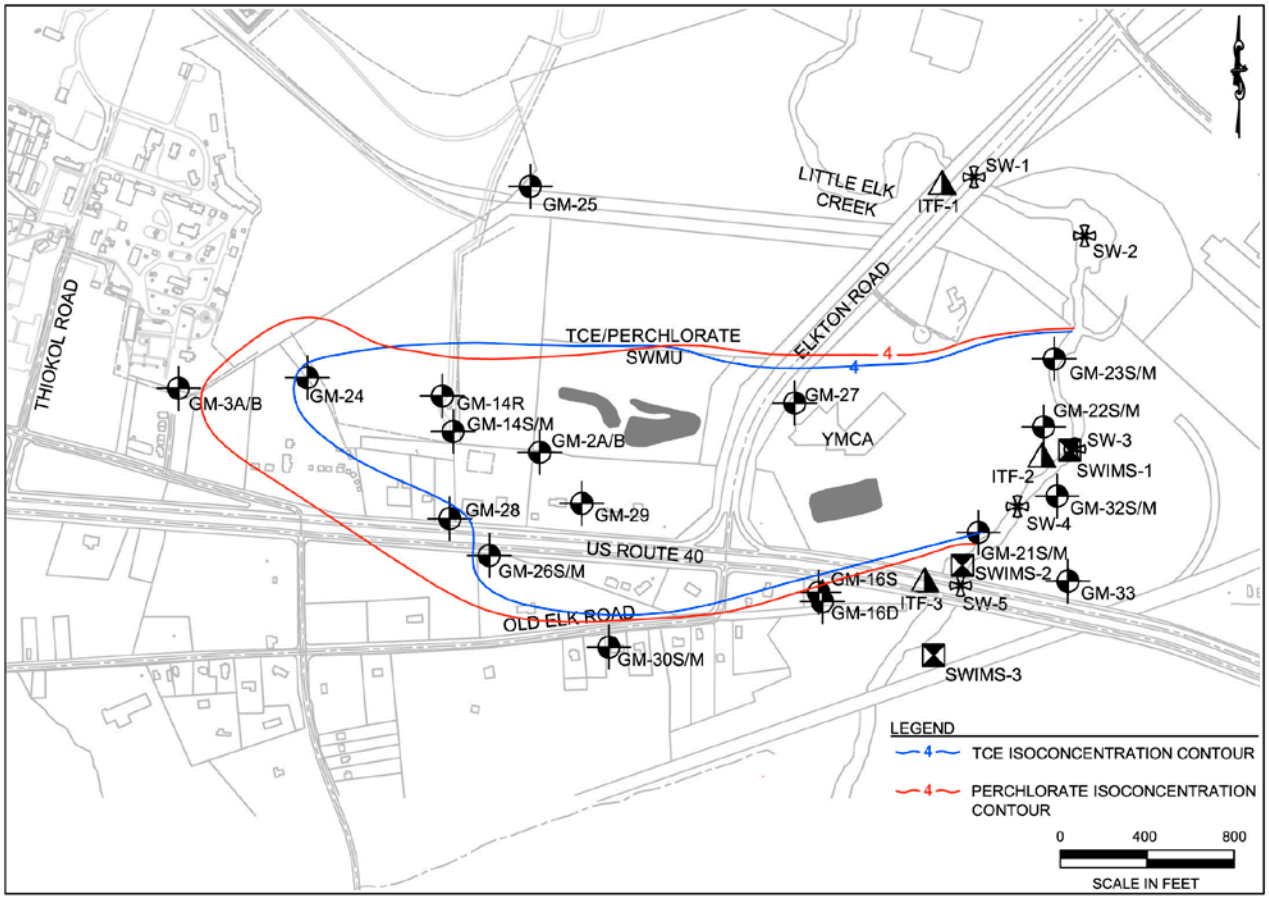

Figure 6. Horizontal extent of the commingled TCE and perchlorate plume at the Maryland manufacturing site.

5.2.2 Previous Remediation Activities

5.2.2.1 <u>A-82 Pump-and-Treat System</u>

As an interim remedial measure, in 1997 recovery well GM-14R and a shallow-tray air stripper system were installed to capture, withdraw, and treat contaminated groundwater from the intermediate aquifer in the vicinity of the source. Treated water is discharged through a pipe carrying the water approximately 1800 ft north to the closest point along Little Elk Creek. Discharge is allowed by a National Pollution Discharge Elimination System permit.

The pump-and-treat (P&T) system has operated since 1998, effectively accounting for the removal of over 800 lb of volatile organic compounds (VOCs) from the aquifer. Perchlorate recovered by the system was reported in the influent waste stream occasionally during the years of monitoring. For example, 31 lb of perchlorate were recovered in 2003 and 12 lb in 2007, but perchlorate is not treated by air stripping and likely remained in the discharge water.

5.2.2.2 In Situ Bioremediation Pilot Test

In 2004, ARCADIS performed a pilot test to demonstrate the effectiveness of injection of a molasses solution into the aquifer to promote in situ bioremediation of CVOCs and perchlorate. The In Situ Reactive Zone (IRZ) pilot test was installed in the vicinity of monitor wells GM-14S/M where TCE and perchlorate levels were 1000 and 1240 µg/L, respectively, at the beginning of the test. The test was monitored for about 1 year during which time TCE concentrations at GM-14M fluctuated but never dropped appreciably. By contrast, the concentration of perchlorate dropped from the baseline level to nondetect after approximately 7 months. Once the added carbon was depleted, mass flux of perchlorate from shallow upgradient portions of the plume caused a rebound in perchlorate levels.

5.2.3 Pre-Demonstration Testing

5.2.3.1 Groundwater and Soil Sampling

The wells of interest during the site screening process included GM-3B, GM-14M, GM-2B, GM-22S and GM-22M. As shown on Figure 6, these wells generally form a line starting close to the plant and moving east (i.e., downgradient) toward the eastern leg of Little Elk Creek. During the site-selection process, samples were collected from these wells and a soil sample was collected from 3 to 5 ft bgs (below the water table) from adjacent to GM-22S (Figure 7).

Figure 7. Location of GM-22S/M near the wooded riparian buffer on the west side of Little Elk Creek.

Perchlorate concentrations ranged from 1200 µg/L near the presumed source to an average of 215 µg/L at GM-22S/M, about 30 ft from the creek. TCE concentrations actually showed an increase from 1300 µg/L near the source to an average of 2015 µg/L at GM-22S/M. Groundwater pH was generally below 6, ORP was +130 to +220 mV across the plume, and TOC and methane were absent. However, the CD enzyme assay from soil near GM-22S was positive. Despite the appearance of conditions suboptimal for natural attenuation of TCE, the decrease in

perchlorate downgradient of the source and the positive enzyme assay result were sufficient to continue the evaluation of this plume as a demonstration site.

5.2.3.2 Laboratory Studies

Microcosm studies were performed with soil and groundwater collected from the vicinity of GM-22S. The bottles were prepared to test three conditions: (1) natural attenuation of low starting perchlorate (~100 µg/L); (2) natural attenuation of perchlorate starting at relatively high concentrations (~5000 µg/L); and (3) enhanced attenuation in the presence of added simple and complex electron donors (i.e., lactate and EOS® solutions, respectively).

In the microcosms spiked to contain a high elevated perchlorate starting concentration, nitrate decreased to below detection while sulfate, chloride, and dissolved oxygen (DO) remained constant over time. The average perchlorate concentration declined from 5400 µg/L to 1416 µg/L, a 70% reduction over the one-year incubation period (Figure 8). In one of the high perchlorate microcosm replicates, perchlorate was reduced to below the detection limit. In the low and high perchlorate killed microcosms, perchlorate, chloride, sulfate, and DO remained constant showing no biodegradation.

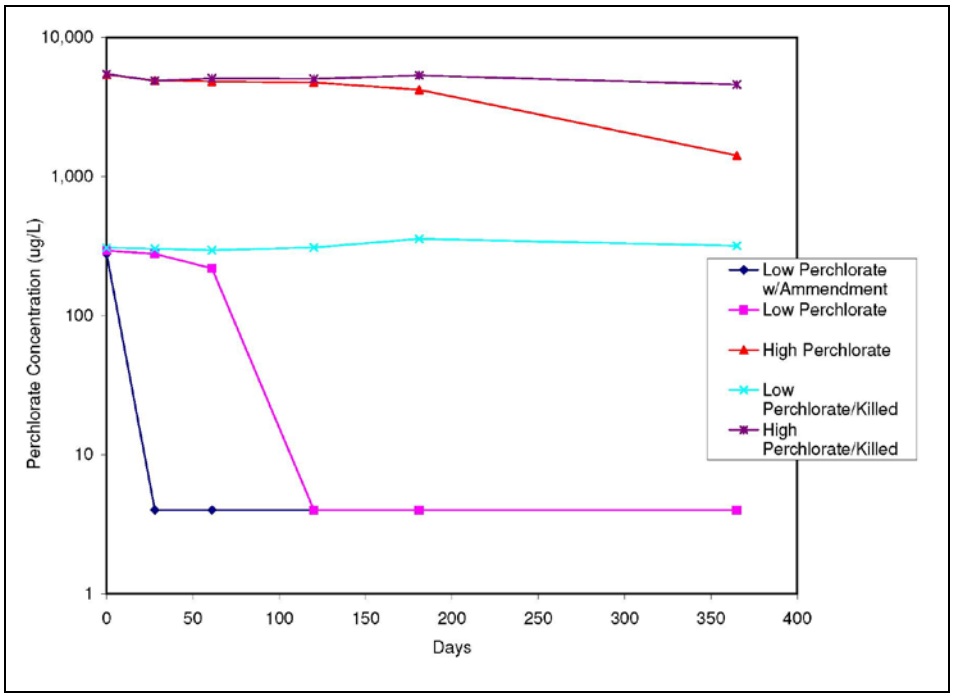

Figure 8. Perchlorate concentrations in microcosms versus time using soil and groundwater from the TCE/perchlorate plume (ESTCP, 2007)**.**

In microcosms with low starting perchlorate, a lag lasting ~61 days was observed followed by a rapid decrease in perchlorate concentration. The zero-order rate between Day 61 and Day 120 was 3.6 µg/L/day and the first-order degradation rate for the same period was 0.068/day. At high starting concentrations, the best fit curve was shown to be zero-order resulting in an ambient perchlorate degradation rate of approximately 9.7 µg/L/day. Although slow, the decrease in perchlorate concentration over one year under ambient conditions and the accelerated

degradation in the presence of substrate demonstrate that microorganisms capable of perchlorate reduction are present in soil and groundwater near the presumed plume discharge area in the vicinity of Little Elk Creek.

5.3 DEMONSTRATION APPROACH

5.3.1 Additional Site Characterization and Performance Monitoring

Solutions-IES augmented the existing monitor well network by installing several new monitor wells to further delineate the plume geometry, fill in gaps in coverage, and provide additional sources of data from which to evaluate MNA and perchlorate mass flux. Four additional monitoring well pairs were constructed in December 2006: three monitoring well pairs east of Elkton Road on the property owned by the YMCA (designated SMW-9S and 9M, SMW-11S and 11M, SMW-13S and 13M) and one well pair west of Elkton Road (SMW-8S and SMW-8M). A well in each well pair was terminated within the shallow and intermediate aquifers. The shallow monitoring wells were generally terminated so that the screen interval was approximately 20 to 30 ft bgs, and each intermediate monitoring well was terminated so that the screen interval was approximately 50 to 60 ft bgs. The new and existing monitoring wells were sampled up to five times during the 23-month performance monitoring period from May 2006 and April 2008 to evaluate aquifer conditions and how those conditions might affect the potential for natural biodegradation of perchlorate.

5.3.2 Site Hydrogeology and Plume Configuration

ARCADIS (2007) described the site hydrogeology as consisting of three units: a shallow unconfined aquifer (depths less than -20 ft msl), the intermediate Potomac Group (depths between -20 and -70 ft msl), and the deep saprolite unit (depths greater than -70 ft msl). The depth to bedrock ranges from about 90 to 150 ft bgs between the plant area and Little Elk Creek to the east. The thickness of the overlying saprolite ranges from 5 to 64 ft. The saprolite is micaceous, silty, and friable, becoming more cohesive and resistant to drilling with depth.

The sediments of the Potomac Group overlie the bedrock/saprolite. A layer of predominantly fine sandy silt (varying in thickness from 18 to 35 ft) 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. Most historical site data have indicated that the plume is migrating east/southeast primarily in the intermediate zone of the Potomac Group. The flow direction basically follows the surface topography. A pumping test on GM-14R located near the presumed source within the TCE/Perchlorate SWMU calculated the hydraulic conductivity ranging from 9.0 ft/d to 31 ft/d. With a reported gradient of 0.002, and effective porosity of 0.20, the groundwater velocity ranges from 0.1 ft/d to 0.3 ft/d (36 ft/yr. to 110 ft/yr.) (ARCADIS, 2003).

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 environment and occurs along Little Elk Creek and its tributaries. Limited data indicate an

alluvial thickness of 0 to 40 ft; these beds are extremely variable in their horizontal and vertical extent. Information gathered during additional assessment activities generally supports previous work.

During the ARCADIS (1999) perchlorate investigation, surface water samples were collected along the length of Little Elk Creek with three locations being within the presumed plume discharge zone (Figure 6). Each of these surface water samples contained low concentrations of perchlorate and TCE suggesting further that groundwater is discharging to Little Elk Creek.

5.4 PERFORMANCE ASSESSMENT

The potential for perchlorate MNA at the site was evaluated using the tiered approach described in the Protocol (ESTCP, 2008). The plume at the TCE/Perchlorate SWMU was divided into transects, which are illustrated in Figure 9 to aid in the evaluation. Contaminant concentrations, biogeochemical conditions, and MBT enumerations were performed along the entire well network as part of the Tier 1 and Tier 2 evaluations. In Tier 3, specialized studies designed to determine biodegradation rates were conducted only on matrices from closer to Little Elk Creek. The complete data set is provided in the Technical Report for this demonstration (ESTCP, 2010b). The results are summarized below.

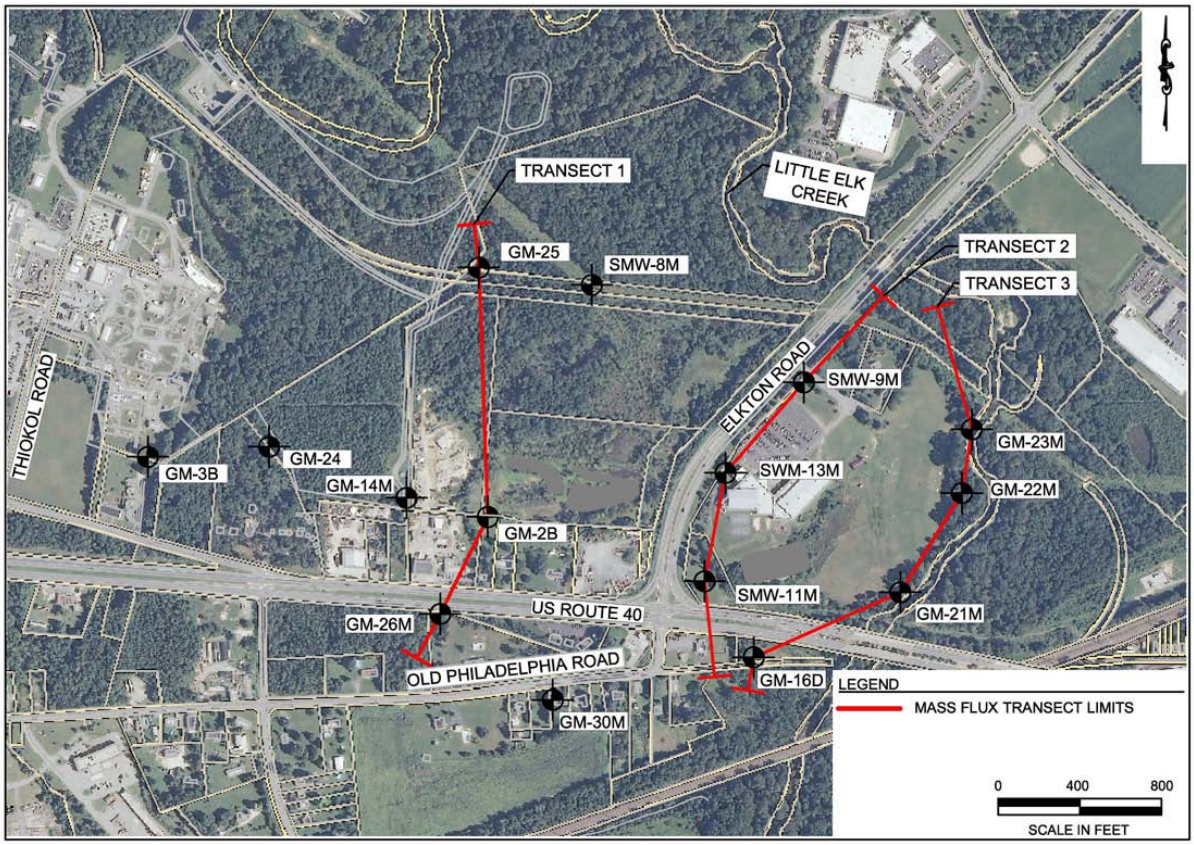

Figure 9. Transects for estimating mass flux across the TCE/perchlorate plume.

5.4.1 Tier 1 and Tier 2 Evaluations

5.4.1.1 Current Source Conditions

The Presumed Source Area is in the vicinity of GM-14S/M. There are currently low concentrations of perchlorate in the groundwater at both depths. In March 2004, prior to the IRZ pilot test, the concentration of perchlorate in GM-14M was 1240 µg/L. It appears that the introduction of organic substrate stimulated perchlorate reduction resulting in an 80 to 90% decrease in concentration. These wells are slightly acidic but contain some residual TOC and show evidence of reducing conditions that could promote further perchlorate degradation. These source area wells also contain measurable populations of bacteria with chlorite dismutase (*cld*) and *pcrA* gene copies. The historical data from several source area wells suggest significant perchlorate decreases over time in this portion of the site. This attenuation could be attributable to a combination of natural abiotic processes, the activity of the pump-and-treat system, and enhanced perchlorate reduction during the former bioremediation pilot study, all in the same general area.

5.4.1.2 Mid-Plume Conditions (Transect 1)

Transect 1 is located approximately 500 to 700 ft downgradient of the presumed source. These wells begin to show the perchlorate contamination pattern that is most prevalent throughout the plume. There is virtually no perchlorate in the shallow portion of the aquifer (<1 to 21 µg/L), but there is elevated perchlorate in the intermediate groundwater (153 to 1053 µg/L). The pH is somewhat acidic, the ORP is oxidative, and there is virtually no TOC present that could enhance biodegradation of perchlorate. There are measureable populations of microorganisms (10^3 to 10^5 eubacteria/mL) in both the shallow and deep portions of the aquifer but no detectable perchlorate-reducing bacteria in this environment, although the *cld* assays did indicate some capability. Although the oxidative conditions, low pH, and absence of TOC do not support bioattenuation of perchlorate, abiotic factors such as dilution and dispersion may account for decreases in perchlorate concentrations observed over time. Conversely, a similar decrease in TCE was not observed.

5.4.1.3 Mid-Plume Conditions (Transect 2)

Transect 2 includes three well pairs installed along Elkton Road to fill out the well network for this project. Conditions in the shallow and intermediate aquifer in areas approximately 1000 to 2000 ft downgradient from the presumed source (i.e., mid-plume) are very similar with the exception that there is some perchlorate (67 to 748 µg/L) in the intermediate zone and virtually none detectable (<1 to 70 µg/L) in shallow groundwater. There is no detectable TOC, groundwater is mostly acidic pH, ORPs are oxidative, and there are low bacterial populations with no evidence of *pcrA* activity. These conditions are not conducive to bioattenuation of perchlorate or TCE.

5.4.1.4 Presumed Discharge Zone (Transect 3 and Interface Samples)

The well pairs situated near Little Elk Creek (GM-21S/M, GM-22S/M and GM-23S/M) are located just before the 30-ft-wide wooded zone that forms a buffer between open playing fields and the creek. Shallow and intermediate groundwater merge in this area as deeper water

migrates upward before discharging into the creek. There is some evidence that not all groundwater is controlled by the creek since TCE has been measured in groundwater on the opposite side, but perchlorate has not been detected beyond the creek. Measurable perchlorate and TCE are in all the shallow and intermediate wells in this distal portion of the plume. The data suggest increased *cld* and *pcrA* activity in this area of the aquifer, and some natural perchlorate biodegradation appears to have occurred. Although the biogeochemical conditions may support perchlorate biodegradation, reductive dechlorination of TCE is minimal.

Groundwater conditions change immediately before discharge into Little Elk Creek. The interface samples taken from 1 to 2 ft below the surface along the edge of the creek contained 6 to 19 mg/L TOC with pH closer to 5.9. The ORP in interface sample ITF-1 was -67 mV, suggesting a reducing environment, and methane was reported in all three interface samples. This portion of the plume appears to be the zone most favorable for biodegradation of perchlorate, which is consistent with the absence of perchlorate in the creek. As before, these conditions do not appear to be sufficient to promote TCE biodegradation to the same degree.

The Tier 1 and 2 evaluations show that groundwater conditions are minimally conducive to biological degradation of perchlorate until closer to discharge into Little Elk Creek. Non-biological attenuation mechanisms with limited biological contribution have resulted in decreases in perchlorate concentrations over distance. Perchlorate mass flux during each of the four performance monitoring events is shown Figure 10. Perchlorate mass flux in the intermediate zone declines significantly during groundwater flow from Transect 1 to 3 (i.e., the downward trend is statistically significant at the 99% level; $F = 0.001$). However, there is a substantial increase in the shallow zone mass flux in Transect 3 as groundwater migrates from the intermediate to the shallow zones near Little Elk Creek. Total mass flux declines from an average of 28 g/d to 18 g/d of perchlorate from Transect 1 to 3.

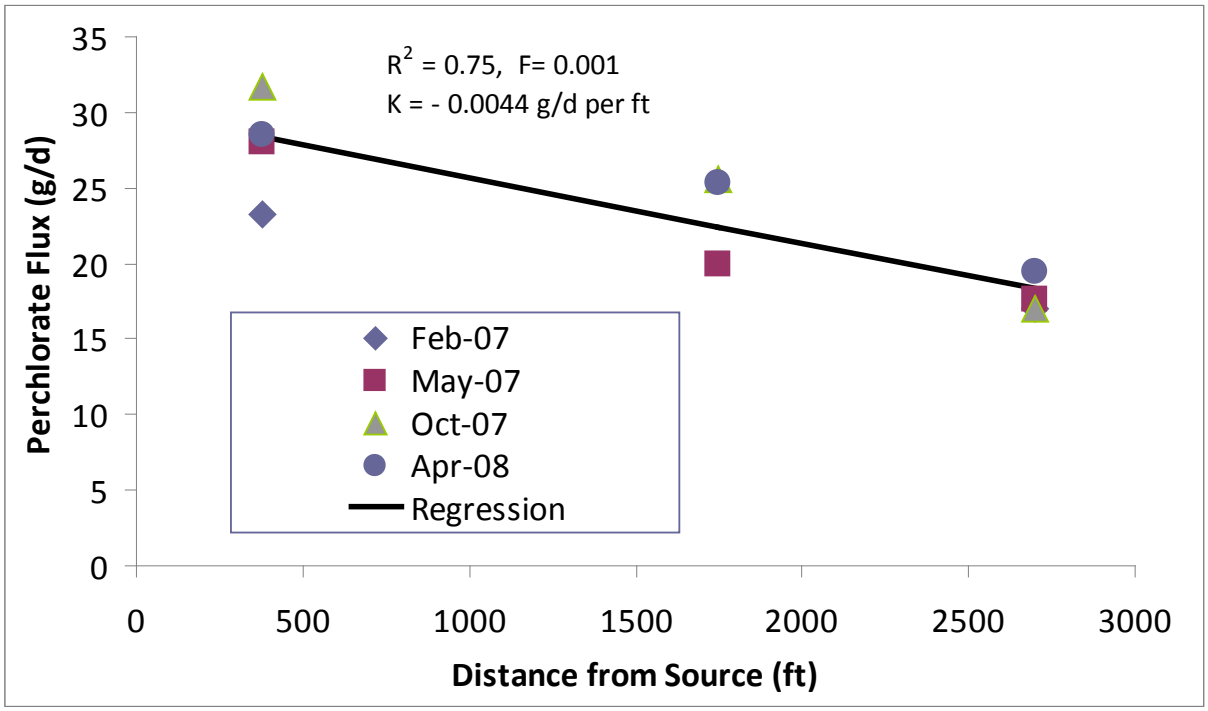

Figure 10. Mass flux versus distance from source.

Overall results from analysis of concentration versus time trends in individual wells are: (1) concentrations are declining with time in the source area wells and are projected to reach cleanup standards in a few years, and (2) concentrations in wells near Little Elk Creek do not show any consistent trend with concentrations in some wells increasing and other wells decreasing. This overall pattern is consistent with a pulse of dissolved perchlorate migrating through the aquifer towards Little Elk Creek. Travel time from the source area to Little Elk Creek is estimated to be roughly 45 years. If flushing by ambient groundwater flow is removing perchlorate from near the source area, this effect might not be observed in wells near the creek for several decades. Some of the apparent increase in perchlorate near the creek could be due to the arrival of perchlorate that was released in the 1950s–1960s. Additional biodegradation tests were designed and performed in Tier 3 to corroborate the lines of evidence suggested by the Tier 1 and 2 evaluations.

5.4.2 Tier 3 Evaluation

Macrocosm and in situ column studies were designed and implemented to estimate perchlorate biodegradation rates in site matrix soil and groundwater from near Little Elk Creek. Macrocosms in 5-gal carboys were constructed on site using shallow soil and groundwater from GM-22S. Replicate carboys were transported to the laboratory and sampled over time for degradation by-products and other indicator parameters. The first-order biodegradation rate calculated from the macrocosm study was 2.9/yr.

In situ columns were installed in the same vicinity and pumped to measure perchlorate degradation during vertical transport through the native aquifer material. First-order biodegradation rates were comparable to the macrocosm rates. As summarized in Table 2, these

tests offer a positive line of evidence supporting the potential for MNA of perchlorate to occur in this area of the TCE/perchlorate contaminant plume.

Table 2. Summary of biodegradation rates in TCE/perchlorate plume matrices from the Maryland manufacturing site.

Test	Type	Rate Constant	Half-Life ($t_{½}$)
Microcosms	Zero-Order	0.92 mg/L/yr.	--
Macrocosms	1st-Order	2.9/yr.	87 days
In Situ Column B	1st-Order	8.5/yr.	30 days
In Situ Column C	1st-Order	7.6/yr.	33 days

In summary, the trends in groundwater flow, biogeochemical parameters, microbial populations and perchlorate concentrations suggest that perchlorate is attenuating and, in some locations, is biodegrading prior to groundwater discharging to Little Elk Creek. The evaluation successfully demonstrated that the perchlorate naturally attenuates, biodegradation is a component of the attenuation, and that perchlorate MNA can be incorporated into the groundwater remediation approach to address perchlorate contamination at the site.

5.5 MANUFACTURING SITE COST ASSESSMENT

A cost breakdown and performance analysis was provided in the Technical Report (ESTCP, 2010b). The total cost of the demonstration was approximately $292,900.

Primary cost elements are summarized below and include:

- Technical Demonstration Plan, white papers/design: ~$17,000 (6%)
- Additional characterization: ~$45,000 (15%)
- Performance monitoring and data acquisition for Tiers 1 & 2: ~$101,900 (35%)
- Tier 1 and 2 evaluations: ~$21,000 (7%)
- Tier 3 data acquisition and evaluation: ~$58,000 (20%)
- Technical reporting: ~$50,000 (17%).

Large portions of the costs were associated with additional site characterization including installation of new monitoring wells pairs and extended performance monitoring. Macrocosm and in situ column studies to confirm biodegradation potential were also large portions of the cost. Project costs not directly related to the individual technical demonstrations such as project management, technical transfer, site screening, treatability study, and protocol development are not included in the cost summary.

6.0 COST COMPARISON

The following sections discuss the cost drivers, compare the costs to evaluate the potential for MNA at the Indian Head and manufacturing facility demonstration sites, and compare costs of other technologies typically used to remediate perchlorate in groundwater. At a minimum, the demonstrations showed that the systematic approach to evaluating perchlorate MNA provided as guidance in the protocol prepared for this project can result in timely and informed application of this remedy at very different sites. The cost comparisons provided in the following sections also demonstrate that MNA of perchlorate can result in life-cycle savings compared to other treatment technologies.

6.1 COST DRIVERS

Components of evaluation of perchlorate MNA that impact cost are listed below:

- More detailed site characterization is needed to demonstrate attenuation, which may mean more complex and costly up-front investigation.
- Specialized testing (e.g., microcosms, macrocosms, in situ columns, stable isotopes) may be needed to corroborate lines of evidence.
- Long-term performance monitoring typically associated with MNA may be more expensive because more parameters may be monitored.
- Potentially longer life cycles to reach remediation goals compared to active remediation measures.
- Changing site conditions over time may require a re-evaluation of MNA and associated additional cost.
- Demonstrating the effectiveness of MNA as protective of human health and the environment to gain public acceptance may be more difficult and therefore, costly.

6.2 COST COMPARISON—INDIAN HEAD VERSUS THE MANUFACTURING SITE DEMONSTRATIONS

Although costs for implementing each of the demonstrations cannot be directly compared due to differences in site conditions, highlighting the cost differences between the Indian Head and the Maryland manufacturing site evaluations leads to a greater understanding of cost drivers and the importance of utilizing the tiered evaluation to systematically evaluate if perchlorate MNA is an appropriate remedial strategy for a particular site. Table 3 summarizes the total project cost and the general allocation of funds between the two sites.

Table 3. Cost breakdown of overall ESTCP Project ER-200428.

Project Cost Not Directly Related to Site	Project Management/Technical Transfer			$105,000
	Site Screening/Treatability Study			$116,000
	Protocol Development			$50,000
Site	**Indian Head**	**Manufacturing Site**		
Technical Demonstration Plan//White Paper/ Design	$51,300	$17,000		$68,300
Additional Site Characterization	$103,600	$45,000		$148,600
Performance Monitoring/Data Acquisition for Tier 1 & Tier 2	$209,300	$101,900		$311,200
Tier 1 and 2 Evaluations	$14,900	$21,000		$35,900
Tier 3 Data Acquisition & Evaluation	$60,000	$58,000		$118,000
Technical Reporting	$70,000	$50,000		$120,000
Total	**$509,100**	**$292,900**	**Project Total**	**$1,073,000**

Some important considerations when comparing the two demonstration sites are:

- Project costs which are not directly related to site demonstration are approximately 25% of total project cost. These costs are related to project management including various meetings required by ESTCP and technical transfer of the perchlorate MNA technology through webinars, presentations and participation on the Interstate Technology & Regulatory Council (ITRC) Perchlorate Team. These costs also include site screening activities including contacting multiple DoD sites, sampling seven sites, conducting laboratory treatability studies, and writing a Protocol to assist endusers in evaluating the potential of perchlorate MNA. Although the time and cost for project management would be incorporated into any remediation, many tasks performed by Solutions-IES for this project such as site screening and creating the Protocol would not be included in a typical project.
- Demonstration costs cannot be directly correlated to the size of the perchlorate plume but are more related to the complexity of the site. Although the perchlorate plume at the Indian Head site is much smaller than the perchlorate plume at the manufacturing facility site, the higher cost at the Indian Head site appears to be driven by the complexity of well installation and sampling, and by evaluating the impact of tidal hydrogeology on perchlorate degradation, and less dependent on the actual size of the plume.
- Additional site characterization that may be required for a tiered evaluation can add substantial costs. A substantially expanded monitoring well/piezometer network was required at the Indian Head Site once it became apparent that the perchlorate plume was discharging to the Littoral Zone. This added cost to the site characterization and remedial demonstration. Although the TCE/perchlorate plume at the manufacturing site was fully defined prior to starting the demonstration, additional monitoring well pairs were installed to help characterize

mid-plume conditions and provide data for mass flux calculations and attenuation rates.

- Sites with historical monitoring data available can possibly realize cost savings related to the Tier 1 and 2 evaluations if the existing data are relevant to the perchlorate MNA evaluation. Often, however, the Sampling and Analysis Plan must be modified or the well network expanded to include additional parameters and locations important to the Tier 1 and Tier 2 evaluations.
- The manufacturing site performance monitoring costs were lower than the Indian Head monitoring costs because the TCE/perchlorate plume was already delineated and subject to a regular monitoring program. The historical monitoring performed at the Indian Head site was related to the Shaw pilot study in a small defined area. Site-wide monitoring data were not available but were eventually obtained by Solutions-IES at additional cost.
- Performance monitoring at each site involved up to five events over a 2- to 3-year period. If historical data are available, the number of events needed to obtain lines of evidence to support MNA could be reduced, which would reduce cost.
- Tier 3 evaluation provided important lines of evidence supporting the potential for perchlorate MNA at each site. The additional cost to conduct these studies was independent of plume size or complexity of the hydrogeology as the Tier 3 costs for each site are nearly the same.

6.3 COST COMPARISONS: PERCHLORATE MNA AND ENGINEERED REMEDIATION APPROACHES

Costs associated with various in situ remediation technologies for perchlorate are discussed in Stroo and Norris (2009) and Krug et al. (2009), but neither directly addresses or compares potential costs to MNA. There are many similarities, particularly associated with up-front assessment and long-term monitoring activities, but the difference with MNA is the absence of any designed intervention. To employ MNA, the goals of the assessment should merge with the goals of MNA. As an example, when considering MNA as a remedial alternative during the assessment phase, an expanded network of monitoring wells may need to be installed to thoroughly evaluate the nature of the contaminants present and the hydrogeology of the site in question. Once installed, altering the site monitoring program or Sampling and Analysis Plan is often all that is necessary to gather data that meet the objectives of Tier 1 and Tier 2 evaluations.

The Tier 3 evaluation including the biodegradation rate estimates may serve a different purpose when considering active or semipassive remediation versus MNA. For these in situ approaches, these studies may be used to help select a substrate to use and then confirm enhanced bioactivity by the substrate selected. Although interesting and possibly useful for predicting the duration of the remediation, biodegradation rate studies performed for this purpose may not be a critical component of the eventual design. However, biodegradation studies can provide an additional line of evidence supporting MNA, which can be very useful when seeking regulatory approval for the technology. Such studies require additional lab and or field work specifically to demonstrate that bioactivity is responsible for the attenuation that is observed.

The remedial action objectives (RAOs) for a site also can have a significant impact on cost and potentially the ability to use MNA at all as a remedial alternative. End users should work very closely with regulators during the evaluation process to determine realistic objectives for perchlorate remediation that are agreeable to the stakeholders. Results should be achievable for the regulatory agency involved in the cleanup. Cost estimates in the following sections use the federal TBC of 24.5 µg/L perchlorate as the target RAO. Solutions-IES used this target concentration when estimating the time to reach the regulatory limit at Indian Head, but used the MDE drinking water standard of 2.6 µg/L for calculations at the manufacturing site.

Costs of several engineered perchlorate remediation technologies were described by Krug et al. (2009) based on a hypothetical base case scenario. Life-cycle costs were projected for an Active Biobarrier Treatment, Passive Injection Biobarrier, and Extraction and Treatment System using estimates of capital cost, installation, operation and maintenance, and long-term monitoring for the treatment of base case perchlorate plume. Capital costs for the engineered remediation systems include system design, well installation, start-up, and testing. Pre-remedial investigations including treatability studies were not included in the capital costs for the engineered remediation systems.

Based on the current project, Solutions-IES projected the life-cycle costs for MNA for the same base case conditions using the table format created by Krug et al. (2009). This is shown in Table 4. The 3-tiered approach developed in this project was included with the capital costs for the perchlorate MNA estimate because the tiered evaluation may not be included in typical pre-remedial activities. The corresponding tables for the alternative technologies (as taken from Krug et al., 2009) were provided in the Indian Head and Maryland Manufacturing Site Technical Reports (ESTCP, 2010a,b).

Table 4. Cost components for perchlorate MNA – base case.

	Year Cost is Incurred							NPV of Cost	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System design	10,000								10,000
Install expanded well network	15,000								15,000
Tier 1, 2, 3 evaluation	50,000								50,000
Installation/start-up testing	0								0
MNA permit & reporting	30,000								30,000
SUBCOST ($)	105,000							102,239	105,000
LONG-TERM MONITORING COSTS									
(Quarterly for 5 years, then annually)	46,000	94,800	94,800	94,800	94,800	23,000	23,000 every yr.		1,000,200
SUBCOST ($)	46,000	94,800	94,800	94,800	94,800	23,000	23,000	752,947	1,000,200
TOTAL COST ($)	151,000	94,800	94,800	94,800	94,800	23,000	23,000	855,186	1,105,200

* Net present value (NPV) was calculated based on a 2.7% discount rate
**No start-up and testing costs are included because no operating equipment is left behind following substrate injection.

Table 5 summarizes the estimated costs for the three technologies described by Krug et al. (2009) compared to MNA shown above.

Table 5. Comparison of capital costs and NPV of costs for operation, maintenance, and monitoring of various technologies for perchlorate-impacted groundwater.

Technology Alternative	Capital Costs ($K)	NPV of 30 Years O&M Costs ($K)	NPV of 30 Years Monitoring Costs ($K)	NPV of 30 Years of Total Remedy Costs ($K)	Total 30-Year Remedy Costs ($K)
Perchlorate MNA	$105	Included with monitoring	$753	$855	$1105
Passive Injection Biobarrier	$280	$990	$350	$1610	$2240
Active Biobarrier	$430	$1200	$350	$1980	$2700
Extraction and Treatment	$490	$1470	$350	$2310	$3160

Note: Costs in thousands of dollars.

The active biobarrier assumes continuous extraction, reinjection, and recirculation of soluble electron donor. The passive injection biobarrier assumes an initial injection of emulsified vegetable oil to promote biodegradation as perchlorate-contaminated groundwater passes through the injection zone. Groundwater extraction and treatment assumes a row of extraction wells used to bring contaminated groundwater to a small-scale aboveground bioreactor for treatment prior to reinjection into the aquifer. MNA assumes expanding an existing well network to delineate the plume and provide groundwater analyses to meet the requirements of a complete three-tiered evaluation. Perchlorate MNA is a cost-effective and reliable remedial alternative that is feasible for many sites. Conclusions of the technology comparison include:

- MNA is approximately one-half the life-cycle cost of the Passive Injection Biobarrier alternative, and approximately one third the cost of the Extraction and Treatment alternative, even though the cost of monitoring is almost double the long-term monitoring costs for the engineered systems.
- An area of savings associated with perchlorate MNA and MNA in general is the relatively low operations and maintenance costs required.
- The tiered evaluation and reporting comprise 76% of the capital cost of an MNA evaluation, with Tier 3 evaluation costs alone comprising almost half the total capital cost. It is important to note that a Tier 3 evaluation was assumed for the base case. In many instances, the lines of evidence supporting perchlorate MNA may be fully established by earlier tiers, and a Tier 3 evaluation may not be necessary.
- Should the tiered analysis prove insufficient to support perchlorate MNA, the information acquired can be used to help evaluate other more active forms of treatment. For example, if the Tier 3 evaluation suggests that there is not enough carbon or microorganisms to support perchlorate MNA and a passive injection

biobarrier is considered, the substrate addition and bioaugmentation may be considered as alternatives for further evaluation and pilot testing.

- Should the tiered analysis suggest that perchlorate MNA is applicable to a portion of the plume crossing a large site, a remedial strategy can be customized to utilize MNA in concert with more active forms of treatment.

6.4 CONCLUSIONS

The principles of MNA that have been used historically to manage and remediate groundwater plumes contaminated with petroleum hydrocarbons and CVOCs were demonstrated to be applicable for perchlorate at two DoD-related facilities. Using expanded monitoring well/piezometer networks to delineate contaminant plumes applies equally well to perchlorate as to other contaminants. Analytical tools and techniques are available to detect low concentrations of perchlorate (i.e., <1 µg/L, if desired) and to detect and quantify the presence and activity of DPRB populations in the environment.

The demonstrations also identified the biogeochemical conditions that would be expected to promote natural perchlorate attenuation. The ORP and TOC conditions favorable to perchlorate MNA were similar at each site. At the Indian Head demonstration, groundwater ORP less than +50 mV with TOC greater than 4 mg/L was conducive to perchlorate degradation, whereas in the manufacturing site demonstration, ORP less than +100 mV and TOC greater than 6 mg/L appeared to support the limited biodegradation that was observed. Minimal competing nitrate and pH>5.5 were also important for natural attenuation to occur. The observations from the commingled TCE/Perchlorate plume at the Maryland manufacturing site indicated that conditions for perchlorate attenuation are less fastidious than for CVOC attenuation. Where biogeochemical conditions do not provide definitive lines of evidence, there are several ways to confirm bioactivity. These include microcosm, macrocosm and in situ column studies, which can be designed to generate biodegradation rate data. Although not tested in this project, changes to the stable isotope signature of perchlorate may also be useful.

MNA of perchlorate is likely to be considerably less costly than engineered passive and active remediation systems. As shown at the Elkton site, changes in mass flux across the site can be competitive with P&T, which is limited by the pumping radius of influence. MNA of perchlorate can be protective of human health and the environment and should be considered as part of any evaluation of alternatives for remediating perchlorate contamination in groundwater.

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