ESTCP
Cost and Performance Report

(ER-201028)

Passive Biobarrier for Treating Co-Mingled Perchlorate and RDX in Groundwater at an Active Range

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14. ABSTRACT
A subsurface biobarrier consisting of emulsified vegetable oil and a buffering agent was tested to enhance biodegradation and reduce the migration of co-mingled RDX, HMX, and perchlorate in a shallow, acidic groundwater aquifer at an operational military range in Dahlgren, Va. Despite heterogeneous subsurface lithology and low hydraulic conductivity in the test site aquifer, RDX, HMX, and perchlorate were reduced by > 92 % in a centerline of monitoring wells extending 40 ft downgradient of the biobarrier when adequate total organic carbon (TOC) was present from the added oil. The accumulation of toxic nitroso- degradation products MNX, DNX, and TNX from RDX was minimal. Moreover, the passive biobarrier resulted in no significant impacts to ongoing range activities. This field trial suggests that an emulsified oil biobarrier is a viable alternative to reduce the migration of co-mingled perchlorate and explosives in groundwater at this and similar ranges. Ideal range locations include open OB/OD areas, target areas, fast cookoff sites, EOD training areas, and other locations where high munition constituent concentrations are possible.

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ACRONYMS AND ABBREVIATIONS

µg/L	microgram(s) per liter
ANOVA	analysis of variance
As	arsenic
bgs	below ground surface
C	carbon
cm/sec	centimeter(s) per second
DNX	hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DO	dissolved oxygen
DoD	U.S. Department of Defense
DPT	direct-push technology
EEA	Explosives Experimental Area
EOD	explosive ordnance disposal
EOS	emulsified oil substrate
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
Fe	iron
ft	foot/feet
ft/d	
gal	gallon(s)
gal/min	gallon(s) per minute
g/g	gram per gram
GAC	granular activated carbon
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IW	injection well
L	liter(s)
L/min	liter(s) per minute
lbs	pounds
LTM	long-term monitoring
K	hydraulic conductivity; sorption coefficient
MCL	Maximum Contaminant Level
mg/kg	milligram(s) per kilogram
mg/L	milligram(s) per liter

Mn	manganese
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
mV	millivolt(s)
MW	monitoring well
N	nitrogen
NO_3^-	nitrate
NPV	net present value
NSWCDD	Naval Surface Warfare Center Dahlgren Division
O_2	oxygen
OB/OD	open burn/open detonation
ORP	oxidation-reduction potential
O&M	operation and maintenance
PRB	permeable reactive barrier
P&T	pump and treat
PV	pore volume
RDT&E	Research, Development, Test, and Evaluation
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
SERDP	Strategic Environmental Research and Development Program
SIP	stable isotope probing
SO_4^-	sulfate
S.U.	standard unit(s)
TAL	target analyte list
TNT	2,4,6-trinitrotoluene
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	total organic carbon
TPA	test plot area
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UXO	unexploded ordnance
VFA	volatile fatty acid
v/v	volume per volume
ZVI	zero-valent iron

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

During this Environmental Security Technology Certification Program (ESTCP) demonstration, a passive subsurface biobarrier was installed to treat the nitramine explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and comingled perchlorate in groundwater at an operational military range. The optimal areas for application of this technology include open burn/open detonation (OB/OD) sites, munitions test ranges, explosive ordnance disposal (EOD) training areas, target areas, munitions disposal sites, and other regions where high concentrations of munitions constituents are likely to occur. The Churchill Range in the Explosives Experimental Area (EEA) of the Naval Surface Warfare Center Dahlgren Division (NSWCDD) in Dahlgren, VA, was chosen as the demonstration site. The barrier, which was placed downgradient of a location where testing activities occur at NSWCDD, consisted of an emulsified oil substrate (EOS) and buffer applied to the subsurface. The buffer was used to increase the natural acidic pH of the groundwater and maintain that pH in the circumneutral range in order to promote rapid biodegradation kinetics of the target contaminants. Important to the mission of operational U.S. Department of Defense (DoD) ranges, the barrier had no surface structure and no significant impact on typical range activities. A key objective of this demonstration was to limit further contaminant migration in groundwater cost-effectively, with minimal impact to range activities.

TECHNOLOGY DESCRIPTION

When injected into a groundwater aquifer, EOS promotes the growth of indigenous bacteria capable of anaerobically biodegrading perchlorate, RDX, and HMX to low concentrations. The effectiveness of the barrier for reducing migration of perchlorate and explosives in groundwater at the EEA of NSWCDD was determined using a series of groundwater monitoring wells (MWs). The 100-ft-long biobarrier was installed by injecting emulsified oil and buffer through a series of 20 injection wells (IWs) placed cross-gradient to groundwater flow. Two injection events were conducted over time. Upgradient, in-barrier, and downgradient wells were monitored for perchlorate, RDX, HMX (and nitroso intermediates of RDX and HMX), field parameters, total organic carbon (TOC, as a measure of oil concentration), fatty acids, dissolved metals, anions, and field parameters for approximately 30 months after the initial emulsified oil injection. The remedial approach was designed to treat the contaminants in the ground with no surface structure and to minimize impacts to ongoing range activities.

DEMONSTRATION RESULTS

This barrier promoted the rapid *in situ* biodegradation of perchlorate, RDX, and HMX (**Figure E1**). Upon emulsified oil injection, RDX concentrations decreased significantly downgradient of the biobarrier, with a degradation “front” slowly moving down the centerline of the plot. The RDX removal averaged 83 ± 17% for the in-barrier wells and 75 ± 21% for the centerline wells from the first emulsified oil injection to the end of the demonstration. However, these averages included periods of time when the TOC from the emulsified oil injection(s) was depleted leading to increased RDX in downgradient wells. When TOC from emulsified oil or its degradation products was adequate, and time was allowed for degradation to occur, RDX concentrations reached extremely low levels in the centerline wells. For example, approximately eight months after the initial oil injection, the RDX within the barrier to a distance of 30 feet (ft) downgradient ranged from <0.03 to six micrograms per liter (µg/L). RDX removal in these wells was >94%.

Similarly, ten months after a second emulsified oil injection, RDX concentrations along the centerline wells ranged from <0.03 µg/L (5/7 wells) to 2 µg/L (2 wells) as far as 40 ft downgradient of the barrier, with removal percentages >98% over this large distance. Thus, this technology was highly effective for promoting RDX biodegradation when adequate TOC and appropriate biogeochemical conditions were achieved.

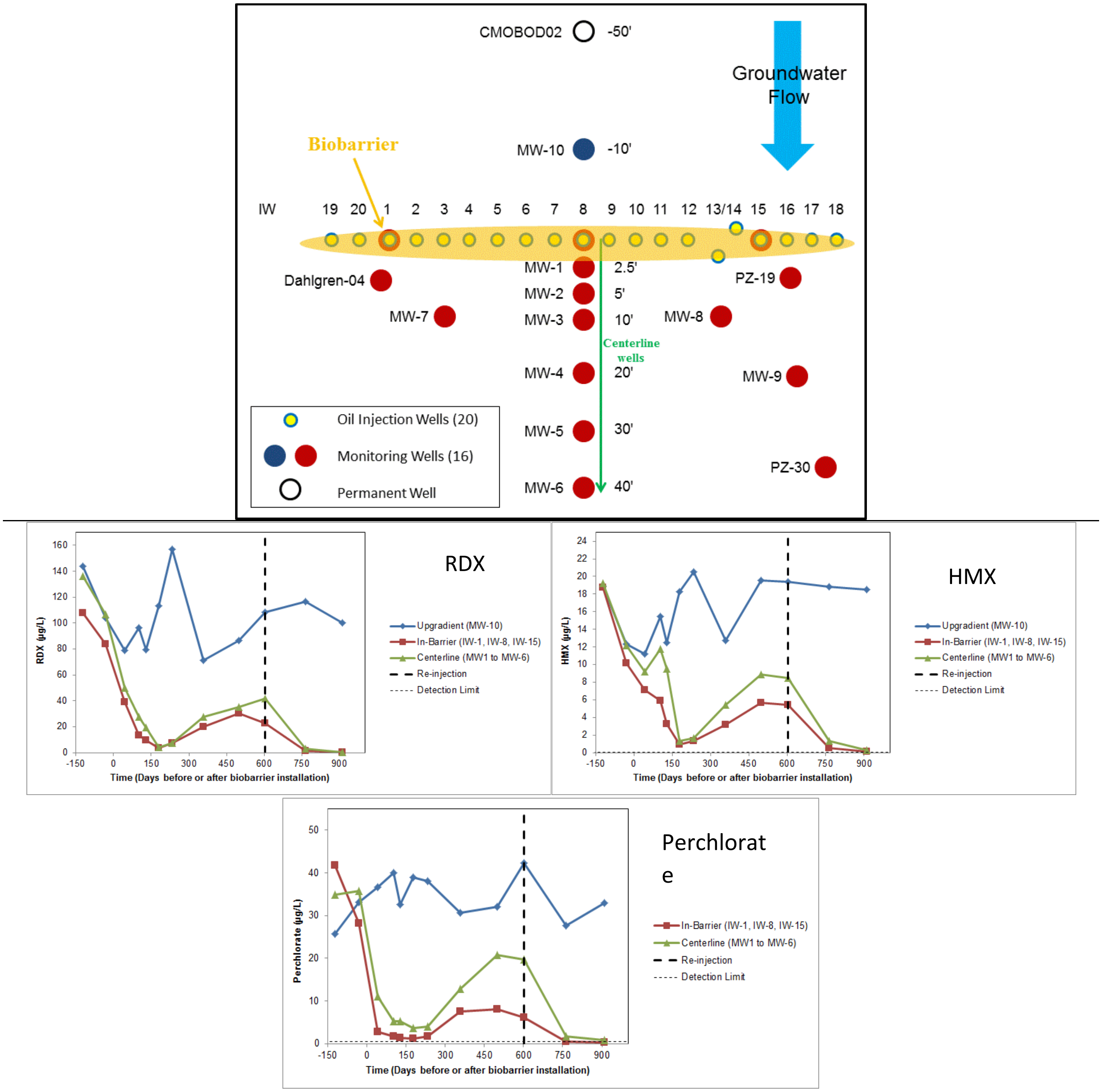

Figure E.1. Schematic Showing the Biobarrier Layout (Top Panel), and the Overall Monitoring Data for RDX, HMX, and Perchlorate.

The RDX metabolites hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) increased as RDX degraded in response to the initial and secondary emulsified oil injections, and conversely decreased as RDX degradation slowed. The trends indicate that the nitroso metabolites were being produced in measurable, albeit not stoichiometric, concentrations and were being further transformed, degraded, or otherwise attenuated, and therefore were not expected to be present at any appreciable concentration further downgradient. To that end, during the final sampling event of the demonstration approximately 30 months after the initial oil injection, MNX, DNX and TNX were below detection (<0.08 µg/L) in 11 of the combined in-barrier and downgradient wells, and were present at a maximum of 1.1 µg/L in the remaining 4 wells that had detectable intermediates. The data suggest that the RDX ring structure was being broken during biodegradation, leading to non-toxic or otherwise labile products.

The concentration of HMX in the groundwater before the demonstration averaged 15 ± 5 µg/L, and concentrations in the upgradient well remained in the same range for the duration of the study (17 ± 3 µg/L). As with RDX, HMX concentrations decreased significantly downgradient of the biobarrier after emulsified oil injection, with a degradation "front" slowly moving down the centerline of the plot. HMX removal was slightly lower than RDX removal, averaging 77 µg/L ± 20% for the in-barrier wells and 61 µg/L ± 32% for the centerline wells from the first emulsified oil injection to the end of the demonstration. However, as noted for RDX, during periods with sufficient TOC, low HMX concentrations were achieved in the centerline wells. For example, approximately six months after the initial oil injection, the HMX within the barrier to a distance of 40 ft downgradient ranged from <0.03 to 4 µg/L with an average of 1.2 µg/L. Similarly, 10 months after the second emulsified oil injection, HMX concentrations along the centerline wells ranged from <0.03 µg/L (6/7 wells) to 2 µg/L (1 well) as far as 40 ft downgradient of the barrier. Similar to RDX, the data suggest that this technology was also highly effective for HMX removal when appropriate biogeochemical conditions were achieved.

The concentration of perchlorate in the groundwater before the demonstration averaged 36 ± 11 µg/L, and concentrations in the upgradient well remained in the same range for the duration of the study (34 ± 5 µg/L). Perchlorate removal was greater than both RDX and HMX, with 91 µg/L ± 9% removal in the barrier wells, and was comparable to total RDX removal along the centerline at 76 µg/L ± 21% from the first emulsified oil injection to the end of the demonstration. During periods with sufficient TOC, low perchlorate concentrations were achieved in the centerline wells. For example, six months after the initial oil injection, the perchlorate within the barrier to a distance of 40 ft downgradient ranged from <0.5 µg/L (4 wells) to 17.2 µg/L (1 well) with an average of 3.2 µg/L. Similarly, 10 months after the second emulsified oil injection, perchlorate concentrations along the centerline wells ranged from <0.5 µg/L (5/7 wells) to 2.2 µg/L (1 well) as far as 40 ft downgradient of the barrier, with an average concentration of 0.9 µg/L—an overall reduction of >97%.

This field trial at NSWCDD suggests that an emulsified oil biobarrier is a viable alternative to reduce the migration of co-mingled perchlorate and explosives in groundwater at this and similar range sites. The optimal areas for application of this technology include OB/OD sites, munitions test ranges, EOD training areas, target areas, munitions disposal sites, and other regions where high concentrations of munitions constituents are likely to occur. Despite heterogeneous subsurface lithology, low pH, and low hydraulic conductivity in the aquifer at NSWCDD, emulsified oil and buffer were well distributed to form a subsurface biobarrier.

RDX, HMX, and perchlorate were reduced by ≥92% in the centerline of MWs extending 40 ft downgradient of the biobarrier after the second injection of emulsified oil, and accumulation of nitroso-degradation products from RDX was minimal. Moreover, the biobarrier required no operation and maintenance (O&M) other than injection and reinjection of oil substrate, and resulted in no impacts to ongoing range activities.

A cost analysis for full-scale application was completed for several different applicable treatment technologies, using a base case in which a shallow aquifer is contaminated with perchlorate and RDX from 10 to 40 ft below ground surface (bgs) with a plume width of 400 ft. The passive emulsified oil biobarrier had the lowest capital costs under this scenario, and had overall 30-year life cycle costs like several other *in situ* alternatives, including a zero-valent iron (ZVI) barrier, a mulch biobarrier, and a semi-passive emulsified oil barrier, each of which ranged from $2.4M to $2.6M. The actual costs of these technologies would depend on the longevity of each treatment under site geochemical conditions. All of the *in situ* technologies were appreciably less costly than an ex situ pump and treat (P&T) option, which was >$3.6M over a 30-year lifespan.

IMPLEMENTATION ISSUES

The general implementation concerns of these end users are likely to include the following: (1) technology scale-up technology and applicability under local site conditions, (2) secondary impacts to the local aquifer, and (3) technology cost versus other remedial options.

This technology is amenable for use at a variety of testing and training ranges. Consideration should be given to emplacing the barrier in an area that is not likely to be impacted either directly by detonations or by unexploded ordnance (UXO). While not feasible at all sites, emplacement of permanent, flush-mounted IWs should be preferred over using Geoprobe® injection methods, both in terms of ease of follow-on injections to maintain barrier effectiveness, and in terms of limiting UXO clearance activities to only those needed for IW installation. At more aggressive ranges, hardened IW vaults may be required to protect the infrastructure.

Emulsified oils have been widely used for other applications, such as treatment of chlorinated solvents, so scale-up for an application with explosives and perchlorate should not be problematic. In the case at NSWCDD, the biobarrier could have easily been scaled from 100 to 300 ft or so, which would have been a full-scale design for one of the two identified plumes. Due to the relatively low hydraulic conductivity of the groundwater aquifer at the NSWCDD site, another way to implement this approach full-scale would be to install a sand/gravel trench barrier cross-gradient to groundwater flow, with lines for the addition of emulsified oil. This trench system would replace the closely-spaced biobarrier IWs, and could be quickly rejuvenated with additional emulsified oil on an annual or semi-annual basis as necessary.

Some of the potential limitations of this approach include (1) cost or technological barriers at increased depth (beyond that easily obtained by a direct-push technology [DPT] rig), (2) difficulty injecting emulsified oils in low permeability formations, and (3) secondary groundwater impacts. Aquifer depth is one of the limiting factors for all fully passive designs, which become increasingly expensive due to close spacing of injection points or technically impractical (e.g., for passive trench barriers) as the depth to the water table increases. In addition, emulsified oils are most effectively injected in aquifers where the hydraulic conductivity >4 x 10^{-3} centimeters per second (cm/sec) (~10 feet per day [ft/day]), and become impractical <~1 x 10^{-4} cm/sec (~0.3 ft/day).

Secondary groundwater impacts typical of passive approaches include mobilization of metals (notably iron [Fe], manganese [Mn], and arsenic [As]) and production and accumulation of methane. In a typical application of emulsified oil, Fe and Mn will be mobilized within the treatment zone to milligrams per liter (mg/L) concentrations, but these metals will generally be oxidized and precipitated rapidly, so that dissolved concentrations return to background levels within several meters downgradient of the IWs. Similar results are expected for methane, which is usually oxidized in an aerobic aquifer via methane-oxidizing bacteria.

The emulsified oil biobarrier is generally a cost-effective option, particularly for an active range where other options such as P&T are technically impractical due to the surface structure and O&M required. Important cost factors for such biobarriers include (1) plume characteristics, particularly the plume width and depth, which will determine the costs of well or trench installation as well as the quantities of emulsified oil required; and (2) hydrogeology and aquifer characteristics, such as the rate of groundwater flow and general geochemistry (e.g., presence of alternate electron acceptors such as oxygen [O_2], nitrate [NO_3^-], and sulfate [SO_4^{2-}]), which will determine the rate of oil consumption and the necessity for other amendments (e.g., buffer or inorganic nutrients).

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1.0 INTRODUCTION

1.1 BACKGROUND

Perchlorate (ClO_4^-) and explosives, particularly hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), are widespread soil contaminants at former and current military facilities, including many operational ranges. Because these compounds are readily transported through soils to the subsurface, they presently impact groundwater and drinking water at numerous military facilities across the country. One important objective for sustaining an operational range is to prevent offsite contaminant migration, while allowing typical range training and testing activities to occur uninterrupted. Organic explosives such as RDX and perchlorate have been shown individually to be amenable to biological degradation under anoxic conditions (Hatzinger, 2005; Hawari *et al.*, 2000). However, there is little overall information on the potential for the joint treatment of these compounds either biologically or through abiotic approaches.

1.2 OBJECTIVE OF THE DEMONSTRATION

During this Environmental Security Technology Certification Program (ESTCP) demonstration, a passive subsurface biobarrier was installed to treat dissolved explosives and perchlorate in groundwater at an operational military range. The optimal areas for application of this technology include open burn/open detonation (OB/OD) sites, munitions test ranges, explosive ordnance disposal (EOD) training areas, target areas, munitions disposal sites, and other regions where high concentrations of munitions constituents are likely to occur. The Churchill Range in the Explosives Experimental Area (EEA) of the Naval Surface Warfare Center Dahlgren Division (NSWCDD) in Dahlgren, VA, was chosen as the demonstration site for this ESTCP project. The barrier, which was placed downgradient of a location where testing activities occur at NSWCDD, consisted of an emulsified oil substrate (EOS) and buffer applied to the subsurface. This barrier promoted the rapid *in situ* biodegradation of perchlorate and explosives, including RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Important to the mission of operational U.S. Department of Defense (DoD) ranges, the barrier had no surface structure (e.g., pumping wells, control building) and no significant impact on typical range activities. A key objective of this demonstration was to apply an effective long-term solution of contaminant migration in groundwater with minimal impact to range activities.

1.3 REGULATORY DRIVERS

There are currently no Federal drinking water standards (Maximum Contaminant Level [MCL]) for the energetics that are the object of this demonstration. However, the U.S. Environmental Protection Agency (USEPA) has listed both RDX and perchlorate on the Draft Drinking Water Candidate Contaminant List[1] and the Unregulated Contaminant Monitoring Regulation List.[2] In addition, the USEPA has issued lifetime Health Advisory Limits (Maximum Contaminant Goal Levels; MCGLs) of 2 micrograms per liter (µg/L) for RDX and 400 µg/L for HMX (USEPA, 2004), and recently announced that a Federal MCL will be established for perchlorate under the Safe Drinking Water Act.[3] The states of Massachusetts and California currently have drinking water MCL values for perchlorate of 1 µg/L and 6 µg/L, respectively.

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[1] http://water.epa.gov/scitech/drinkingwater/dws/ccl/ccl3.cfm.

[2] http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/factsheet.cfm.

[3] https://www.epa.gov/dwstandardsregulations/perchlorate-drinking-water.

The State of Virginia has issued Groundwater Protection Standards for RDX, HMX, perchlorate, 2,4,6-trinitrotoluene (TNT), and a variety of TNT degradation intermediates. The specific criteria for compounds detected on the Churchill Range at NSWCDD are 1.08 µg/L for RDX, 1,800 µg/L for HMX, and 70 µg/L for perchlorate. Several DoD sites have already come under regulatory pressure to stop activities that may result in contamination of groundwater with these compounds, as well as to begin remediating contaminated groundwater and overlying soil. This technology is designed to help the DoD meet these challenges while continuing to operate the ranges to maintain military preparedness.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Techniques to remove explosives from surface soils, including soil washing, composting, soil bioreactors, iron (Fe) amendment, and enhanced *in situ* soil treatment, are well established (Comfort *et al.*, 2003; Fuller *et al.*, 2003; Griest *et al.*, 1993; Zhang *et al.*, 2001), but there are presently few proven methods to treat energetic compounds in groundwater. In addition, although *in situ* bioremediation technologies for perchlorate in water have been developed and implemented (Hatzinger, 2005; Stroo and Ward, 2008), there is little relevant field information concerning joint treatment of perchlorate and nitramine explosives in groundwater (Fuller *et al.*, 2007; Schaefer *et al.*, 2007; Weeks *et al.*, 2003). During this demonstration, we tested and validated a passive remedial approach for treating co-mingled perchlorate and RDX in groundwater at an operational DoD range. This test was specifically designed to minimize impact on range activities, while determining the potential for long-term protection of downgradient groundwater.

Previous studies conducted in our laboratory revealed that perchlorate and nitramine explosives (RDX and HMX) can be treated together in groundwater using select organic substrates, including EOS (Schaefer *et al.*, 2007). Other approaches, such as application of various forms of zero-valent iron (ZVI) and nickel catalysts, also were effective for the nitramines, but not for perchlorate. More recently, microcosms prepared with aquifer samples from the EEA at NSWCDD revealed that degradation of both RDX and perchlorate at this location can be stimulated via the addition of emulsified oil as well as other substrates, including ethanol and glucose.

Emulsified oil substrates consist of small, stable oil droplets that are completely miscible in water (Borden *et al.*, 2008a). When injected into the subsurface, these oil droplets move into the aquifer and slowly adsorb to solid particles, resulting in a thin coating of oil on aquifer solids in the barrier area (**Figure 2.1**). A volume of chase water is usually added after the emulsified oil injection to adequately disperse the solution into a continuous barrier. The spacing of injection points and volume of emulsified oil required to form a barrier, as well as barrier longevity, depend on the existing hydrological and geochemical conditions. A recently published emulsified oil design tool, which resulted from an ESTCP project, provides guidance concerning barrier installation (Borden *et al.*, 2008b). This tool was used to aid in the design of the biobarrier. Once the barrier is installed, the emulsified oil provides a long-term source of organic carbon and electron donors to support reductive degradation of contaminants. The primary application of this technology to date is for chlorinated ethenes, and in one DoD demonstration for perchlorate and 1,1,1-trichloroethane (Borden, 2007).

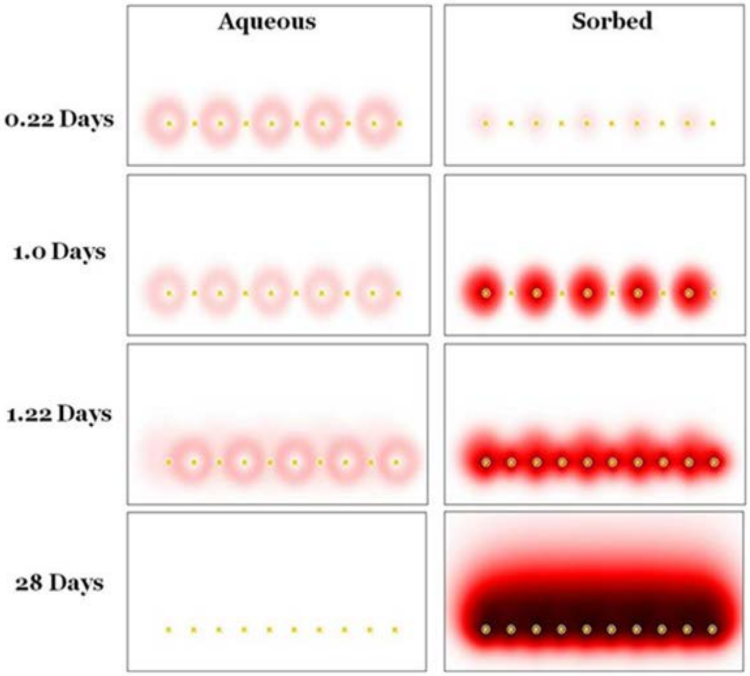

Figure 2.1. Disposition of Emulsified Oil after Injection into Groundwater as a Function of Time.

During this demonstration, EOS was injected into the subsurface to form a passive biobarrier. The oil substrate promotes the growth of indigenous bacteria capable of biodegrading perchlorate and RDX to low concentrations (RDX <0.25 µg/L and perchlorate <1 µg/L based on our laboratory data). To our knowledge, emulsified oil barriers have not been evaluated and validated in the field for enhancing biodegradation of explosives or for mixed explosives and perchlorate. The technology has also not been applied and verified at the field-scale to address groundwater contamination on an active range, although this approach appears well-suited for preventing offsite migration of pollutants from some range activities, such as OB/OD.

The effectiveness of the barrier for reducing migration of perchlorate and explosives in groundwater at the EEA of NSWCDD was determined using a series of groundwater monitoring wells (MWs). A graphic showing the basic field layout design is provided in **Figure 2.2**. The biobarrier was installed cross-gradient to groundwater flow. Upgradient, barrier, and downgradient groundwater were monitored for perchlorate, RDX, HMX, and their nitroso-degradation intermediates, field parameters, total organic carbon (TOC, as a measure of oil concentration), fatty acids, dissolved metals, anions, and field parameters for approximately 30 months following the initial emulsified oil injection. Depending on hydrological and geochemical characteristics, emulsified oil barriers can effectively provide reducing conditions for more than five years (ESTCP, 2006).

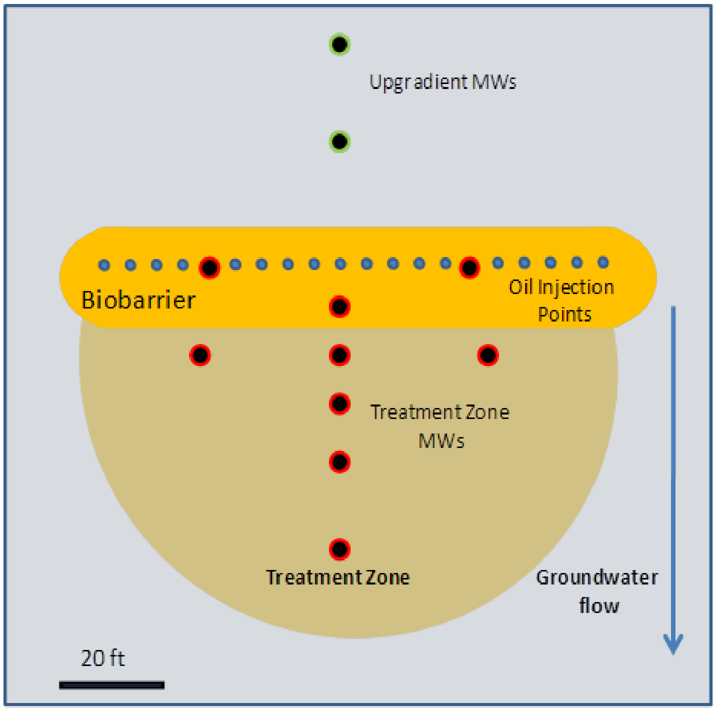

Figure 2.2. Schematic of Generalized Biobarrier Design and Monitoring Well Network.

The actual design was based on specific site conditions.

Studies were also undertaken to identify the specific bacterial communities in the NSWCDD aquifer biodegrading RDX through advanced molecular analysis with stable isotope probing (SIP; Roh *et al*., 2009). The application of this method provides valuable information on the identity of key microorganisms responsible for degrading RDX in the aquifer under different electron-accepting conditions, and the portion of the molecule that they utilize (e.g., ring-N, nitro-N, or ring-C).

In summary, this project demonstrates and verifies a passive remedial approach for treating RDX and perchlorate in groundwater at an operational DoD range. During the project, an advanced molecular technique was utilized to assess the organisms responsible for *in situ* energetics biodegradation. Most critically, the project was designed to show that groundwater treatment and protection can be implemented on an operational range without significantly affecting mission-critical range activities.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.2.1 Advantages

The main advantages of utilizing an *in situ* approach for RDX and perchlorate treatment are:

1. Appreciably reduced cost and infrastructure compared to traditional pump and treat (P&T) approaches.

2. Complete destruction of explosives and perchlorate rather than transfer to a secondary medium, such as granular activated carbon (GAC).

In addition, the use of a passive design in which emulsified oil is applied to the subsurface is advantageous in the following ways:

1. There is no requirement for pumping wells or aboveground infrastructure typical for active pumping designs. Such infrastructure is impractical in a range environment.
2. Minimal engineering design is required compared to an active *in situ* system.
3. There are significantly reduced system operation and maintenance (O&M) requirements and costs, including electrical and biofouling control costs.
4. Long-term effectiveness of the biobarrier is expected depending on groundwater geochemistry and hydrology (>5 years possible).

2.2.2 Limitations

As with all technologies, there are also limitations with passive treatment approaches:

1. Technology becomes expensive to implement in deep aquifers (>50 ft) due to the costs of injecting the substrate at depth.
2. The groundwater oxidation-reduction potential (ORP) will be significantly reduced, which is necessary to create conditions conducive to treatment explosives and perchlorate, but also causes secondary geochemical impacts, such as mobilization of metals (e.g., dissolved Fe(II) and Mn(III)] from dissolution of Fe and manganese [Mn] oxides), sulfide production, and other changes in groundwater geochemistry that impact local groundwater quality.
3. Absence of hydraulic control, which can be gained with pumping wells in an active *in situ* system. One must rely on the natural gradient to move contaminant through the barrier.
4. Necessity for closely spaced injections of emulsified oil in tight formations.

Additional details on the advantages and limitations of passive approaches for substrate addition compared to semi-passive and active approaches can be found in Stroo and Ward (2009), which evaluates options for *in situ* perchlorate treatment.

3.0 PERFORMANCE OBJECTIVES

Performance objectives for this demonstration are summarized in **Table 3.1**, and detailed descriptions of objectives are provided in **Sections 3.1** through **3.5**.

Table 3.1. Performance Objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Effectiveness of RDX treatment	Pre- and post-treatment contaminant concentrations in groundwater wells using EPA Method 8330.	• Reduction in downgradient groundwater in one or more MW(s) to <1.08 µg/L • Overall downgradient RDX reduction >95% • Statistical comparison: - Pre- and post-barrier installation - Upgradient versus downgradient MWs	
Effectiveness of perchlorate treatment	Pre- and post-treatment contaminant concentrations in groundwater wells using EPA Method 314.0.	• Reduction in one or more downgradient MWs to <2 µg/L • Overall downgradient perchlorate reduction >95% • Statistical comparison: - Pre- and post-barrier installation - Upgradient versus downgradient MWs	
Distribution of emulsified oil	Measurement of TOC	TOC elevated in MWs 2.5 ft and 5 ft downgradient	
Geochemical changes to create conditions necessary for contaminant degradation	Measurements of DO Measurements of ORP	DO <1 mg/L in all treatment wells ORP <-100 mV in all treatment wells	
Longevity of biobarrier	TOC and treatment efficacy over time	Barrier effective two years after installation	
Qualitative Performance Objectives			
Barrier Installation	Total time for installation Feedback from field technician Maintenance logs and time	<5 days for barrier installation Minimal maintenance costs	

mg/L – milligram(s) per liter, mV – millivolt(s)

3.1 EFFECTIVENESS OF RDX AND PERCHLORATE TREATMENT

The effectiveness of the biobarrier technology for groundwater remediation was a function of the degree to which RDX and perchlorate concentrations decreased. HMX degradation was also measured.

Remediation success depended on the residual contamination during and after application of the treatment remedy. The overall duration of the biobarrier performance was also of interest during this project and was quantified via extended testing.

3.1.1 Data Requirements for RDX and Perchlorate Treatment

As summarized in **Section 2** and detailed further in **Section 5**, an emulsified oil biobarrier was installed at NSWCDD, cross-gradient to groundwater flow. A series of groundwater wells were installed upgradient, downgradient, and within the oil barrier. The groundwater wells were installed prior to emulsified oil injection in order to establish baseline concentrations in each well. Two rounds of baseline data were then collected prior to barrier installation. After barrier installation, groundwater samples were collected 10 times over the next 30 months. All RDX and HMX analyses were conducted by EPA Method 8330[4] and perchlorate analyses by EPA Method 314.0.[5]

3.1.2 Success Criteria for RDX and Perchlorate Treatment

The success criteria were reductions in RDX (based on the Virginia Groundwater Protection Standard) and perchlorate (the lowest state standard in the United States—2 µg/L in Massachusetts) in groundwater to <1.08 µg/L and <2 µg/L, respectively, in one or more downgradient MWs. The value for perchlorate is more stringent that the Virginia Groundwater Protection Standard of 70 µg/L. A second standard-independent objective was an overall reduction in RDX and perchlorate concentrations of >95% in downgradient MWs from the pre-treatment to the post-treatment phase. Treatment effectiveness was measured by comparing RDX and perchlorate concentrations: (1) in each of the impacted downgradient MWs before and after barrier installation, and (2) in the upgradient MW with those in the downgradient treatment zone during each sampling event. Similar comparisons were also made for HMX, and rates of RDX and HMX degradation were calculated.

3.2 ADEQUATE DISTRIBUTION OF EMULSIFIED OIL

Homogeneous oil distribution was deemed important to the success of this biobarrier approach for RDX and perchlorate treatment. The distribution of emulsified oil was quantified by measuring TOC increases in the wells installed within the biobarrier. In addition, both TOC and volatile fatty acids (VFAs; breakdown products of emulsified oil) were measured in downgradient MWs.

3.2.1 Data Requirements for Oil Distribution

TOC was measured at CB&I's Analytical Laboratory in Lawrenceville, NJ, by Standard Method SM-5310[6] and VFAs were measured by EPA Method 300.0m.[7] Distribution of oil and resulting products were assessed by comparing RDX and perchlorate concentrations: (1) in each of the downgradient MWs before and after barrier installation and (2) in the upgradient MW with those in the downgradient treatment area during each selected sampling event.

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[4] https://www.epa.gov/hw-sw846/sw-846-test-method-8330a-nitroaromatics-and-nitramines-high-performance-liquid.

[5] EPA Method 314.0.

[6] https://standardmethods.org/store/ProductView.cfm?ProductID=38.

[7] https://www.epa.gov/quality/perchlorate-water-ion-chromatography-modified-epa-method-3000-revision-21-august-1993.

3.2.2 Success Criteria for Oil Distribution

The success criteria for oil distribution was (1) a significant increase in TOC within the barrier monitoring and the first two downgradient wells (2.5 ft and 5 ft downgradient of the barrier) after emulsified oil injection, and (2) increased levels of VFAs in the downgradient wells during the initial six months of the demonstration.

3.3 GEOCHEMICAL CHANGES

The addition of emulsified oil as an *in situ* biobarrier typically creates reducing conditions due to microorganisms consuming oxygen, nitrate, and other available electron acceptors during oxidation of oil components. The reducing conditions are necessary for degradation of explosives and perchlorate.

3.3.1 Data Requirements for Geochemical Changes

The parameters measured to assess potential geochemical changes were as follows: (1) dissolved oxygen (DO, or dissolved O_2) by field meter, and (2) ORP by field meter. In addition to these parameters, other geochemical parameters were measured including pH, anions, and dissolved Fe, Mn, and arsenic (As).

3.3.2 Success Criteria for Geochemical Changes

The success criteria for measured geochemical changes were as follows: (1) dissolved O_2 <1 milligrams per liter (mg/L) in all impacted downgradient wells, and (2) ORP reduced to <-100 millivolts (mV) in all wells throughout the demonstration.

3.4 BARRIER LONGEVITY

The proposed biobarrier for groundwater remediation was expected to remain effective for a minimum of two years, based on groundwater flow, electron acceptor concentrations, and other variables.

3.4.1 Data Requirements for Barrier Longevity

The biobarrier longevity was judged based upon (1) the measurement of elevated TOC in the biobarrier wells and the wells immediately downgradient, and (2) reduced concentrations of RDX and perchlorate in the wells immediately downgradient of the barrier.

3.4.2 Success Criteria for Barrier Longevity

The biobarrier longevity was considered adequate if (1) TOC remained elevated in the biobarrier wells and the wells immediately downgradient, and (2) RDX and perchlorate remained below Virginia Groundwater Protection Standards in the wells immediately downgradient of the barrier for two years after barrier installation (or for explosives and perchlorate, two years after the initial reductions are observed assuming some lag period after initial oil injection).

3.5 EASE OF BARRIER INSTALLATION

One key goal was to minimize downtime on the active range, therefore minimizing the time required for biobarrier installation and operation was critical.

3.5.1 Data Requirements for Barrier Installation and Operation

The total length of time for biobarrier installation was recorded. System reliability was evaluated qualitatively by discussions with field personnel and quantitatively by evaluating total downtime for any unplanned activities (e.g., reinjection of emulsified oil) and total costs of the unplanned activities.

3.5.2 Success Criteria for Barrier Installation and Operation

The qualitative success criteria for system installation was downtime of less than five days for the facility, including installation of required MWs and emulsified oil injection. Success for operation was “minimal” unplanned maintenance/repair and cost. Quantitatively, the system should require no more than 15% additional field technician time per month than planned for routine checks and assessment.

4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

NSWCDD is located in King George County, VA, along the Potomac River approximately 40 miles south of downtown Washington, D.C., and 28 miles east of Richmond, VA (**Figure 4.1**) (URS, 2010). NSWCDD, which was originally established in 1918 as a testing site for naval ordnance, is presently focused on research, development, test, and evaluation (RDT&E) of ordnance, integrated warfare systems, weapons and ammunition, sensors and directed energy, and force protection. Apart from testing and disposal activities associated with their RDT&E mission, NSWCDD accepts obsolete or waste munitions from other military facilities for treatment and serves as a center for emergency EOD for the public sector. The explosives requiring disposal are thermally treated at the OB/OD units located at the Churchill Range of the EEA at NSWCDD.

Figure 4.1. Map Showing the Location of the NSWCDD Site.

The EEA, commonly referred to as "Pumpkin Neck," is one of the two main areas comprising NSWCDD. The Upper Machodoc Creek passes through NSWCDD, cutting the facility into the two areas: the Mainside consisting of 2,677 acres, and the EEA comprising 1,614 acres (Bell, 1996). The EEA is composed of >60% forest and marshland, with two open areas (Churchill Range and Harris Range) for munitions testing and disposal activities (**Figure 4.2**).

The Churchill Range includes OB and OD areas, a Fast Cookoff area, and other facilities for ordnance and energetics testing, including drop test towers, and static thrust stands. This ESTCP demonstration was conducted on the Churchill Range at a location downgradient of the Fast Cookoff area where RDX and perchlorate contamination is present.

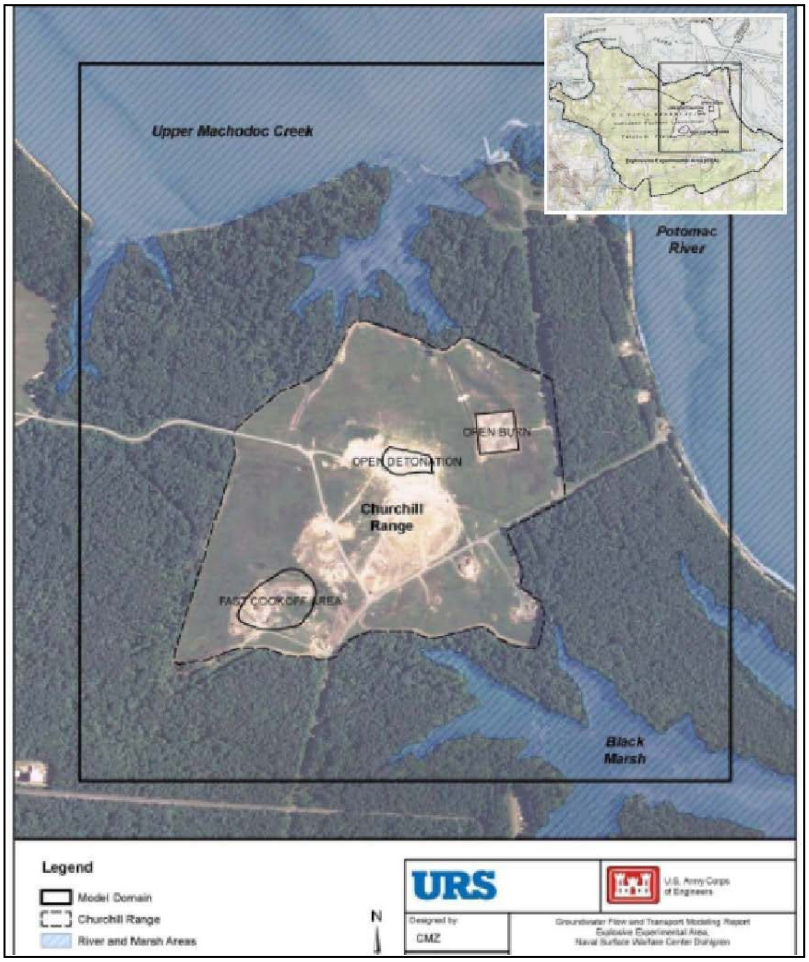


Figure 4.2. Map Showing the Churchill Range of NSWCDD.

The inset provides the location of the range within the EEA (URS, 2010).

4.2 SITE GEOLOGY AND HYDROGEOLOGY

4.2.1 Basic Geology

The geology of the EEA was studied by the U.S. Geologic Survey (USGS) in the mid-1990s (Bell, 1996), and has been the subject of additional investigative work by the URS Group Inc. (URS, 2010). The surface of the EEA varies in elevation from ~0 to 30 ft above mean sea level (amsl), and the surface topography is basically flat. The geology of the site consists of two sequences of fluvial-estuarine deposits (Pleistocene) that overlie marine deposits (Pleistocene-Eocene) of the Nanjemoy-Marlboro confining unit (Bell, 1996). The surficial water bearing unit is the Columbia aquifer, which is the unit within which the demonstration was conducted.

The Columbia aquifer unconformably overlies the upper confining unit (clay with significant organic deposits) across most of the EEA and ranges from <8 to ~34 ft thick. The Columbia aquifer consists of sand, silt, and clay with a pebble deposit at the bottom (on top of the underlying confining layer). The upper confining layer was observed to be absent in the central region of the OB/OD area; rather the Columbia aquifer appears to directly overlie the Nanjemoy-Marlboro confining unit in this region, which consists of glauconitic fine-grained sands of the Nanjemoy formation (Bell, 1996; URS, 2010).

4.2.2 Groundwater Monitoring Wells

Fifteen permanent groundwater MWs are present in the Churchill Range Area. Two of these wells (EEA-S17, EEA-S18) were installed by the USGS in 1993, as part of the overall site investigation work, during which time 28 wells were drilled across the entire EEA (Belle, 1993). Eight additional wells (GWOBOD02–GWOBOD09) were installed by USGS in the Churchill Range area in 1998, and five wells (CMOBOD01–CMOBOD05) were subsequently installed in 2007, by URS during site assessment studies. All of these wells are screened in the Columbia Aquifer.

4.2.3 Groundwater Depth

The depth to water on the range varies seasonally, but generally is from 0.1 to 8 ft below ground surface (bgs) depending on location and season, with the water table rising in the spring and declining in the summer/fall (URS, 2010). Based on 2007 data and previous groundwater maps of the area, there is usually a groundwater divide that runs through the center of the range in an east-west direction. To the north of the divide, groundwater flows in a northerly direction and discharges primarily to the Upper Machodoc Creek and Potomac River, generally flowing with surface topography. The OB area on the range is near the top of the groundwater divide, with some groundwater flow going in a west-northwest direction and some southwesterly flow, depending on the location of the groundwater mound (URS, 2007). To the south of the divide, groundwater flows in a southerly direction and discharges to the Black Marsh and various tidal creeks to the south and southeast.

4.2.4 Groundwater Flow

Slug tests conducted by USGS in the early 1990s in 18 wells screened in the Columbia Aquifer across the entire EEA revealed hydraulic conductivities (K) ranging from 0.1 to 21 feet per day (ft/day), with a median value of 1.4 ft/day (Bell, 1996). However, only two of these wells were located in the Churchill Range Area. Assuming an average aquifer porosity of 0.30, and measured horizontal hydraulic gradient of 0.002, the rates of horizontal flow across the entire EEA were determined to vary from 0.003 to 0.7 ft/day (~1–300 ft/year) (Bell, 1996). Using the same values for porosity and horizontal gradient, and the K values specifically from the Churchill Range wells, the horizontal flow in this area might be expected to range from 4 to 300 ft/yr. Data suggest that there is significant variability in both groundwater flow direction and rates across the EEA and the much smaller area of the Churchill Range.

4.2.5 Groundwater Chemistry

The basic groundwater geochemistry in the Columbia Aquifer across the EEA was evaluated by the USGS in 1996 (Bell, 1996). The water is considered to be typical of shallow groundwater in the coastal plain of Virginia. Overall, the groundwater in the EEA is slightly acidic, with a median pH value of 4.9, and a range from 4.2 to 6.8. Consistent with the low pH, alkalinity in the aquifer is low, averaging 22 mg/L as calcium carbonate (CaCO3). The bulk of the aquifer is aerobic (although with some anoxic areas), with a median DO of 4.3 mg/L, and a range from 0.2 to 9 mg/L.

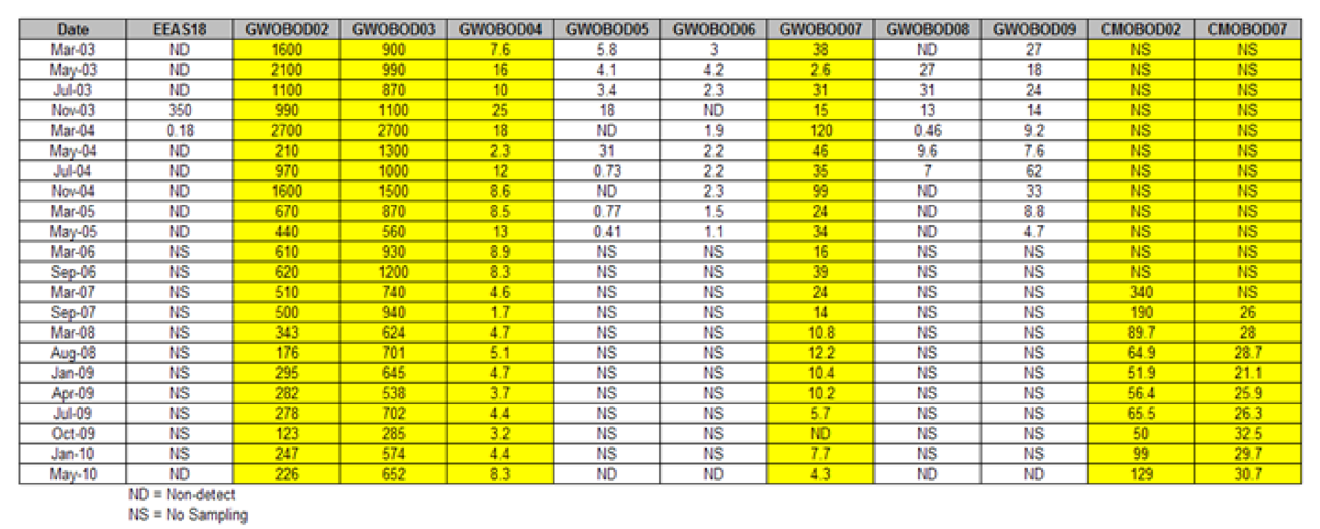
As with hydrogeological conditions across the EEA, the overall groundwater chemistry shows significant variability, in part related to the influence of the Potomac River in some wells, and in other instances the influence of the Nanjemoy-Marlboro confining unit (particularly in the central EEA where the Columbia Aquifer directly overlies this unit).

4.3 CONTAMINANT DISTRIBUTION

RDT&E activities on the Churchill Range have resulted in contamination of soil and groundwater at some locations. A recent soil characterization conducted by URS in the OB/OD area revealed that the contamination of surface soils with explosives and perchlorate is randomly distributed, which is consistent with the activities performed in this region. The average concentrations of perchlorate and RDX in the regions sampled were 54.9 milligrams per kilogram (mg/kg) (320 mg/kg maximum) for perchlorate and 3.3 mg/kg (43 mg/kg maximum) for RDX (URS, 2010). Because of the random distribution of constituents, and the likelihood that some energetic materials are present as variably-sized particles rather than as dissolved or adsorbed phase chemicals, infiltration of these contaminants to groundwater is likely to be intermittent in time and variable in space.

A recent study by URS documented perchlorate and RDX concentrations in groundwater at the Churchill Range from 1998 to 2010 (URS, 2010). These data are presented in **Table 4.1** (perchlorate) and **Table 4.2** (RDX). Based on the data presented, several wells onsite have had elevated concentrations of both perchlorate and RDX during the study period. These include wells GWOBOD02 and GWOBOD03. A series of model simulations were conducted by URS (2010) to assess groundwater flow from source areas and future plume migration pathways with relevant concentrations (**Figure 4.3**).

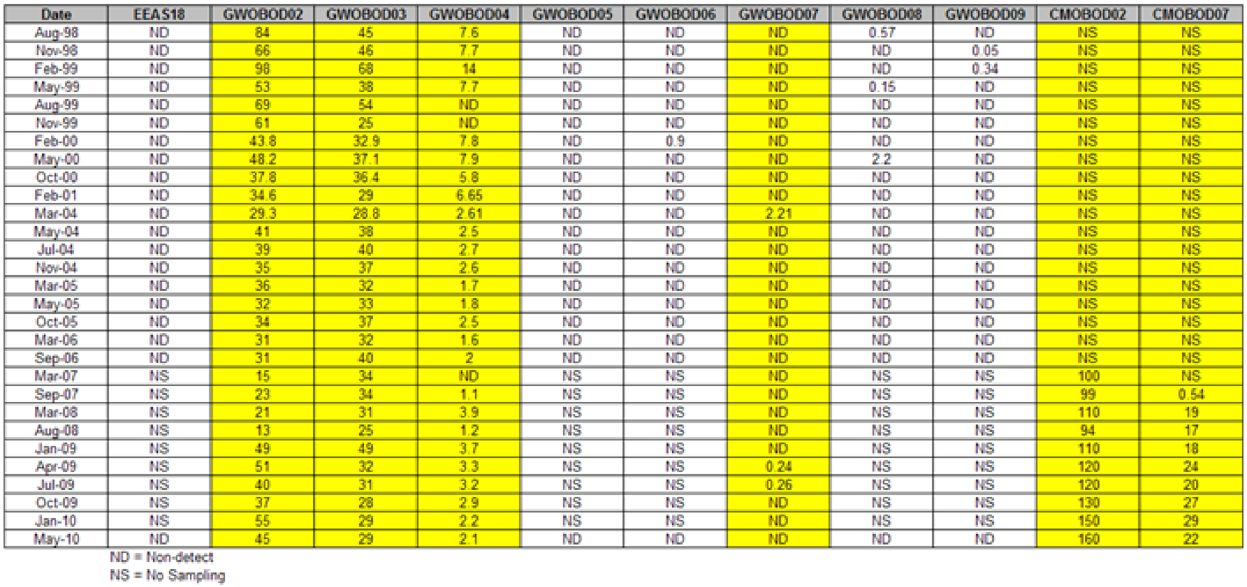
Table 4.1. Observed Historical Groundwater Perchlorate Concentrations in the Churchill Range (2003–2010). *(URS, 2010; µg/L)*



Date	EEAS18	GWOBOD02	GWOBOD03	GWOBOD04	GWOBOD05	GWOBOD06	GWOBOD07	GWOBOD08	GWOBOD09	CMOBOD02	CMOBOD07
Mar-03	ND	1600	900	7.6	5.8	3	38	ND	27	NS	NS
May-03	ND	2100	990	16	4.1	4.2	2.6	27	18	NS	NS
Jul-03	ND	1100	870	10	3.4	2.3	31	31	24	NS	NS
Nov-03	350	990	1100	25	18	ND	15	13	14	NS	NS
Mar-04	0.18	2700	2700	18	ND	1.9	120	0.46	9.2	NS	NS
May-04	ND	210	1300	2.3	31	2.2	46	9.6	7.6	NS	NS
Jul-04	ND	970	1000	12	0.73	2.2	35	7	62	NS	NS
Nov-04	ND	1600	1500	8.6	ND	2.3	99	ND	33	NS	NS
Mar-05	ND	670	870	8.5	0.77	1.5	24	ND	8.8	NS	NS
May-05	ND	440	560	13	0.41	1.1	34	ND	4.7	NS	NS
Mar-06	NS	610	930	8.9	NS	NS	16	NS	NS	NS	NS
Sep-06	NS	620	1200	8.3	NS	NS	39	NS	NS	NS	NS
Mar-07	NS	510	740	4.6	NS	NS	24	NS	NS	340	NS
Sep-07	NS	500	940	1.7	NS	NS	14	NS	NS	190	26
Mar-08	NS	343	624	4.7	NS	NS	10.8	NS	NS	89.7	28
Aug-08	NS	176	701	5.1	NS	NS	12.2	NS	NS	64.9	28.7
Jan-09	NS	295	645	4.7	NS	NS	10.4	NS	NS	51.9	21.1
Apr-09	NS	282	538	3.7	NS	NS	10.2	NS	NS	56.4	25.9
Jul-09	NS	278	702	4.4	NS	NS	5.7	NS	NS	65.5	26.3
Oct-09	NS	123	285	3.2	NS	NS	ND	NS	NS	50	32.5
Jan-10	NS	247	574	4.4	NS	NS	7.7	NS	NS	99	29.7
May-10	ND	226	652	8.3	ND	ND	4.3	ND	ND	129	30.7

ND = Non-detect
NS = No Sampling

Table 4.2. Observed Historical Groundwater RDX Concentrations in the Churchill Range (1998–2010). *(URS, 2010; µg/L)*



Date	EEAS18	GWOBOD02	GWOBOD03	GWOBOD04	GWOBOD05	GWOBOD06	GWOBOD07	GWOBOD08	GWOBOD09	CMOBOD02	CMOBOD07
Aug-98	ND	84	45	7.6	ND	ND	ND	0.57	ND	NS	NS
Nov-98	ND	66	46	7.7	ND	ND	ND	ND	0.05	NS	NS
Feb-99	ND	98	68	14	ND	ND	ND	ND	0.34	NS	NS
May-99	ND	53	38	7.7	ND	ND	ND	0.15	ND	NS	NS
Aug-99	ND	69	54	ND	ND	ND	ND	ND	ND	NS	NS
Nov-99	ND	61	25	ND	ND	ND	ND	ND	ND	NS	NS
Feb-00	ND	43.8	32.9	7.8	ND	0.9	ND	ND	ND	NS	NS
May-00	ND	48.2	37.1	7.9	ND	ND	ND	2.2	ND	NS	NS
Oct-00	ND	37.8	36.4	5.8	ND	ND	ND	ND	ND	NS	NS
Feb-01	ND	34.6	29	6.65	ND	ND	ND	ND	ND	NS	NS
Mar-04	ND	29.3	28.8	2.61	ND	ND	2.21	ND	ND	NS	NS
May-04	ND	41	38	2.5	ND	ND	ND	ND	ND	NS	NS
Jul-04	ND	39	40	2.7	ND	ND	ND	ND	ND	NS	NS
Nov-04	ND	35	37	2.6	ND	ND	ND	ND	ND	NS	NS
Mar-05	ND	36	32	1.7	ND	ND	ND	ND	ND	NS	NS
May-05	ND	32	33	1.8	ND	ND	ND	ND	ND	NS	NS
Oct-05	ND	34	37	2.5	ND	ND	ND	ND	ND	NS	NS
Mar-06	ND	31	32	1.6	ND	ND	ND	ND	ND	NS	NS
Sep-06	ND	31	40	2	ND	ND	ND	ND	ND	NS	NS
Mar-07	NS	15	34	ND	NS	NS	ND	NS	NS	100	NS
Sep-07	NS	23	34	1.1	NS	NS	ND	NS	NS	99	0.54
Mar-08	NS	21	31	3.9	NS	NS	ND	NS	NS	110	19
Aug-08	NS	13	25	1.2	NS	NS	ND	NS	NS	94	17
Jan-09	NS	49	49	3.7	NS	NS	ND	NS	NS	110	18
Apr-09	NS	51	32	3.3	NS	NS	0.24	NS	NS	120	24
Jul-09	NS	40	31	3.2	NS	NS	0.26	NS	NS	120	20
Oct-09	NS	37	28	2.9	NS	NS	ND	NS	NS	130	27
Jan-10	NS	55	29	2.2	NS	NS	ND	NS	NS	150	29
May-10	ND	45	29	2.1	ND	ND	ND	ND	ND	160	22

ND = Non-detect
NS = No Sampling

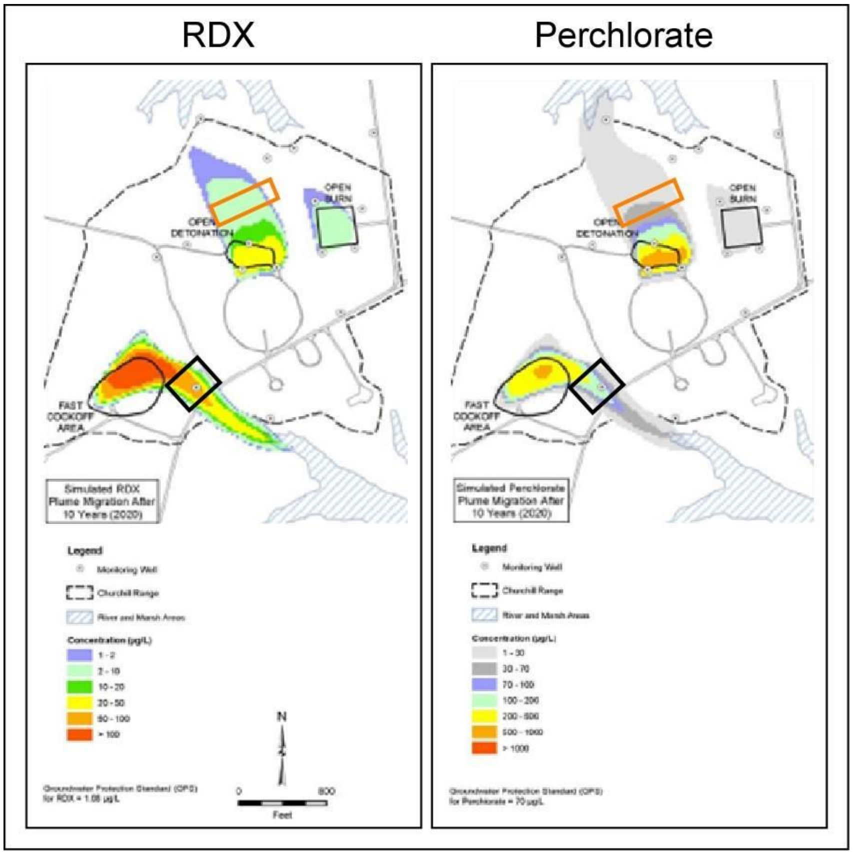


Figure 4.3. Modeled Plume Migration Maps for RDX and Perchlorate. *(URS, 2010).*

The primary demonstration site is indicated by a bold black square.

4.4 TEST PLOT LOCATION

Based on the model simulations from URS (2010), previous site characterization documents, and discussions with site environmental personnel at NSWCDD, a site on the southwestern side of the Churchill Range was chosen as a candidate location for the *in situ* biobarrier test plot area (TPA). This area is in the vicinity of well CMOBOD02 to the southeast of the Fast Cookoff area and to the northeast of the Black Marsh (see “black box” in **Figure 4.3**). Well CMOBOD02 had perchlorate and RDX concentrations in the range desired for this work (each >100 µg/L at initiation of project; see **Tables 4.1 and 4.2**), and historically has had elevated concentrations of both contaminants. Based on the modeling simulations, the contamination in this well (and the general surrounding area) is suspected to emanate from the Fast Cookoff area rather than either the OB or OD areas to the north, and appears to occur over a reasonably small areal extent. Another reason to select this general region for the barrier is that the estimated conductivity values (URS, 2010) are high compared to other regions of the site, and that this region is significantly south of the east-west groundwater divide, with a gradient that appears to be primarily to the southeast. The groundwater flow direction closer to the divide, near the OB/OD area, is more likely to be subject to seasonal effects.

Additional site characterization focused on the proposed TPA was conducted due to the few wells in the area. This work included (1) collection of aquifer solids and groundwater for a series of treatability studies; (2) installation, surveying, and sampling of 28 new piezometers screened in the Columbia aquifer to the east and southeast of the Fast Cookoff area; (3) geologic logging of all cores collected during piezometer installation; (3) collection of groundwater elevations from all wells and piezometers on two separate occasions; (4) slug and pump tests in well CMOBOD02; and (5) installation of data loggers into multiple wells to evaluate any tidal influence on groundwater elevation (due to the proximity of the site to the Potomac River). The results from local site assessment and treatability work are provided in the project final report.

5.0 TEST DESIGN

The following subsections provide detailed description of the system design and testing conducted to address the performance objectives described in **Section 3.0**.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The effectiveness of an emulsified oil barrier for *in situ* treatment of perchlorate and explosives was tested during this project. The experimental plan consisted of initial data review, site assessment, and treatability studies to determine the best location and design for the biobarrier, and the most effective EOS for application at the EEA. The biobarrier was installed cross-gradient to groundwater flow. The effectiveness of the barrier for reducing migration of perchlorate and explosives in groundwater was determined using a series of groundwater MWs, including two upgradient wells, two wells within the biobarrier, and eight downgradient wells spaced from 2.5 to 40 ft downgradient of the barrier. The wells were monitored for perchlorate; RDX and other explosives; field parameters; TOC; fatty acids; dissolved metals; and anions. Two initial baseline rounds of groundwater sampling were conducted prior to barrier installation. Once biobarrier installation was complete, 10 groundwater sampling events were conducted that included all demonstration MWs, over 30 months. The details of barrier installation and sampling are provided in **Section 5.4**.

Overall, this project was designed to demonstrate that a passive remedial approach can be highly effective and cost-effective for treating explosives and perchlorate in groundwater at an operational DoD range. The site investigation, treatability work, barrier design, MW network, and sampling plan were designed to meet this objective. Molecular techniques developed through previous and current Strategic Environmental Research and Development Program (SERDP) research were also utilized to assess the organisms responsible for *in situ* energetics biodegradation as described in the final report. Those data are not presented herein. Most critically, the project showed that groundwater treatment and protection can be implemented cost-effectively on an operational range without affecting mission-critical activities.

5.2 BASELINE CHARACTERIZATION

Prior to site selection, CB&I reviewed existing site investigation documents and all available hydrogeologic, contaminant concentration, and geochemical data for the EEA at the NSWCDD site. Based on these data, a TPA was selected in the vicinity of well CMOBOD02, but a significant amount of additional data were required to effectively locate, design, and install the biobarrier and the required MW network for the field demonstration plot. The following text summarizes baseline characterization activities that were performed in support of the final demonstration design.

In order to properly place the biobarrier for effective treatment of the groundwater, site characterization work was performed during 2010 and 2011 to (1) better define the extent of contamination in the region; and (2) to confirm the local hydrogeology, including lithology, hydraulic conductivity, and the estimated velocity and direction of groundwater flow. A summary of the results are provided below, with more details provided in the project final report.

A total of 28 piezometers were installed in three separate events in order to better determine the approximate extent of groundwater contamination in the vicinity of MW CMOBOD02, to verify the source of contamination, and better define both the subsurface lithology of the region and the general path of groundwater flow. The location of these piezometers is provided in **Figure 5.1**.

Figure 5.1. Map Showing the Well and Piezometer Locations on the Churchill Range of NSWCDD (November 2011).

5.2.1 Test Site Geology

Continuous soil core samples were collected in 4-ft intervals using a direct-push technology (DPT) rig at each piezometer location. The collected soil cores were logged by a CB&I geologist and used to determine the construction and placement of the piezometers. The soil collected within the cores was visually classified using the Unified Soil Classification System (USCS). The soil borings typically revealed a surficial 0.5–3 ft layer of dark silt or lean clay.

This material overlaid a poorly-graded sand interbedded with clayey sand and lean clay lenses, consistent with the Columbia Aquifer sediments. Beneath the poorly-graded sand, an impermeable fat clay layer approximately 2–8 ft thick was present overlying the marine, glauconitic sand of the Nanjemoy-Marlboro confining unit, marking the end of the boring.

Based on the analysis of recovered soil, the average site-wide thickness of the interbedded, water conductive layers was 5.9 ft, with approximately 4.7 ft of the layer consisting primarily of sandy material. On average, the conductive layer began at approximately 3.1 ft bgs and ended at approximately 9.0 ft bgs, below which the impermeable fat clay and marine glauconitic sand exist. It should be noted that the regional geology is highly variable in grain size as well as layer thickness due to the nature of fluvial-estuarine deposits.

Groundwater was typically encountered between 1.5 and 5.8 ft bgs during the May 2011 groundwater survey, and 0.5 to 3.8 ft bgs in October 2011. The average depth to groundwater across the Churchill Range was 3.8 ft bgs in May 2011, and 2.1 ft bgs in October 2011, indicating a seasonal fluctuation of approximately 1.5–2 ft. It should be noted that the October site characterization event occurred following an exceptionally wet fall season (including passage of Hurricane Irene and Tropical Storm Lee), which caused widespread inundation of the Churchill Range site. Groundwater measurements compiled during the characterization events were used to create potentiometric surface maps, which confirmed a general groundwater gradient to the south-southeast in the area under evaluation. The October 2011 data are provided in **Figure 5.2**.

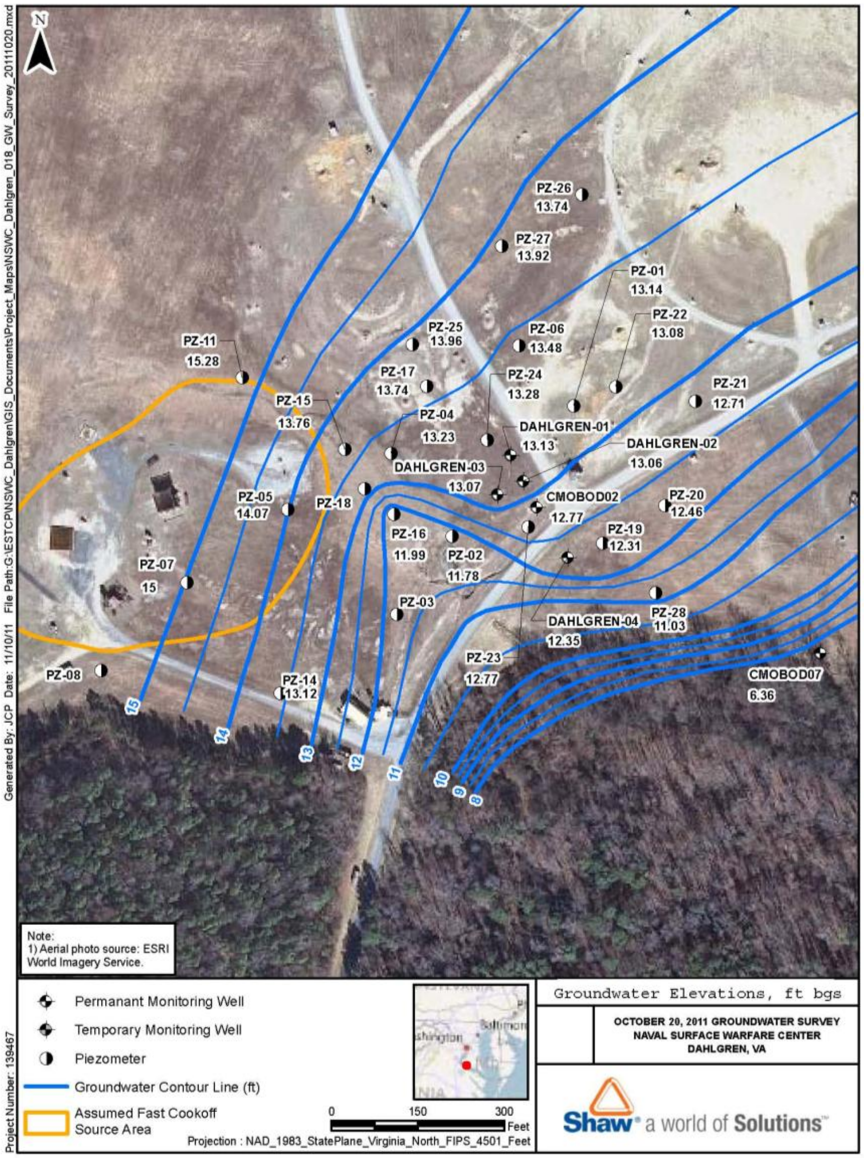


Figure 5.2. **Potentiometric Surface Map of the Churchill Range in October 2011.**

5.2.2 Groundwater Chemistry

In November 2008, several wells were sampled on the Churchill Range to conduct studies for SERDP Project ER-1607. Basic geochemistry was collected for wells GWOBOD02, GWOBOD03, CMOBOD02, and EEA-S17 (as an uncontaminated control well), along with analysis of metals, explosives, anions, and cations. The basic geochemical parameters for these Churchill Range wells in 2008 are provided in **Table 5.1**. During the 2010 and 2011 sampling events, pH and DO measurements were collected from each of the piezometers prior to collecting groundwater samples using a field meter and in-line flow cell. These measurements were used to create maps depicting geochemical conditions at the Churchill Range. The pH measurements east of the Fast Cookoff area ranged from 3.9 to 6.4, averaging approximately 4.9. Dissolved oxygen measurements ranged from 0 to 9.6 mg/L, averaging approximately 5.3 mg/L.

Table 5.1. Water Quality Data from Four Permanent Wells on the Churchill Range.

	Parameter						
Well ID	**pH (SU)**	**ORP (mV)**	**DO (mg/L)**	**Sp. Cond. (µS/cm)**	**Cl^- (mg/L)**	**NO_3^- (mg/L)**	**SO_4^- (mg/L)**
GWOBOD02	4.20	289	1.5	0.079	8.4	1.2	9.5
GWOBOD03	4.45	236	3.7	0.073	6.7	0.9	6.4
CMOBOD02	4.76	424	4.1	0.052	3.8	<0.1	4.3
EEA-S17	4.02	293	1.9	0.039	2.2	0.3	8.5

µS/cm – micro-Siemens per cm, Cl^- – chloride, ID – identification, NO_3^- – nitrate, SO4- – sulfate

5.2.3 Test Site Groundwater Flow and Direction

Based on the proximity of the Potomac River, an In-Situ Level TROLL® 700 pressure transducer was placed in well CMOBOD02 to record pressure fluctuations. The transducer was installed to determine the impact on the Churchill Range of tidal influences. The overall trend for the transducer data over ten days was a gradual downward drop in the groundwater elevation of approximately 0.6 ft. Minor fluctuations (on the order of 1/100-ft) were observed in the groundwater data indicating a slight tidal influence, though not on a scale that would significantly disrupt the groundwater flow direction.

During the May 2011 event, an In-Situ Level Troll 700 was placed in MW CMOBOD02 to record the draw down and recharge of the groundwater during sample collection. The transducer data was recorded with the intention of calculating an estimation of the K value within the surrounding material through the use of the recharge data. Data was recorded throughout the pumping at 5-second intervals.

In addition to the pump test data, slug testing was performed on MW CMOBOD02 during the October 2011 site investigation to determine the localized K value. The slug test and pumping test data were analyzed by the Bouwer and Rice method (Bouwer, 1989; Bouwer and Rice, 1976) based on the unconfined nature of the Columbia aquifer and the partial penetration of the MW. Well construction, pump test, and slug test data were inserted into a USGS spreadsheet (USGS, 2010) designed to calculate K values from the acquired slug test data.

The pump test recharge data collected in May 2011 from well CMOBOD02, the nearest permanent well to the proposed location of biobarrier installation, revealed a K value of approximately 4.3 ft/day. The slug testing performed by CB&I in October 2011 on well CMOBOD02 revealed a K value averaging approximately 4.4 ft/day.

Groundwater flow velocity was calculated using a standard groundwater flow equation (Fetter, 1988):

$$V = \frac{Ki}{n_e} \qquad (1)$$

V = groundwater velocity
K = hydraulic conductivity
I = gradient
n_e = porosity

Using an estimated aquifer porosity of 0.30, calculated K values of 4.3–4.4 ft/day, and a localized hydraulic gradient of 0.004 over the 900-ft study area for the potential biobarrier, the expected horizontal flow velocity in this area is approximately 0.059 ft/day, or 21.4 ft/year. The K value and horizontal flow rate calculated based on the slug test data falls within the ranges reported in previous groundwater reports for the area (URS, 2010; Bell, 1996). The direction of groundwater flow is estimated to be south-southeast, based on measured hydraulic gradients and observed contaminant distributions.

5.2.4 Explosives and Perchlorate in Test Site Groundwater

Groundwater samples were collected for analysis of explosives by EPA Method 8330 and perchlorate by EPA Method 314.0 during all three site characterization events. The data from the October 2011 sampling event were compiled and contour maps of RDX (**Figure 5.3),** perchlorate **(Figure 5.4)**, and HMX (**Figure 5.5)** were prepared based on the data. The data indicate that the majority of the contamination in groundwater flowing towards the Black Marsh originates from multiple point sources to the east of the Fast Cookoff Area and to the south and west of the central “arena.” The contour maps are the best interpretation of the data. Based upon all available data, two initial locations were selected for the installation of the biobarrier: a primary location and a back-up location. The first location for the placement of the biobarrier was on the southeast side of the main access road in the vicinity of PZ-20. This location is shown as a yellow line in **Figures 5.3–5.5.** This barrier location intercepted perchlorate, RDX, and HMX from an apparent source zone. The expected concentrations in the barrier area were >60 µg/L for RDX, >100 µg/L for perchlorate, and >25 µg/L for HMX. The direction of groundwater flow in this region was to the southeast (**Figure 5.2**). The primary issue with this location was the fact that the underlying clay layer was detected at only 6.5 ft bgs in the core log for PZ-20—the only piezometer installed in the immediate vicinity—which could result in dry wells during some of the demonstration period.

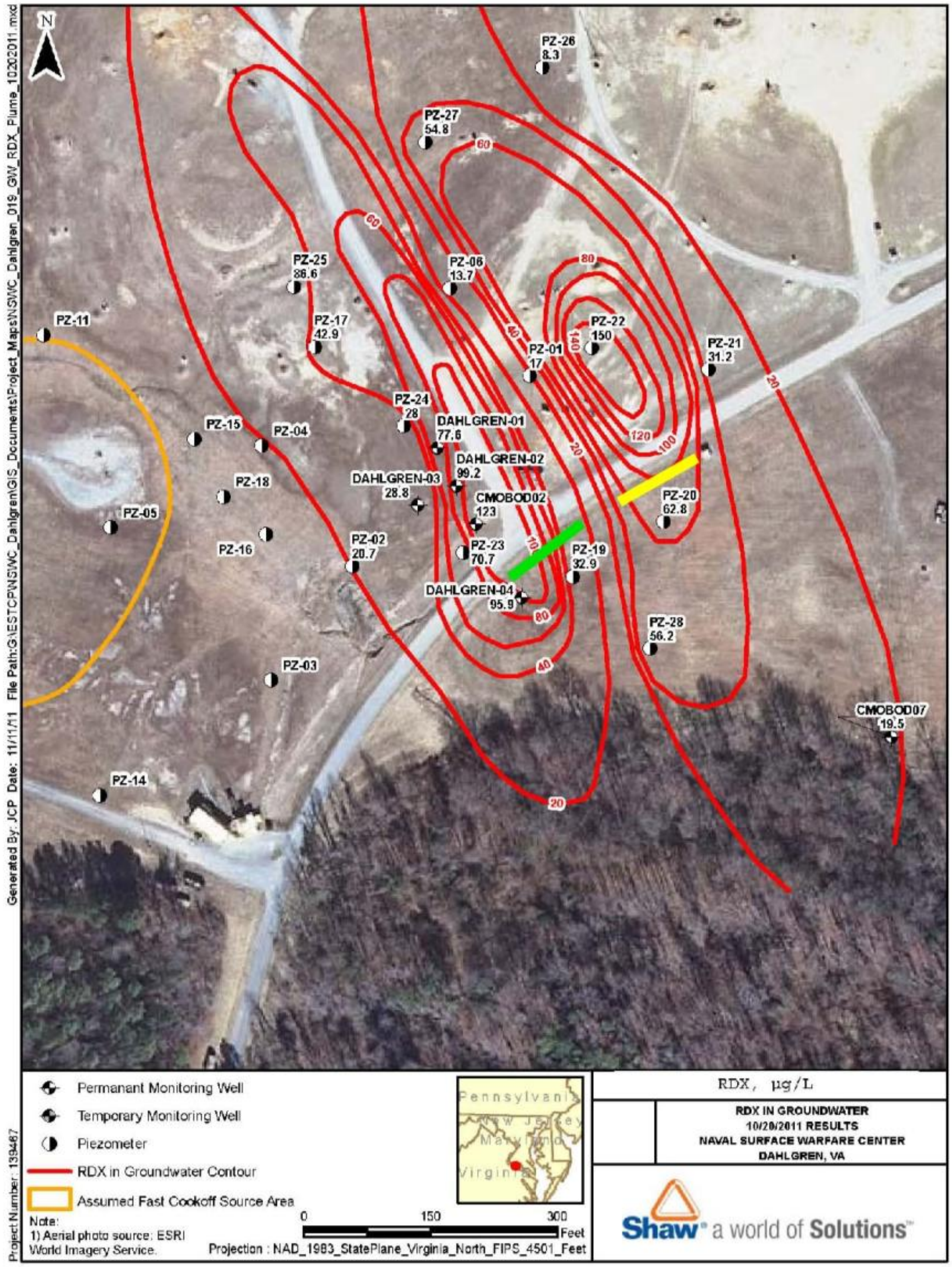


Figure 5.3. Plume Map for RDX in the Southeast Area of the Churchill Range.

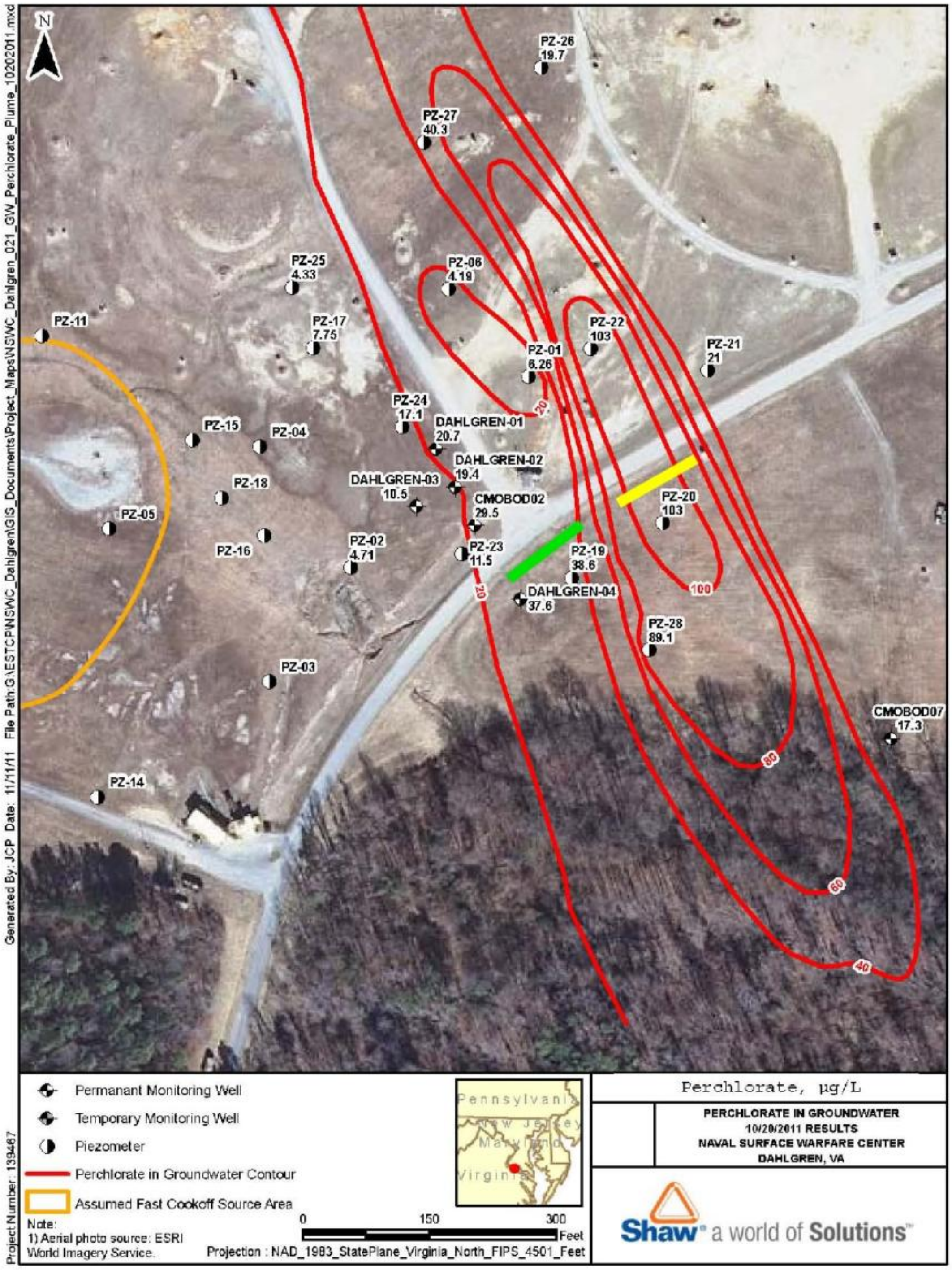


Figure 5.4. Plume Map for Perchlorate in the Southeast Area of the Churchill Range.

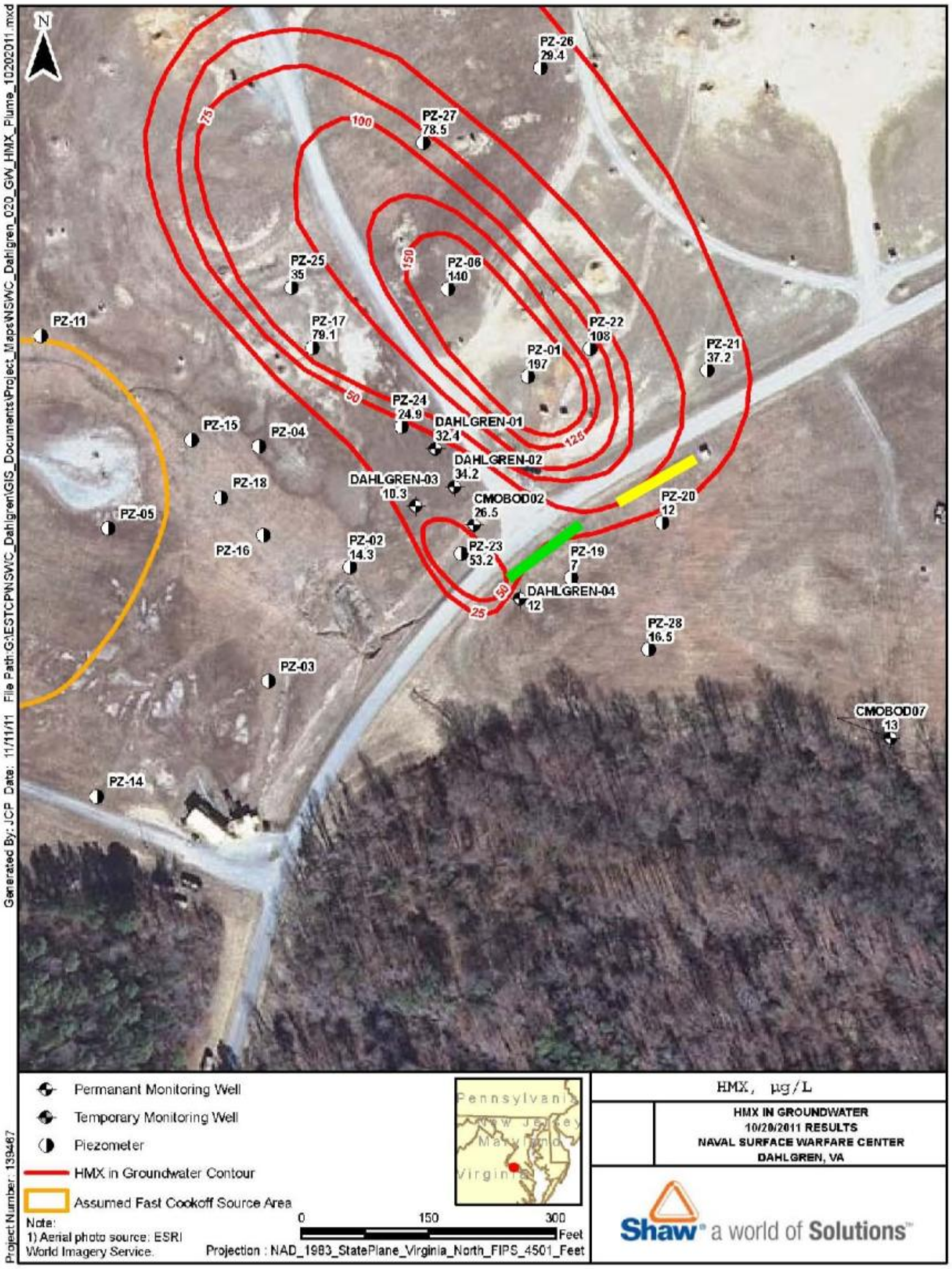


Figure 5.5. Plume Map for HMX in the Southeast Area of the Churchill Range.

The second selected location for the demonstration was ~120 ft southwest in the vicinity of PZ-19 and Dahlgren 04. This location is shown as a green line in **Figures 5.3–5.5.** This barrier location also intercepted an apparent plume with perchlorate and RDX, although perchlorate concentrations were lower than in the previous area. The expected concentrations in the barrier area were >40 µg/L for RDX (perhaps as high as 100 µg/L) and >20 µg/L for perchlorate.

HMX was also expected in this area at concentrations ranging from ~7 to 25 µg/L. The core logs from PZ-19 and Dahlgren 04 suggested that the confining clay layer in this region occurred at 10–12 ft bgs, with mixed conductive materials and clay zones above. Thus, this region appeared to provide a slightly greater conductive zone based on available data. After careful consideration, the second location (green line) was chosen to locate the barrier rather than the initial site (yellow line), based primarily on the depth to the lower clay layer and the potential for dry wells during the summer months.

5.3 TREATABILITY RESULTS

Laboratory treatability studies were conducted with samples obtained from the TPA. The objectives of the treatability studies were: (1) to determine if indigenous bacteria can be stimulated via emulsified oil addition to biodegrade perchlorate and RDX to below their respective practical quantitation limits (PQLs); (2) to evaluate the effectiveness of different oil formulations, particularly the potential for pH buffered emulsified oils to enhance degradation rates; (3) to estimate the extent of oil adsorption to site sediments; and (4) to estimate kinetics of *in situ* perchlorate and RDX biodegradation.

The treatability study results supported the application of an emulsified oil biobarrier for *in situ* treatment of RDX, HMX, and perchlorate in the TPA. The following is a summary of the treatability study results:

- Perchlorate, RDX, and HMX were rapidly biodegraded in microcosms receiving EOS (EOS®-Low Salt blend) to concentrations <0.5 µg/L for perchlorate and RDX, and <10 µg/L for HMX. No loss of RDX or perchlorate was observed in the unamended microcosms under aerobic or anoxic incubation conditions.
- Perchlorate, RDX, and HMX also were biodegraded in aquifer columns receiving two different emulsified oil blends, one of which includes buffering materials (EOS® AquaBupH™) to raise pH. Significant loss of RDX also was observed in the unamended control column in this study, which was attributed to a combination of abiotic and biotic processes. It is unclear whether these processes are occurring in the field at some rate (similar losses were not observed in microcosms) or rather are an artifact of the homogenization process used for the column solids (potentially releasing natural organic matter, Fe, or enhancing sorption sites). Based on the extensive and persistent RDX contamination in the EEA area, it is likely that any natural attenuation processes were significantly accelerated in the columns. Unlike RDX, no loss of perchlorate or nitrate was observed in the unamended control column.
- The best oil amendment in the columns based on degradation rates of perchlorate was determined to be a 75:25 (volume per volume [v/v]) mixture of EOS®-Low Salt and EOS® AquaBupH™. This mixture also maintained the groundwater pH at the desired value of around 6 standard units (S.U.).
- The emulsified oils generated conditions in the column that caused increases in Fe and Mn, as expected, but only minor mobilization of As (<20 µg/L).

- The emulsified oil retention by the soil calculated according to Borden *et al.* (2008b), was 0.0019 gram per gram (g/g). This is comparable with previously published values (e.g., 0.0037 g/g) (Borden, 2007).

Based on the laboratory and field results, all data indicated that an emulsified oil barrier should be an effective technology for *in situ* degradation of RDX, HMX, and perchlorate at the NSWCDD site.

5.4 FIELD TESTING

During this project, an EOS was injected into the subsurface to form a passive biobarrier. The effectiveness of the barrier for reducing migration of perchlorate and explosives in groundwater at the EEA was determined using a series of groundwater MWs. Samples were collected twice prior to initial biobarrier installation (February 2013), and then for 30 months following installation. Upgradient and downgradient groundwater was monitored for perchlorate, RDX, HMX, and other explosives, field parameters, TOC (as a measure of oil concentration), fatty acids, dissolved metals, anions, and field parameters. Precipitation data was obtained from site personnel for the 20-month period (October 2013–June 2015). The details of the field plot design are provided below, and a schematic of the plot is given in **Figure 5.6.**

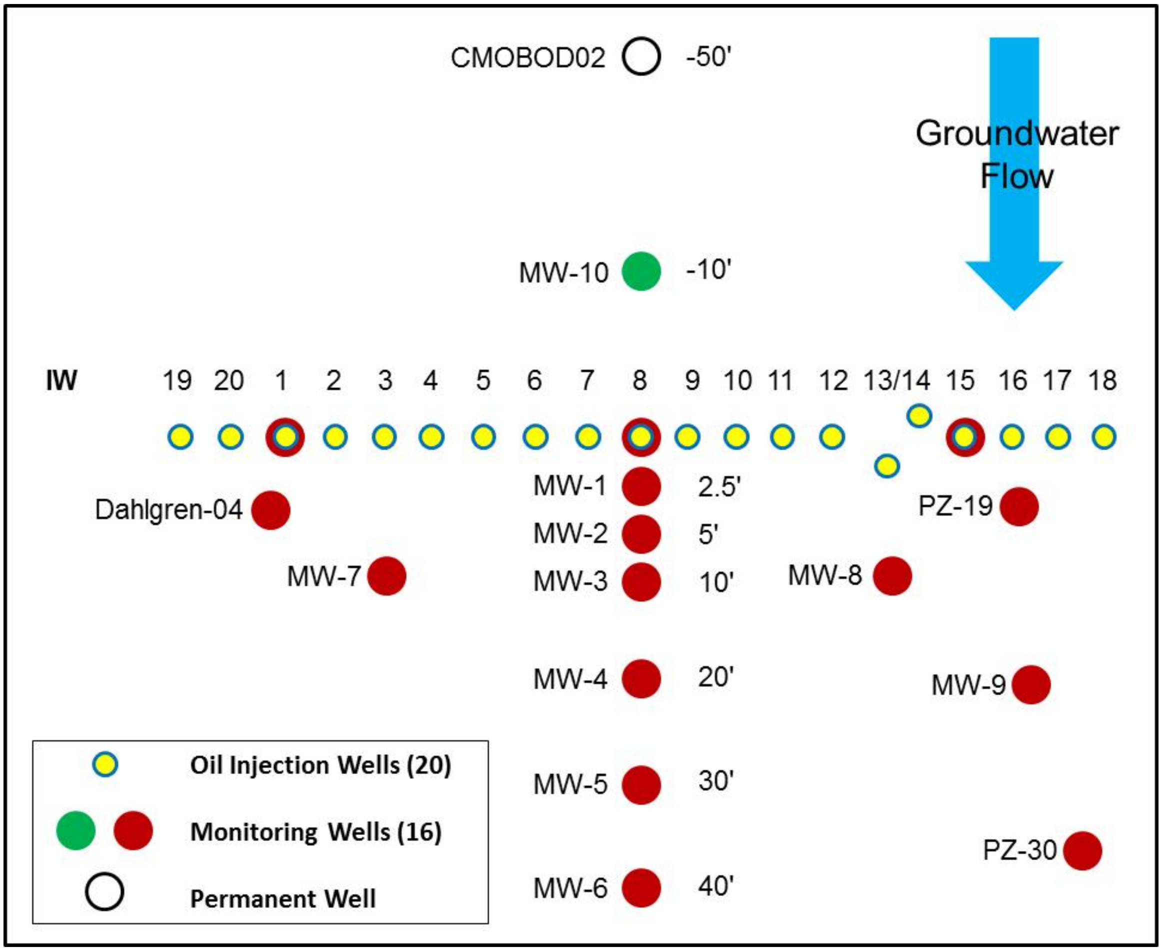
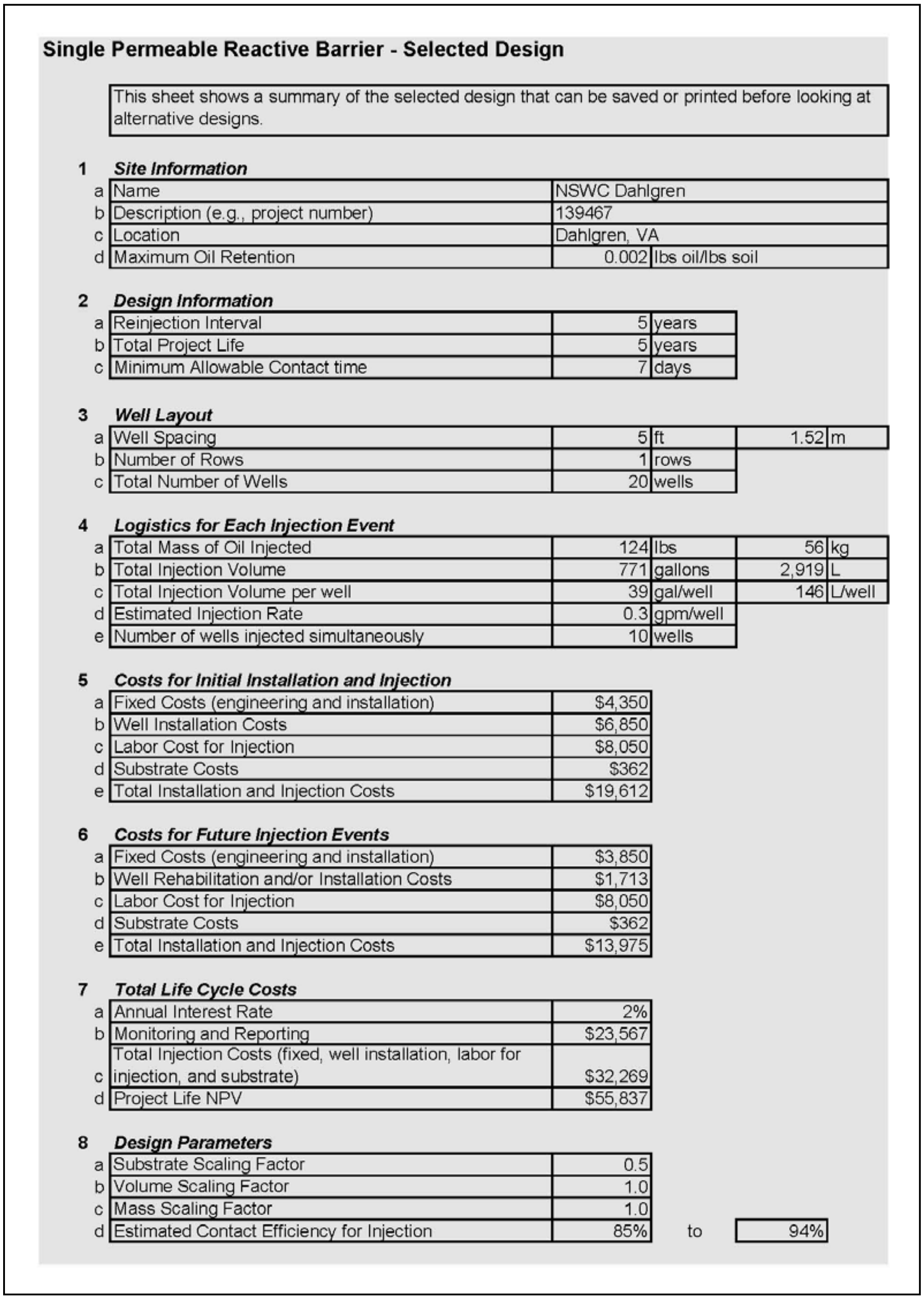


Figure 5.6. Schematic of Demonstration Plot Layout.

5.4.1 Demonstration Layout

The “Emulsified Oil Design Tool,” prepared by Dr. Robert Borden at North Carolina State University, was used to determine injection point spacing, oil volume, and the influence of a number of site variables and injection options on injection cost. A summary of the design parameters are presented in **Figure 5.7.**



Single Permeable Reactive Barrier - Selected Design

This sheet shows a summary of the selected design that can be saved or printed before looking at alternative designs.

1 *Site Information*

a	Name	NSWC Dahlgren			
b	Description (e.g., project number)	139467			
c	Location	Dahlgren, VA			
d	Maximum Oil Retention	0.002	lbs oil/lbs soil		

2 *Design Information*

a	Reinjection Interval	5	years
b	Total Project Life	5	years
c	Minimum Allowable Contact time	7	days

3 *Well Layout*

a	Well Spacing	5	ft	1.52	m
b	Number of Rows	1	rows		
c	Total Number of Wells	20	wells		

4 *Logistics for Each Injection Event*

a	Total Mass of Oil Injected	124	lbs	56	kg
b	Total Injection Volume	771	gallons	2,919	L
c	Total Injection Volume per well	39	gal/well	146	L/well
d	Estimated Injection Rate	0.3	gpm/well		
e	Number of wells injected simultaneously	10	wells		

5 *Costs for Initial Installation and Injection*

a	Fixed Costs (engineering and installation)	$4,350
b	Well Installation Costs	$6,850
c	Labor Cost for Injection	$8,050
d	Substrate Costs	$362
e	Total Installation and Injection Costs	$19,612

6 *Costs for Future Injection Events*

a	Fixed Costs (engineering and installation)	$3,850
b	Well Rehabilitation and/or Installation Costs	$1,713
c	Labor Cost for Injection	$8,050
d	Substrate Costs	$362
e	Total Installation and Injection Costs	$13,975

7 *Total Life Cycle Costs*

a	Annual Interest Rate	2%
b	Monitoring and Reporting	$23,567
c	Total Injection Costs (fixed, well installation, labor for injection, and substrate)	$32,269
d	Project Life NPV	$55,837

8 *Design Parameters*

a	Substrate Scaling Factor	0.5		
b	Volume Scaling Factor	1.0		
c	Mass Scaling Factor	1.0		
d	Estimated Contact Efficiency for Injection	85%	to	94%

Figure 5.7. Summary of Emulsified Oil Biobarrier Design Parameters.

The demonstration plot consisted of 20 emulsified oil injection wells (IWs) spaced in a single row on 5-ft centers, three of which served as in-barrier MWs after oil injection (**Figure 5.6**). The main MW network consisted of one upgradient MW and six downgradient MWs, spaced from -10 to +40 ft along the centerline of the expected groundwater flow through the biobarrier. An additional seven MWs were spaced on either side of the centerline within and on the edge of the expected zone of influence of the injected oil. Existing well CMOBOD02, which was ~50 ft upgradient of the biobarrier, was also sampled during the course of the demonstration. This well (4-inch diameter) was the only well that was not installed for the demonstration.

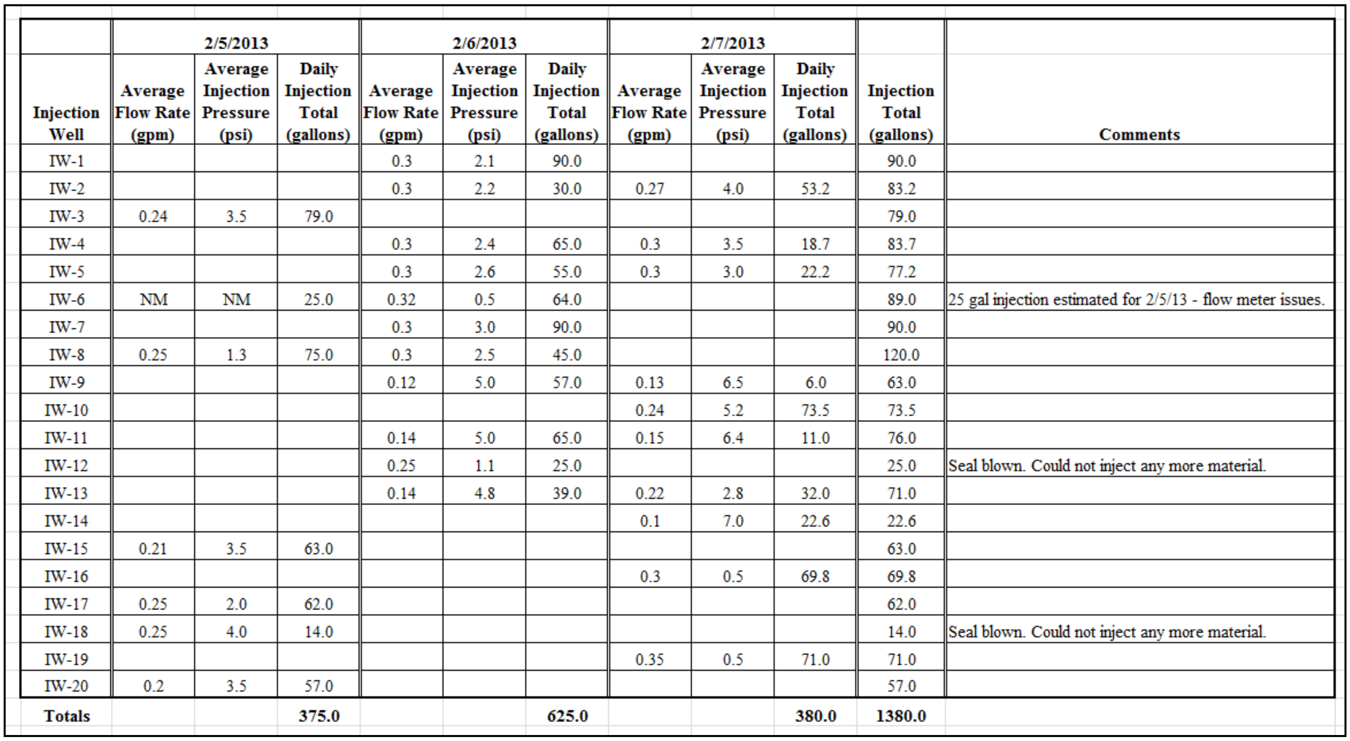
5.4.1.1 Baseline Sampling

After the wells were installed, two rounds of baseline sampling were performed (see **Section 5.5** for sampling and analysis details and **Section 5.6** for analytical results).

5.4.1.2 Biobarrier Installation

At the conclusion of the baseline sampling, the emulsified oil was injected. Injection records for each of the 20 IWs during the initial injection are presented in **Table 5.2**. The oil mixture utilized was a 4% (v/v) solution of EOS® 550LS ("low salt") dissolved in site groundwater (primarily from well CMOBOD02) and amended with 0.75% (v/v) EOS® CoBupH™, a slow-release magnesium hydroxide colloidal solid. The CoBupH™ product was developed by the manufacturer after initial laboratory treatability testing and was substituted for the AquaBupH™ used in the laboratory studies, which also contained emulsified oil. The groundwater and amendments were mixed in three separated batches in a 600-gallon (gal) poly tank. Each batch of injection solution was continually mixed with a submersible pump to keep the CoBupH™ particles in solution.

Table 5.2. Initial Emulsified Oil Injection Logs (February 2013).



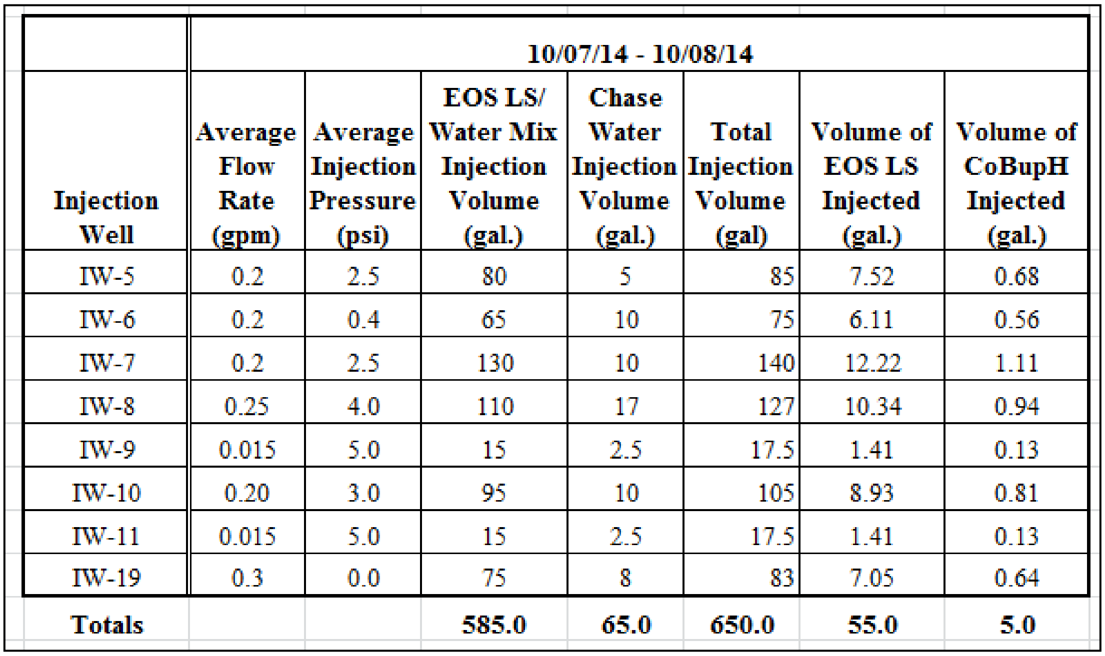
	2/5/2013			2/6/2013			2/7/2013				
Injection Well	**Average Flow Rate (gpm)**	**Average Injection Pressure (psi)**	**Daily Injection Total (gallons)**	**Average Flow Rate (gpm)**	**Average Injection Pressure (psi)**	**Daily Injection Total (gallons)**	**Average Flow Rate (gpm)**	**Average Injection Pressure (psi)**	**Daily Injection Total (gallons)**	**Injection Total (gallons)**	**Comments**
IW-1				0.3	2.1	90.0				90.0	
IW-2				0.3	2.2	30.0	0.27	4.0	53.2	83.2	
IW-3	0.24	3.5	79.0							79.0	
IW-4				0.3	2.4	65.0	0.3	3.5	18.7	83.7	
IW-5				0.3	2.6	55.0	0.3	3.0	22.2	77.2	
IW-6	NM	NM	25.0	0.32	0.5	64.0				89.0	25 gal injection estimated for 2/5/13 - flow meter issues.
IW-7				0.3	3.0	90.0				90.0	
IW-8	0.25	1.3	75.0	0.3	2.5	45.0				120.0	
IW-9				0.12	5.0	57.0	0.13	6.5	6.0	63.0	
IW-10							0.24	5.2	73.5	73.5	
IW-11				0.14	5.0	65.0	0.15	6.4	11.0	76.0	
IW-12				0.25	1.1	25.0				25.0	Seal blown. Could not inject any more material.
IW-13				0.14	4.8	39.0	0.22	2.8	32.0	71.0	
IW-14							0.1	7.0	22.6	22.6	
IW-15	0.21	3.5	63.0							63.0	
IW-16							0.3	0.5	69.8	69.8	
IW-17	0.25	2.0	62.0							62.0	
IW-18	0.25	4.0	14.0							14.0	Seal blown. Could not inject any more material.
IW-19							0.35	0.5	71.0	71.0	
IW-20	0.2	3.5	57.0							57.0	
Totals			**375.0**			**625.0**			**380.0**	**1380.0**	

A centrifugal pump was used to pump the injection solution from the tank through a manifold system that was designed to deliver the emulsified oil/buffer solution to up to seven wells at a time. The injection system included a flow meter/totalizer upstream of the manifold, and individual flow meters and pressure gauges at each of the well heads where injections were being performed. Flow was initiated to each IW and monitored continuously for flow rate and pressure.

A total of 1,380 gal of the emulsified oil/buffer solution was injected. Each well received an average of 69 (±25) gal of the injection solution, with the total volume varying from 14 gal in IW-18 where the well seal failed, to 120 gal in IW-8 (**Table 5.2**). Once injections were complete at each well, a small volume of unamended chase water (3–5 gal of the same groundwater used in the injection solution) was added to the well to clear the injection solution from the well, and push the amendments further into the formation. The variation in injection volume per well reflected the flow rate and pressure observed at each well during the injection, which in turn was consistent with the geologic heterogeneity of the site. In general, the emulsified oil solution was added to 5–7 wells at a time using the manifold system, and the injection was planned so that adjacent wells were not amended at the same time to minimize pressure in the local aquifer. Because of the geology of the TPA, which included significant clay layers between more permeable zones, the average flow rate to the wells was generally maintained between 0.1 and 0.5 gallons per minute (gal/min). The pressure at the well head of each IW was kept <5 pounds per square inch (psi) during the injection to avoid failure of the well seals or daylighting to the surface away from the well. The emulsified oil injection in all 20 IWs was completed over 3.5 days, and provided no disruption to range activities, as the site was on standby for quarterly groundwater sampling. This time could easily be reduced at sites where the local aquifer is more conductive, and faster pumping rates could be achieved.

A second oil injection was performed after 20 months when there were indications that contaminant removal effectiveness was reduced downgradient of the biobarrier. Injection logs are shown in **Table 5.3**. For this injection, a solution containing 9.5% (v/v) EOS® 550LS was mixed in site groundwater with 0.75% (v/v) EOS® CoBupH™. The injectate was introduced into a subset of the seven centermost barrier wells (IW-5–IW-11) and IW-19, which was near the area of a planned push-pull test to be performed at the conclusion of the field demonstration. A total of 585 gal of the emulsified oil/buffer solution was injected. The total volume injected into each of the wells varied form 15 gal in IW-9 and IW-11, to 130 gal in IW-13. A small volume (2.5–17 gal) of clean chase water was injected into each well after the emulsified oil/buffer solution to move the solution further into the formation.

Table 5.3. Second Emulsified Oil Injection Logs (October 2014).



Injection Well	Average Flow Rate (gpm)	Average Injection Pressure (psi)	EOS LS/ Water Mix Injection Volume (gal.)	Chase Water Injection Volume (gal.)	Total Injection Volume (gal)	Volume of EOS LS Injected (gal.)	Volume of CoBupH Injected (gal.)
	10/07/14 - 10/08/14						
IW-5	0.2	2.5	80	5	85	7.52	0.68
IW-6	0.2	0.4	65	10	75	6.11	0.56
IW-7	0.2	2.5	130	10	140	12.22	1.11
IW-8	0.25	4.0	110	17	127	10.34	0.94
IW-9	0.015	5.0	15	2.5	17.5	1.41	0.13
IW-10	0.20	3.0	95	10	105	8.93	0.81
IW-11	0.015	5.0	15	2.5	17.5	1.41	0.13
IW-19	0.3	0.0	75	8	83	7.05	0.64
Totals			**585.0**	**65.0**	**650.0**	**55.0**	**5.0**

5.5 FIELD SAMPLING

The contaminant concentrations in the demonstration plot was monitored for 30 months, with two rounds of baseline sampling in the four months prior to oil injection, and ten round of sampling after oil injection. Sampling details are provided below.

5.5.1 Biobarrier Monitoring

Two initial rounds of baseline sampling were conducted prior to barrier installation. Once biobarrier installation was complete, ten groundwater sampling events were conducted that include all wells shown in **Figure 5.6**. The final sampling schedule is shown in **Table 5.4.**

Table 5.4. Sampling and Field Events Schedule.

YEAR	MONTH	NOTES
2012	OCT	Baseline Sampling
2013	JAN	Baseline Sampling
	FEB	Oil Injection
	MAR	Sampling
	MAY	Sampling
	JUNE	Sampling
	AUG	Sampling
	OCT	Sampling
2014	FEB	Sampling
	JUNE	Sampling
	OCT	Sampling / Oil Injection
2015	MAR	Sampling
	AUG	Sampling

5.5.2 Analysis of RDX Degrading Bacteria

Stable isotope probing (SIP) was used to distinguish key degradative microorganisms under natural conditions based upon their incorporation of stable isotope-labeled carbon (^{13}C-RDX) or nitrogen (^{15}N-RDX) from the contaminants into their nucleic acids (e.g., deoxyribonucleic acid [DNA]). Application of this technique was initially developed during SERDP Projects ER-1378 and ER-1607. The methods and data for this analysis are provided in the project final report.

5.5.3 System Shutdown and Demobilization

At the conclusion of the demonstration, the status of all piezometers was discussed with NSWCDD environmental personnel. The flush-mounted piezometers used as IWs and MWs for the biobarrier were left in place after the demonstration with concurrence from NSWCDD personnel. All other piezometers were removed or cut below ground level and the holes filed with bentonite. No other demobilization activities were required.

5.6 SAMPLING PLAN

5.6.1 Groundwater Sampling

Groundwater samples were collected by CB&I personnel utilizing low-flow purging in general accordance with USEPA Low-Flow Ground-Water Sampling Procedures (Puls and Barcelona, 1995). Prior to each sampling event, the well identification was checked and recorded on a field sheet, then groundwater elevation measurements was collected using an electronic water level probe (ORS Model #1068013 or equivalent) prior to collecting groundwater samples. Measurements were obtained from the top-of-casing and recorded to the nearest 0.01-ft in the field logbook. The tubing used to sample the wells was dedicated and, therefore, did not require decontamination.

A peristaltic pump was used to withdraw water from the wells at a flow rate of 0.1–0.5 L/min, and the water level in the well was monitored. It was desirable, although not always achievable, that the groundwater pumping led to <0.3 meters of drawdown in the well, so the pumping rate was adjusted accordingly (i.e., if drawdown was too great, the pumping rate was reduced). For some of the NSWCDD wells, drawdown was >0.3 meters, even at 0.1 L/min, due to low groundwater yield. The extent of drawdown in each well was recorded during stabilization.

The well was pumped through a flow cell connected to an in-line multi-parameter groundwater meter (e.g., Horiba Model U-22 or equivalent). Parameters, including temperature, conductivity, DO, ORP, turbidity, and pH were measured as a function of pumping time, and the values recorded on a field sheet every 5–10 minutes. Water was purged from the well until all parameters were stable for three consecutive readings. Stability was defined as a variation of <1% for pH, <3% for temperature and specific conductivity, and <10% for DO, ORP, and turbidity. When parameters were stable according to the above guidelines, sampling time was recorded and all samples were collected. Some wells produced groundwater so slowly that collection of samples occurred after the well was pumped “dry” and then allowed to refill several times. These wells also resulted in only partial collection of field parameters, as the flow cell could not effectively be filled and flushed. The final data collected on each field sheet was recorded in the project database as the measured readings in each well. All field meters were calibrated each day of sampling, and recalibrated as needed.

5.6.2 Analytical

Groundwater samples were collected and analyzed for basic field parameters, as described in Section 5.6.1, as well as the analytes listed in Table 5.5. The analytes, methods, sample bottles and preservatives are also provided in Table 5.5. Samples were collected for all analytes from all wells for all sampling events, resulting in 204 data points/analyte, excluding missing samples due to dry wells. CB&I's Analytical and Testing Laboratory in Lawrenceville, NJ, performed analysis for explosives (EPA Method 8330), perchlorate (EPA Method 314.0), anions (EPA Method 300.0[8]), VFAs (EPA Method 300.0m), TOC (SM-5310-B, -C, -D), and dissolved gases (EPA Method 3810m). An outside laboratory approved by CB&I performed analysis for target analyte list (TAL) metals (EPA Method 200.7[9]). Additional sample documentation, identification, and laboratory quality assurance (QA)/quality control (QC) procedures are provided in the project final report.

Table 5.5. Analytical Methods and Total Samples Collected during the Field Demonstration.

	Analyte	**Method/ Laboratory**	**Preservative**	**Bottle**
Process Parameters	**ORP** **DO** **pH** **Conductivity** **Temperature**	Field Meter	--	--
	Anions	EPA Method 300.0 CB&I	4°C	100 mL polyethylene screw-cap (x1)
	TOC	SM-5310-B, -C, -D CB&I	4°C with H_3PO_4	100 mL polyethylene screw-cap (x1)
	VFAs	EPA Method 300.0m CB&I	4°C	40 mL VOA vial (x2) No headspace
Target Analytes	**Explosives (RDX, HMX, nitroso intermediates)**	EPA Method 8330 CB&I (modified)	4°C Some with HCl added after arrival at laboratory	950 mL amber glass screw-cap (x2)
	Perchlorate	EPA Method 314.0 CB&I	Cellulose acetate syringe filter (0.2 µm) and 4°C	50 mL sterile polyethylene screw-cap tube (x2)
Groundwater Quality Analytes	**TAL Metals (Fe, Mn, As)**	EPA Method 200.7 External	Capsule filter, 4°C with HNO_3	100 mL polyethylene screw-cap (x1)
	Dissolved Gases (methane)	EPA Method 3810, RSK175 CB&I	4°C with HCl	40 mL VOA vial (x2) No headspace

°C – degrees Celsius, mL – milliliter(s), VOA – volatile organic analysis

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[8] https://www.epa.gov/sites/production/files/2015-08/documents/method_300-0_rev_2-1_1993.pdf.
[9] https://www.epa.gov/sites/production/files/2015-08/documents/method_200-7_rev_4-4_1994.pdf.

5.7 SAMPLING RESULTS

The primary focus of the data analyses during the demonstration was to observe both temporal and spatial trends in perchlorate and RDX concentrations (as well as HMX and breakdown products). Treatment effectiveness was measured by comparing RDX and perchlorate concentrations: (1) in each of the emulsified oil-impacted downgradient MWs before and after barrier installation, and (2) in the upgradient MW with those in the downgradient treatment zone during each respective sampling event.

Preliminary quantification of temporal and spatial (along the groundwater flow path, thereby providing an assessment of residence time on perchlorate and RDX concentrations) biodegradation rates were determined via regression analysis using a pseudo zero or first order model. Decreases of each target contaminant in each well were assessed using appropriate statistical analyses (e.g., analysis of variance [ANOVA]). Removal of RDX and perchlorate was compared to previous field demonstrations of other *in situ* remediation technologies in terms of degradation rates, half-lives, and overall percent reductions, as appropriate.

The demonstration objective was considered to be met if there were reductions in RDX and perchlorate in groundwater to <1.08 µg/L and <2 µg/L, respectively, in one or more downgradient MWs. These values correspond to the Virginia Groundwater Protection Standards for RDX and the lowest state standard for perchlorate (Massachusetts MCL). The Virginia Groundwater Protection Standard for perchlorate is 70 µg/L. Optimally, it was desired that all downgradient wells impacted by the biobarrier would reach these standards. A second standard-independent objective was an overall >95% reduction in RDX and perchlorate concentrations in the downgradient MWs between the pre-treatment to the post-treatment phases.

The mobilization of metals (Fe, Mn, As) and production of methane, and the downgradient dissipation of these compounds also was evaluated. Data for these compounds were analyzed by comparing their concentrations in each of the impacted downgradient MWs before and after barrier installation, and relative to the upgradient MW, both as a function of elapsed demonstration time and distance from the barrier. This section provides the sampling data for pH, TOC, ORP, explosives, explosive degradation products, perchlorate, and dissolved metals. The reader is referred to the project final report for the complete data for this project.

5.7.1 Oxidation Reduction Potential (ORP)

The ORP in the plot was somewhat less variable with respect to overall trends within the demonstration plot. Before the emulsified oil injection, the ORP averaged +245 ± 82 mV (n = 31) across the plot. The ORP in MW-10 upgradient of the barrier remained oxidizing at +171 ± 86 (n = 12) during the demonstration. After barrier injection, ORP values along the downgradient centerline (0–40 ft downgradient) dropped quickly, then slowly increased over time (**Figure 5.8**). ORP did vary over time at various places within the test plot. Among the in-barrier wells, ORP remained negative throughout the demonstration (-72 ± 64 mV; n = 30) (**Figure 5.9**). The average ORP along the centerline wells over the course of the entire demonstration was negative -9 ± 111 (n = 58), but with periods of positive ORP between initial injection and the second injection.

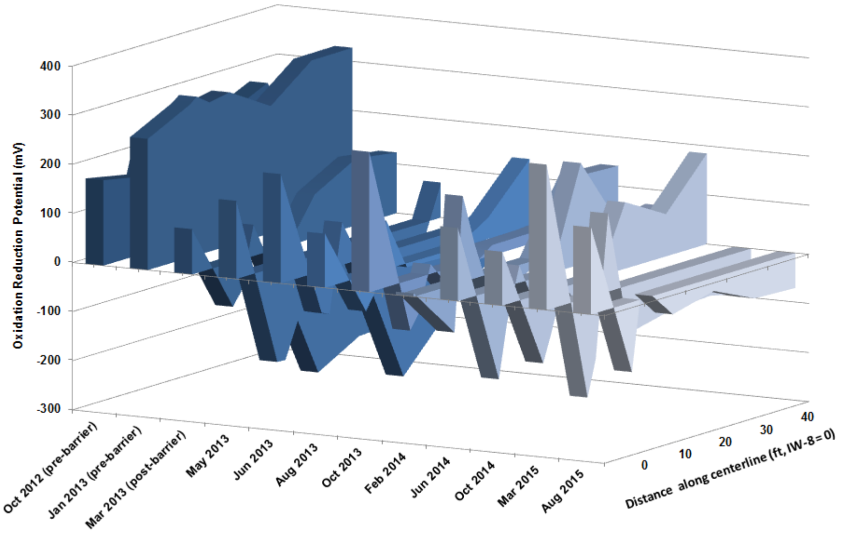

Figure 5.8. ORP along the Demonstration Plot Centerline.

Emulsified oil was re-injected after the October 2015 sampling event.

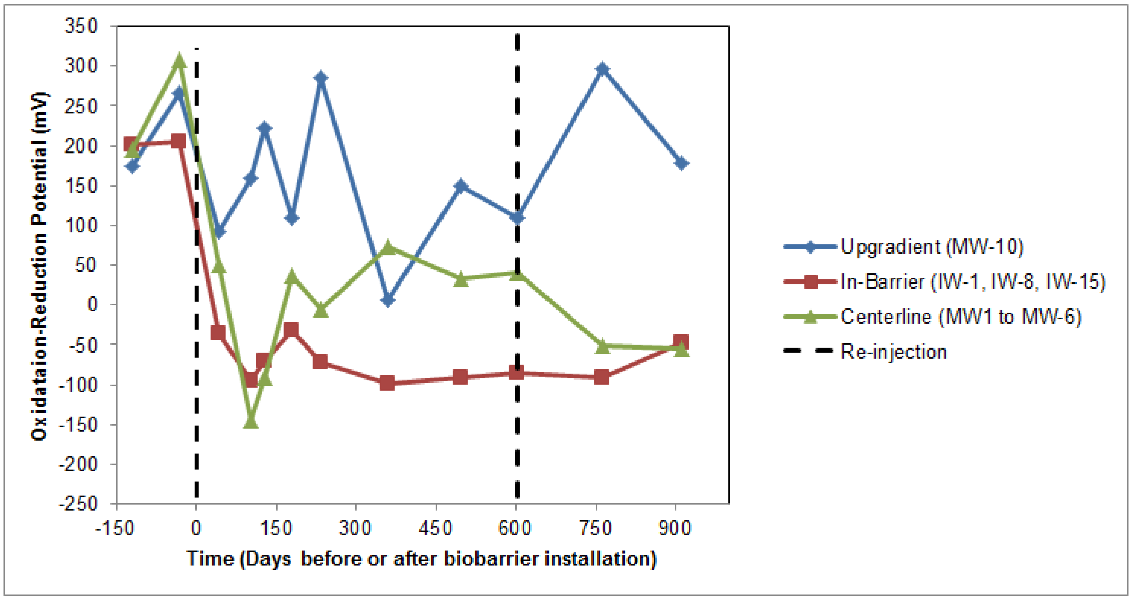

Figure 5.9. ORP over Time in the Demonstration Plot.

All upgradient, in-barrier, and centerline downgradient wells are represented.

These data support the use of emulsified oil injection to generate the reducing conditions required for both perchlorate and RDX biodegradation.

5.7.2 pH

The groundwater in the aquifer was acidic before the demonstration, with an average pH within the test plot of 4.6 ± 0.4 S.U. (n = 31). Groundwater in upgradient monitoring well MW-10, which was not impacted by the emulsified oil and buffer injection, remained acidic during the demonstration period, with an average pH of 4.6 ± 0.2 S.U. (n = 12). The pH along the centerline of the demonstration plot generally increased upon injection of the buffering agent along with the emulsified oil (**Figure 5.10**), as did the majority of the rest of the plot area. The in-barrier wells maintained a neutral pH value of 7.1 ± 1.2 S.U. (n = 30), while the centerline wells remained approximately one unit above the *in situ* pH for the duration of the demonstration (5.6 ± 0.7 S.U.; n = 58) (**Figure 5.11**).

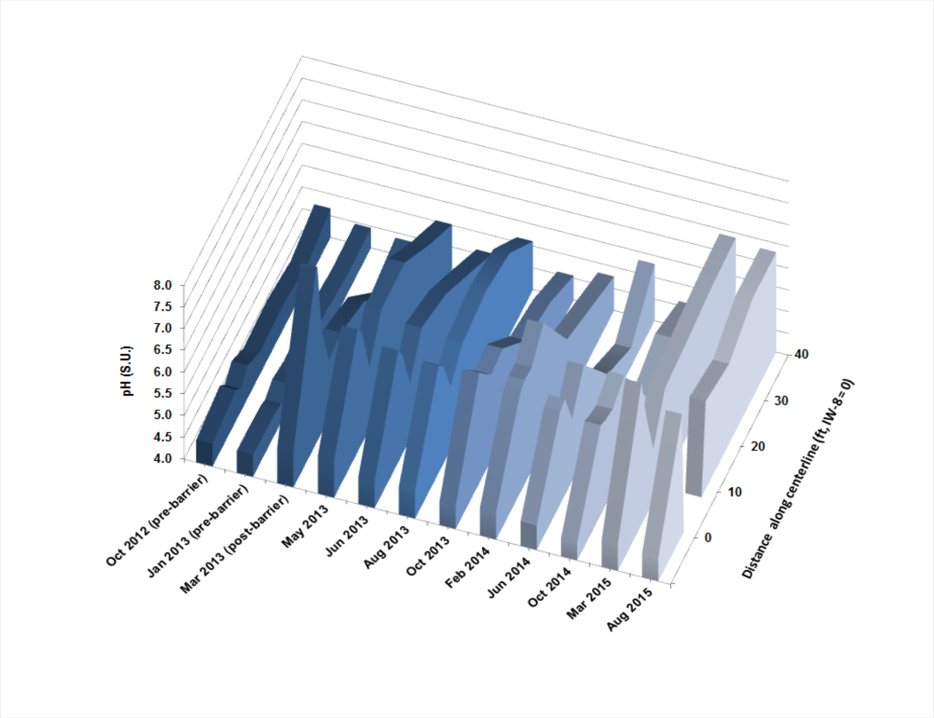

Figure 5.10. Groundwater pH along the Demonstration Plot Centerline.

Emulsified oil was re-injected after the October 2014 sampling event.

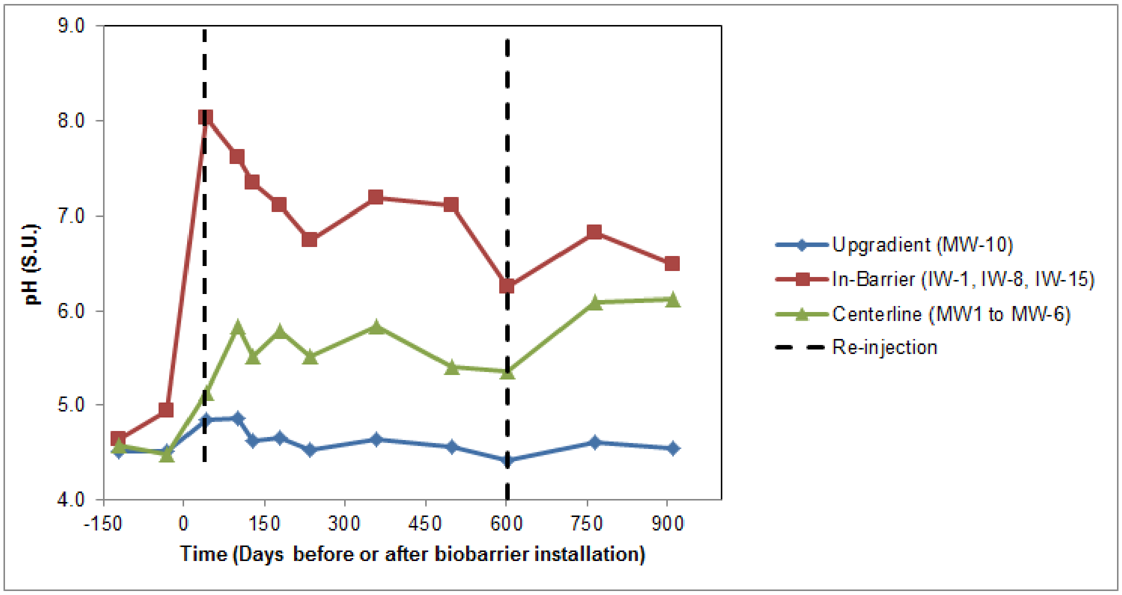

Figure 5.11. Groundwater pH over Time in the Demonstration Plot.

The upgradient, in-barrier, and centerline downgradient wells are represented.

These data indicate that inclusion of the CoBupH™ slow-release buffering agent during the barrier installation allowed elevation of the *in situ* pH to values that were conducive to perchlorate biodegradation (Wang *et al.*, 2008), and likely also led to better RDX biodegradation than what would have occurred at lower pH values.

5.7.3 Total Organic Carbon (TOC)

The average TOC in the *in situ* groundwater was 2.4 ± 0.9 mg/L (n = 32), and the upgradient well remained in this range during the demonstration (2.0 ± 0.2 mg/L, n = 12). As expected, TOC was elevated, although quite variable, in the barrier (50 ± 60 mg/L, n = 29) and along the centerline (11 ± 18 mg/L, n = 58) during the demonstration after emulsified oil injection (**Figure 5.12**).

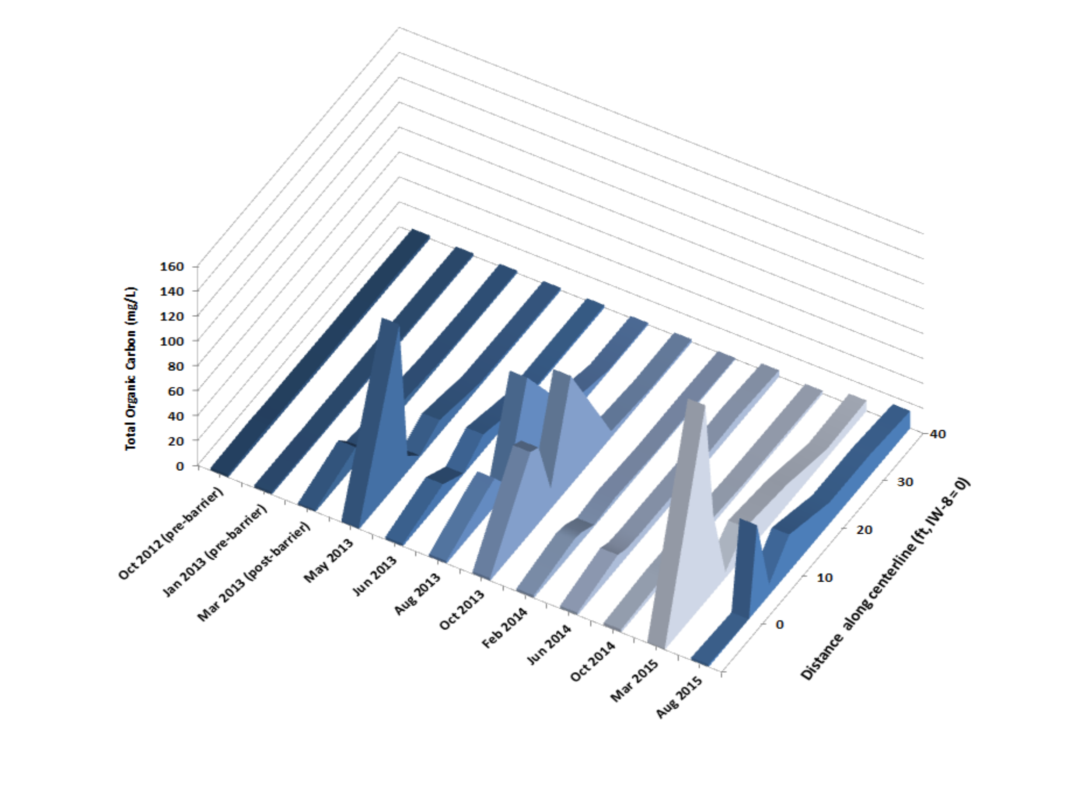

Figure 5.12. TOC in Groundwater along the Demonstration Plot Centerline.

Emulsified oil was re-injected after the October 2014 sampling event.

TOC rose and remained elevated in the in-barrier wells (**Figure 5.13**). The average TOC along the centerline also rose after the initial emulsified oil injection, but then decreased substantially to slightly above the upgradient concentrations prior to the second oil injection. As expected, a large increase in TOC was again observed after the second, more concentrated substrate injection in October 2014. During the final sampling event in August 2015, the TOC was elevated along the entire 40-ft length of centerline wells with an average concentration of 25.8 ± 21.7 mg/L (n = 6), with concentrations as high as 14 mg/L being observed 40 ft downgradient of the biobarrier.

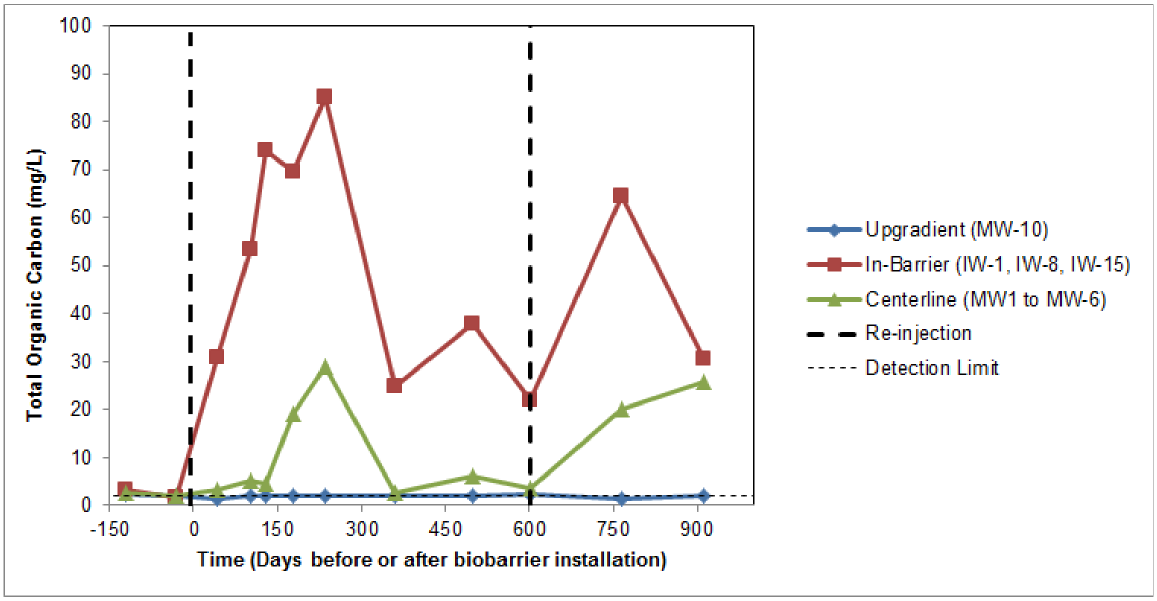

Figure 5.13. TOC in Groundwater over Time in the Demonstration Plot.

The upgradient, in-barrier, and centerline downgradient wells are represented.

5.7.4 RDX, HMX, and Metabolites

5.7.4.1 RDX and metabolite concentrations

No explosives (except RDX, RDX metabolites, and HMX) measurable by our modified EPA Method 8330 were detected at any time during the project above the detection limit (0.03 µg/L).

The concentration of RDX in the groundwater before the demonstration averaged 104 ± 29 µg/L (n = 32), and concentrations in the upgradient well remained in the same range for the duration of the study (105 ± 26, n = 12). Concentrations of the RDX breakdown products hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) were <0.5 µg/L before the emulsified oil injection and in the upgradient well for the duration of the demonstration.

Upon emulsified oil injection, RDX concentrations decreased significantly downgradient of the biobarrier (**Figure 5.14**), with a degradation “front” slowly moving down the centerline of the plot. A rebound in concentrations was observed before the second emulsified oil injection. The average in-barrier RDX concentration after emulsified oil injection was 15 ± 19 µg/L (n = 30), whereas the centerline concentration averaged 22 ± 24 µg/L (n = 58). RDX concentrations in the upgradient, in-barrier, and centerline downgradient wells are presented in **Figure 5.15**.

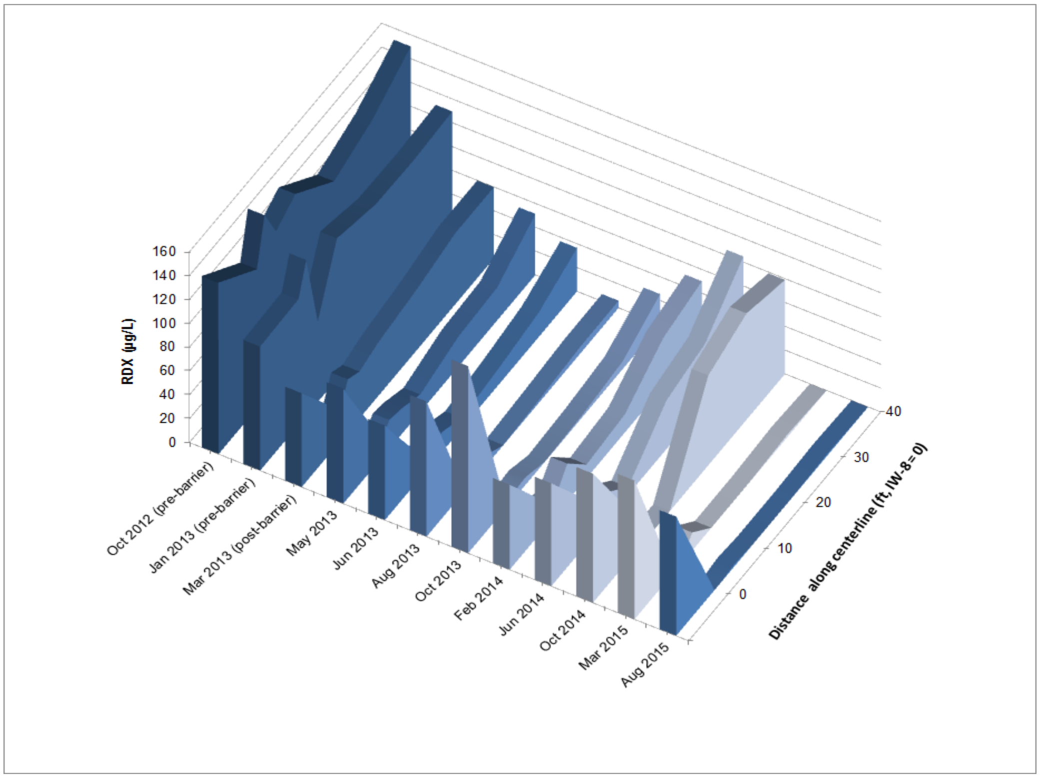

Figure 5.14. RDX along the Centerline of the Demonstration Plot.

Emulsified oil was re-injected after the October 2014 sampling event.

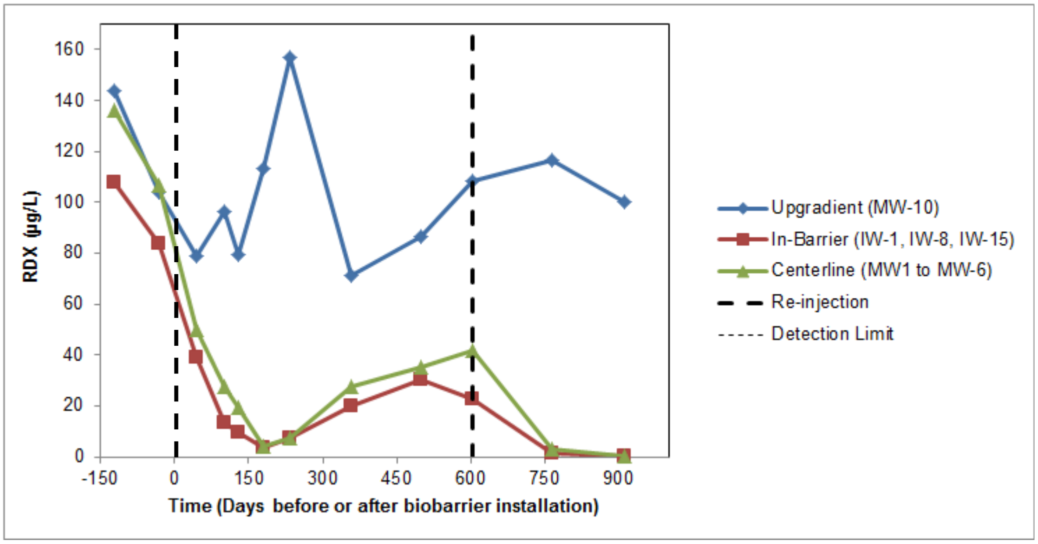

Figure 5.15. RDX Concentrations Groundwater over Time in the Barrier and along the Centerline.

The upgradient, in-barrier, and centerline downgradient wells are represented.

The RDX removal averaged 83 ± 17% for the in-barrier wells and 75 ± 21% for the centerline wells from the first emulsified oil injection to the end of the demonstration. However, these averages include periods of time when the TOC from the emulsified oil injection(s) was depleted with a subsequent and expected increase in RDX in downgradient wells. When TOC was present and adequate time was allowed for degradation to occur, RDX concentrations reached extremely low levels in the centerline wells. For example, during October 2013, approximately eight months after the initial oil injection, the RDX within the barrier to a distance of 30 ft downgradient ranged from <0.03 to 6 µg/L. RDX removal in these wells was >94%. Similarly, in August 2015, ten months after the second emulsified oil injection, RDX concentrations along the centerline wells ranged from <0.03 µg/L (5/7 wells) to 2 µg/L (2 wells) as far as 40 ft downgradient of the barrier, with removal percentages >98%. These data indicate this technology was highly effective for RDX removal when appropriate biogeochemical conditions were achieved in the aquifer.

The RDX metabolite concentrations over time are presented in **Figure 5.16**. As expected, MNX, DNX, and TNX increased as RDX degraded in response to the initial and secondary emulsified oil injections, and conversely decreased as RDX degradation slowed. The average concentration of MNX, DNX, and TNX within the barrier over the duration of the demonstration averaged 2.7 ± 3.6 µg/L (n = 30), 1.7 ± 1.8 µg/L (n = 30), and 5.4 ± 8.9 µg/L (n = 30), respectively. The corresponding values along the centerline were 2.6 ± 3.2 µg/L (n = 58), 1.2 ± 1.8 µg/L (n = 58), and 4.2 ± 8.2 µg/L (n = 58), respectively. The trends indicate that the nitroso metabolites were being produced in measurable—though clearly not stoichiometric—concentrations, and were also being further transformed, degraded, or otherwise attenuated, and therefore not expected to be present at any appreciable concentration further downgradient. To that end, during the final sampling event of the demonstration in August 2015, MNX, DNX, and TNX were below detection (<0.08 µg/L) in 11 of the combined in-barrier and downgradient wells, and were present at a maximum of 1.1 µg/L in the remaining 4 wells that had detectable intermediates. The results, therefore, suggest that the RDX ring structure was being broken during biodegradation, leading to non-toxic or otherwise labile products (Crocker *et al.*, 2006; Halasz and Hawari, 2011).

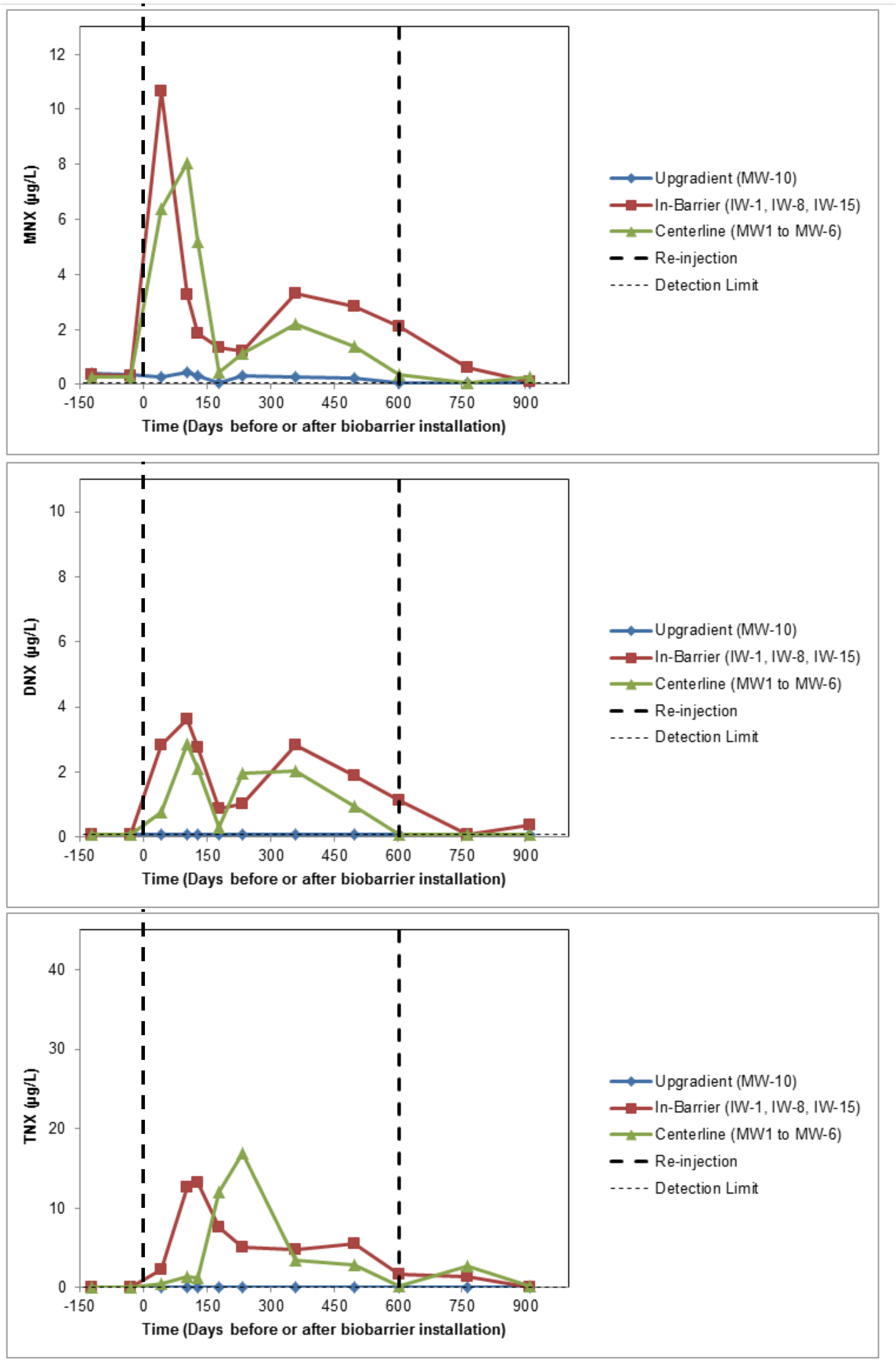

Figure 5.16. RDX Metabolite Concentrations in Groundwater over Time in the Barrier and along the Centerline.

The upgradient, in-barrier, and centerline downgradient wells are represented.

5.7.4.2 RDX degradation rates

Pseudo-first order degradation rates were calculated using the estimated horizontal flow velocity in this area of approximately 0.059 ft/d to convert distance in the demonstration plot to residence or travel time. For instance, the first monitoring well, MW-1, was located 2.5 ft from the barrier. This equates to a 42-day residence time. For the in-barrier wells, a 2-ft zone of influence of the injected emulsified oil was assumed, resulting in a residence time of 34 days. The concentration difference between the upgradient well (MW-10) and each location within the plot at each time point was calculated (µg/L), and this value was divided by the residence time, resulting in a pseudo-first order degradation rate with units of µg/L/d.

Using the methodology described above, the RDX degradation rates over time were calculated. While the rates varied by location within the demonstration plot, they appeared to fluctuate within a moderately narrow range, especially in the latter half of the demonstration and in wells 5 ft or greater downgradient from the barrier. Rates increased significantly after the initial emulsified oil injection, and also after the second injection, although to a lesser degree and more so in the wells closest to the barrier. The average degradation rate in the in-barrier wells was 2.5 ± 1.1 µg/L/d (n = 30), while the average rate along the centerline was 0.4 ± 0.4 µg/L/d (n = 58).

The most relevant comparison to this demonstration was a passive mulch biowall evaluated for treatment of RDX at the Pueblo Chemical Depot (Newell, 2008). No rates were calculated, but >93% removal was observed, down to concentrations <0.5 µg/L. These results are similar to those observed during this demonstration.

Two previous semi-passive anaerobic biostimulation demonstrations—one at the Picatinny Arsenal (using cheese whey as the electron donor) and one at the Nebraska Ordnance Plant (using acetate as the electron donor)—did not calculate RDX degradation rates, but reported >95% reductions in RDX concentration (Hatzinger and Lippincott, 2012; Wade *et al.*, 2010), and degradation to <1 µg/L, again similar to this demonstration.

Anaerobic RDX biodegradation assessed via push-pull testing yielded rates of approximately 10–20-fold higher at the Umatilla Chemical Depot (0.7–1.1 ft/d), albeit much more labile fructose was used as the electron donor (Michalsen, 2015; Michalsen *et al.*, 2013). This type of approach would not be viable on an active range due to the rapid consumption of this soluble substrate and necessity for frequent reinjection.

5.7.4.3 HMX concentrations

The concentration of HMX in the groundwater before the demonstration averaged 15 ± 5 µg/L (n = 32), and concentrations in the upgradient well remained in the same range for the duration of the study (17 ± 3 µg/L, n = 12). HMX concentrations decreased significantly downgradient of the biobarrier after emulsified oil injection (**Figure 5.17**), with a degradation “front” slowly moving down the centerline of the plot. A rebound in concentrations was observed before the second emulsified oil injection. The average in-barrier HMX concentration after emulsified oil injection was 3 ± 3 µg/L (n = 30), whereas the centerline concentration averaged 6 ± 5 µg/L (n = 58). HMX concentrations in the upgradient, in-barrier, and centerline downgradient wells over time are presented in **Figure 5.18**.

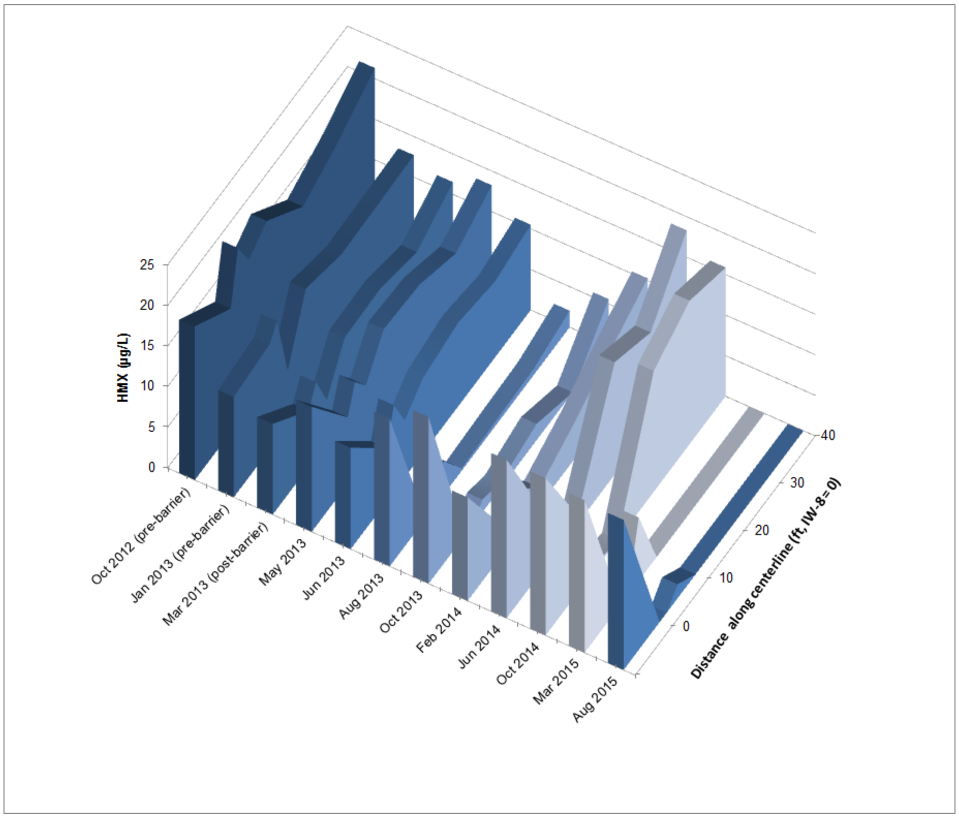

Figure 5.17. HMX along the Centerline of the Demonstration Plot.

Emulsified oil was re-injected after the October 2014 sampling event.

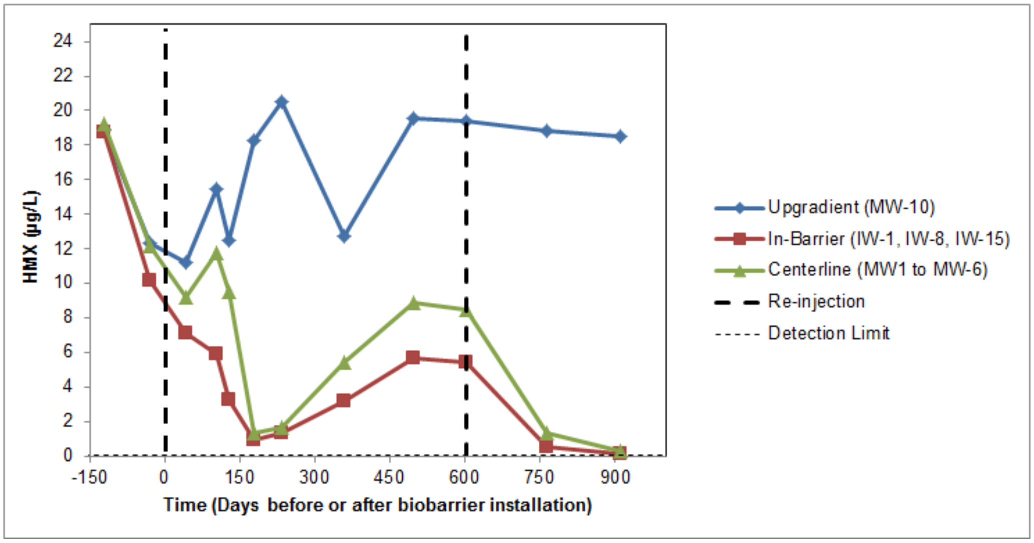

Figure 5.18. HMX Concentrations in Groundwater over Time.

The upgradient, in-barrier, and centerline downgradient wells are represented.

HMX removal was slightly lower than RDX removal, averaging 77 ± 20% for the in-barrier wells and 61 ± 32% for the centerline wells from the first emulsified oil injection to the end of the demonstration. However, as noted for RDX, during periods with sufficient TOC, low HMX concentrations were achieved in the centerline wells. For example, during August 2013, approximately six months after the initial oil injection, the HMX within the barrier to a distance of 40 ft downgradient ranged from <0.03 to 4 µg/L with an average of 1.2 µg/L. Similarly, in August 2015, ten months after the second emulsified oil injection, HMX concentrations along the centerline wells ranged from <0.03 µg/L (6/7 wells) to 2 µg/L (1 well) as far as 40 ft downgradient of the barrier. These data indicate this technology was also highly effective for HMX removal, when appropriate biogeochemical conditions were achieved in the aquifer.

5.7.4.4 HMX degradation rates

The same methodology as was used for RDX was employed to determined pseudo-first order degradation rates for HMX. As with RDX, the rates varied by location within the demonstration plot, but fluctuated within a moderately narrow range. Rates increased in response to the emulsified oil injections. The average degradation rate in the in-barrier wells was 0.4 ± 0.2 µg/L/d (n = 30), while the average rate along the centerline was 0.1 ± 0.1 µg/L/d (n = 58). Taking the average rates from all wells downgradient from MW-10 yields an HMX degradation rate of 0.1 ± 0.2 µg/L/d (n = 148).

Comparable performance for HMX treatment was observed using the passive mulch biowall at the Pueblo Chemical Depot (Newell, 2008) and semi-passive anaerobic biostimulation at the Picatinny Arsenal cited above (Hatzinger and Lippincott, 2012; Wade *et al.*, 2010). Degradation rates and half-lives were not calculated in these previous studies.

5.7.5 Perchlorate

5.7.5.1 Perchlorate concentrations

The concentration of perchlorate in the groundwater before the demonstration averaged 36 ± 11 µg/L (n = 32), and concentrations in the upgradient well remained in the same range for the duration of the study (34 ± 5 µg/L, n = 12). The first injection of emulsified oil resulted in rapid decreases in perchlorate concentrations downgradient of the biobarrier (**Figure 5.19**). Concentrations increased somewhat before the second emulsified oil injection. The average in-barrier perchlorate concentration after emulsified oil injection was 3 ± 4 µg/L (n = 30), whereas the centerline concentration averaged 9 ± 12 µg/L (n = 58). Perchlorate concentrations in the upgradient, in-barrier, and centerline downgradient wells are presented in **Figure 5.20**.

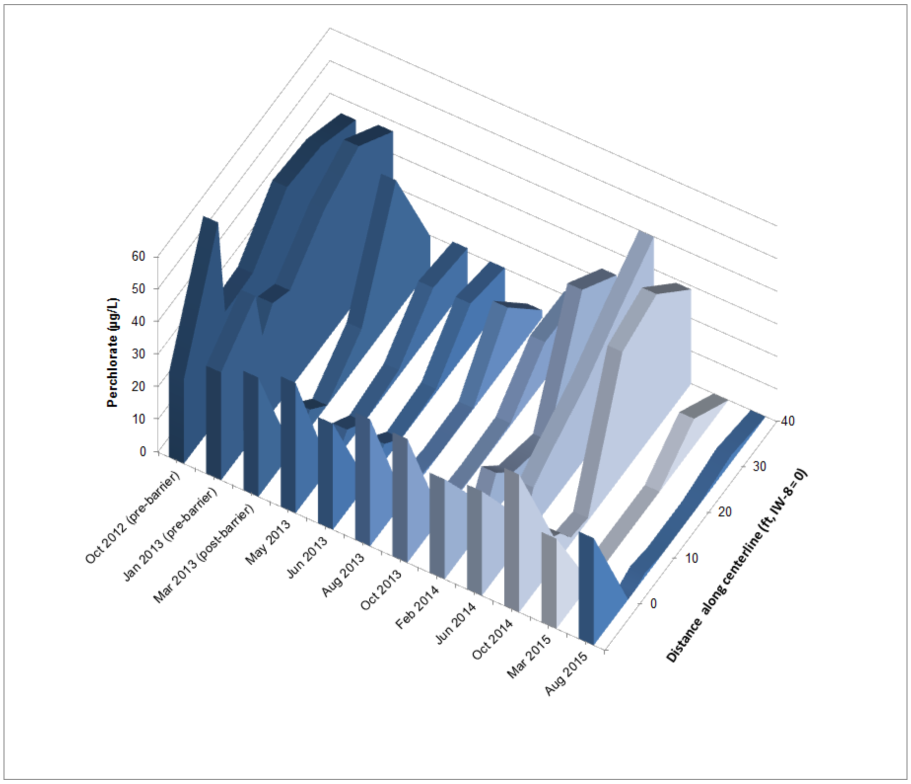

Figure 5.19. Perchlorate Concentration along the Centerline of the Demonstration Plot.

Emulsified oil was re-injected after the October 2014 sampling event.

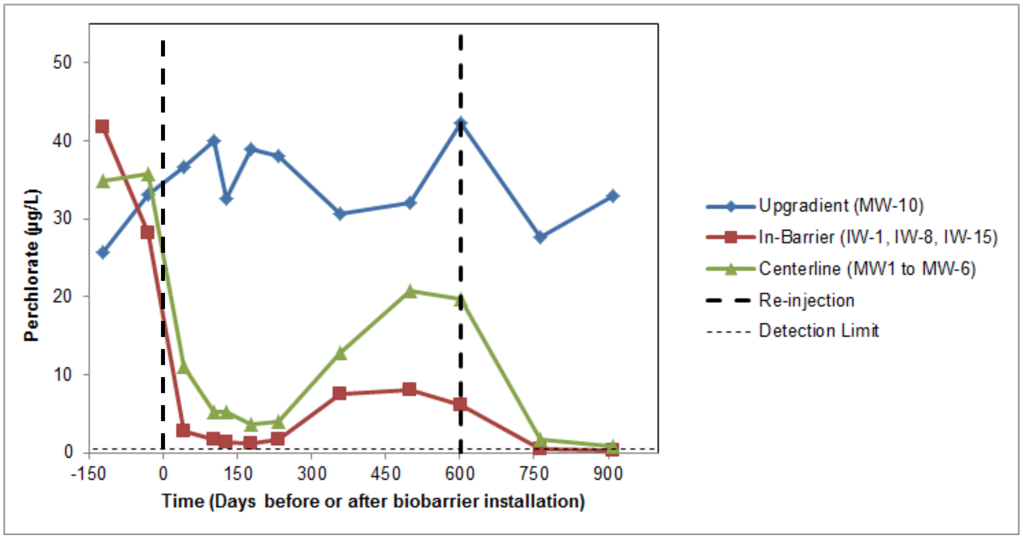

Figure 5.20. Perchlorate Concentrations in Groundwater over Time.

The upgradient, in-barrier, and centerline downgradient wells are represented.

Perchlorate removal was greater than both RDX and HMX, with 91 ± 9% removal in the barrier wells, and was comparable to total RDX removal along the centerline at 76 ± 21% from the first emulsified oil injection to the end of the demonstration. During periods with sufficient TOC, low perchlorate concentrations were achieved in the centerline wells. For example, during August 2013, approximately six months after the initial oil injection, the perchlorate within the barrier to a distance of 40 ft downgradient ranged from <0.5 µg/L (4 wells) to 17.2 µg/L (1 well) with an average of 3.2 µg/L. Similarly, in August 2015, ten months after the second emulsified oil injection, perchlorate concentrations along the centerline wells ranged from <0.5 µg/L (5/7 wells) to 2.2 µg/L (1 well) as far as 40 ft downgradient of the barrier, with an average concentration of 0.9 µg/L. These results demonstrate that this passive biobarrier approach is highly effective for removal of both perchlorate and nitramine explosives, when appropriate biogeochemical conditions were achieved in the aquifer.

5.7.5.2 Perchlorate degradation rates

The same methodology used for RDX and HMX was employed to determined pseudo-first order degradation rates for perchlorate. Perchlorate degradation rates increased after the initial emulsified oil injection, but did not seem to be appreciably affected by the second injection. The average degradation rate in the in-barrier wells was 1 ± 0.2 µg/L/d (n = 30), while the average rate along the centerline was 0.2 ± 0.2 µg/L/d (n = 58). The average rate from all downgradient wells was 0.3 ± 0.4 µg/L/d (n = 148).

Emulsified oil in a permeable reactive barrier (PRB) was examined previously for comingled chlorinated solvents and perchlorate (Borden *et al.*, 2002). Removal >95% was observed, but no rates were reported. Similarly, *in situ* anaerobic biostimulation for perchlorate was demonstrated at the Aerojet Superfund Site in Sacramento, CA (Geosyntech, 2002). A perchlorate half-life of 0.5–1.2 days was reported. The shorter half-life compared to the demonstration may be due to the use of ethanol as the electron donor, compared to emulsified oil in the present demonstration. Anaerobic biostimulation was also demonstrated at Aerojet General Corporation using citrate as the electron donor (Hatzinger and Diebold, 2009). No rates were reported, but removal of approximately 89% of the perchlorate was observed in the treatment area—comparable to the passive emulsified oil biobarrier.

5.7.6 Dissolved Metals

Dissolved Fe, Mn, and As in the site groundwater prior to the demonstration averaged 188 ± 420 µg/L (n = 32), 22 ± 26 µg/L (n=32), and 3 ± 1 µg/L (n = 32), respectively. Upgradient concentrations in well MW-10 remained relatively stable during the demonstration, averaging 3 ± 1 µg/L (n = 12) for As, 38 ± 48 µg/L (n = 12) for Fe, and 7 ± 3 µg/L (n = 12) for Mn.

Dissolved metals increased in response to the reducing conditions resulting from the emulsified oil injections, and were moderately variable from well to well and at each time point. Dissolved Fe, Mn, and As over time are presented in **Figure 5.21, Figure 5.22**, and **Figure 5.23**, respectively. Dissolved Fe increased approximately 100-fold, averaging 16,348 ± 16,064 µg/L (n = 29) in the in-barrier wells, and 21,453 ± 25,714 µg/L (n = 58) in the centerline wells. Dissolved Mn concentrations did not increase as much as Fe, with in-barrier wells rising to 41 ± 53 µg/L (n = 29), and centerline wells rising to 35 ± 50 µg/L (n = 58).

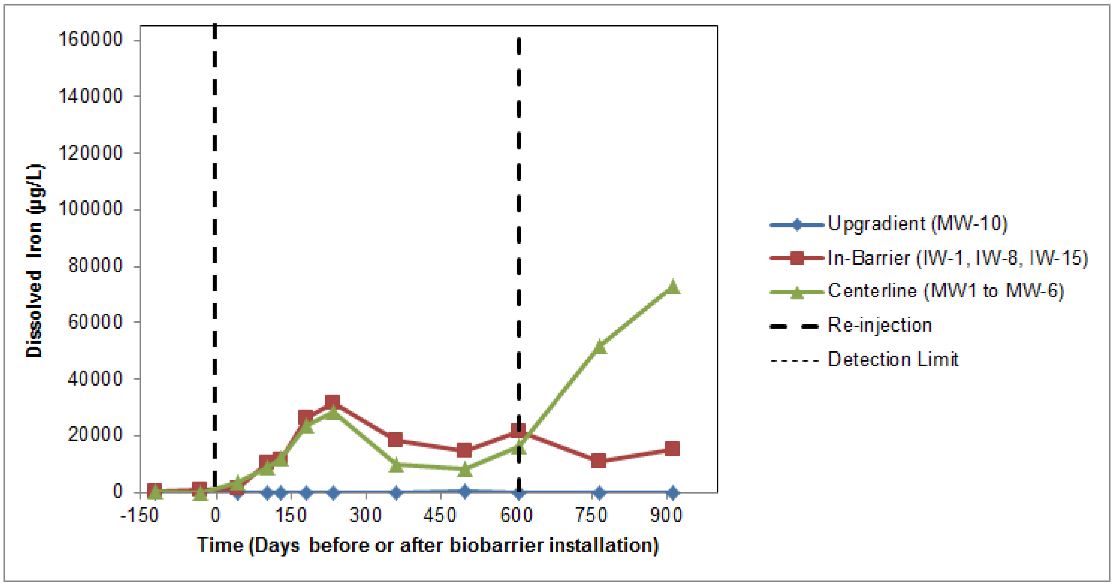

Figure 5.21. Dissolved Iron (Fe) Concentrations over Time.

The upgradient, in-barrier, and centerline downgradient wells are represented.

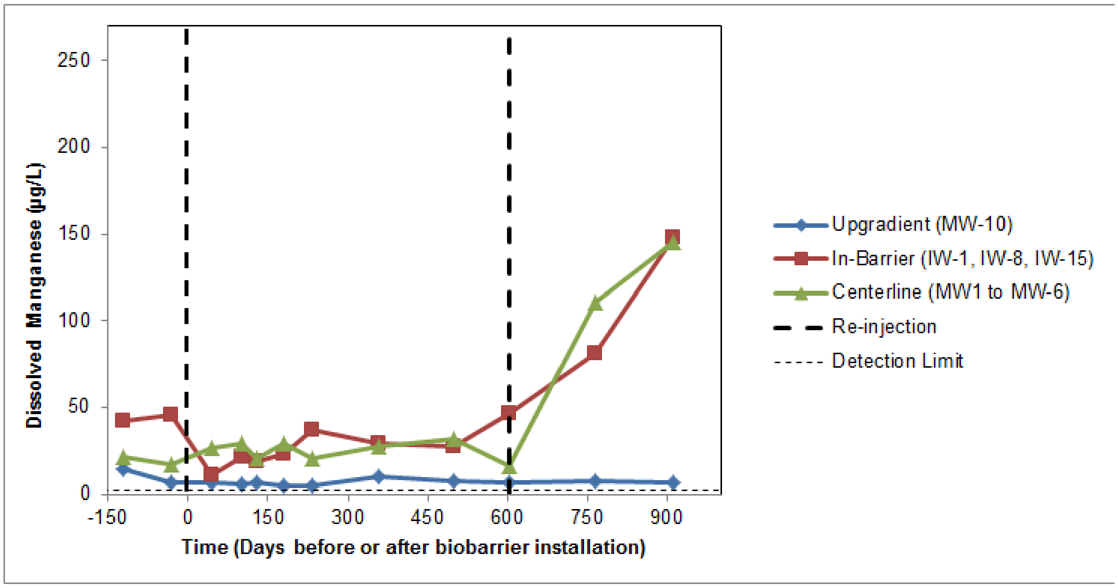

Figure 5.22. Dissolved Manganese (Mn) Concentrations over Time.

The upgradient, in-barrier, and centerline downgradient wells are represented.

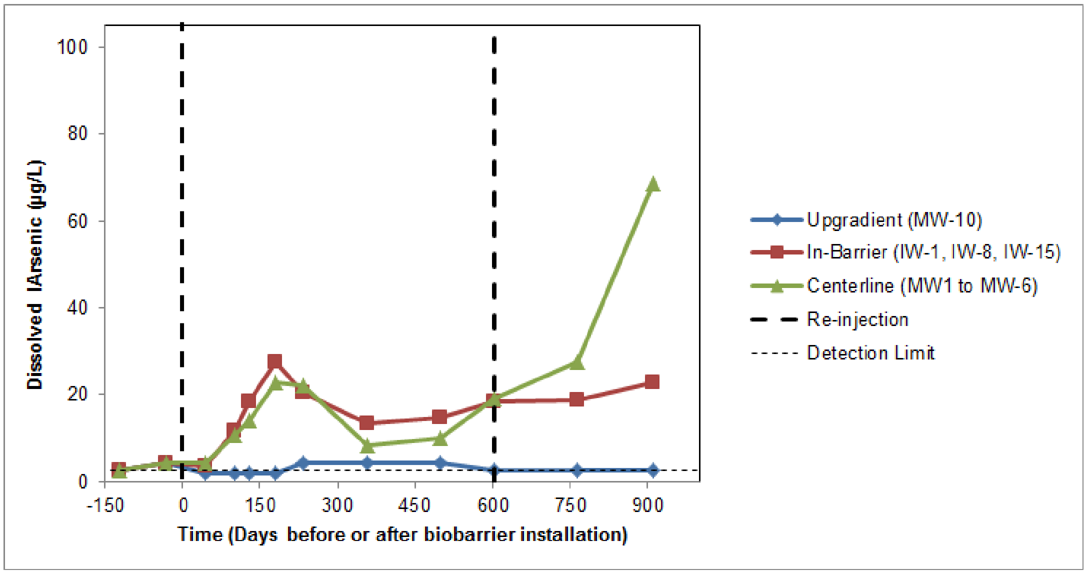

Figure 5.23. Dissolved Arsenic (As) Concentrations over Time.

The upgradient, in-barrier, and centerline downgradient wells are represented.

Dissolved As increased in the in-barrier wells to 17 ± 9 µg/L (n = 29), and in the centerline wells to 20 ± 22 µg/L (n = 58). This represents an approximately 5- to 6-fold increase over pre-demonstration concentrations. These concentrations would be expected to return to background levels downstream of the demonstration plot as the groundwater re-aerates, causing the dissolved As to oxidize and precipitate, likely forming highly insoluble mineral phases with Fe.

The most significant increase in each of the dissolved metals occurred after the second injection of emulsified oil, when a more concentrated solution was applied. This is consistent with the stimulation of higher rates of Fe and Mn reduction in the local aquifer. As in most applications where high levels of TOC are added to an aquifer, some mobilization of metals is to be expected. However, attenuation of all of these metals is anticipated downgradient as groundwater re-oxygenates.

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6.0 PERFORMANCE ASSESSMENT

6.1 PERFORMANCE OBJECTIVES

The performance objectives for this demonstration are summarized in **Table 6.1.** Detailed assessments of each performance objective are provided in **Sections 6.2** through **6.6**.

Table 6.1. Performance Objective Assessment.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Effectiveness of RDX treatment	Pre- and post-treatment contaminant concentrations in groundwater wells using EPA Method 8330.	• Reduction in downgradient groundwater in one or more MW(s) to <1.08 µg/L	**SUCCESS** • Wells as far as 40 ft from the barrier achieved RDX <1.08 µg/L at some point post-injection • Also achieved HMX <1.08 µg/L to 40 ft downgradient at some time points
		• Overall downgradient RDX reduction >95%	**PARTIAL SUCCESS** • In-barrier wells reached >95% reduction in RDX 50% of the demonstration period and >99% reduction for 43% of the demonstration period • The averaged centerline wells (from 2.5 to 40 ft downgradient) achieved >95% reduction in RDX for 35% of the demonstration • Similar removal percentages for HMX
		• Statistical comparison: - Pre- and post-barrier installation - Upgradient versus downgradient MWs	**SUCCESS** • Over demonstration duration, upgradient RDX concentrations were statistically higher than RDX concentrations in the in-barrier wells, and in the centerline wells at the - P <0.0001 • Upgradient RDX was statistically higher than RDX detected 40 ft downgradient (P <0.005)

Table 6.1. Performance Objective Assessment (Continued).

Performance Objective	Data Requirements	Success Criteria	Results
Effectiveness of perchlorate treatment	Pre- and post-treatment contaminant concentrations in groundwater wells using EPA Method 314.0.	• Reduction in one or more downgradient MWs to <2 µg/L	**SUCCESS** • Wells as far as 40 ft from the barrier achieved perchlorate <2 µg/L at some point post-injection
		• Overall downgradient perchlorate reduction >95%	**PARTIAL SUCCESS** • In-barrier wells reached >95% reduction in perchlorate 60% of the demonstration period • centerline wells (from 2.5 to 40 ft downgradient) achieved >95% reduction in perchlorate for 48% of the demonstration
		• Statistical comparison: - Pre- and post-barrier installation - Upgradient versus downgradient MWs	**SUCCESS** • Over demonstration duration, upgradient perchlorate concentrations were statistically higher than perchlorate concentrations in the in-barrier wells, and in the centerline wells at the - P <0.0001 significance • Upgradient perchlorate was statistically higher than perchlorate detected 40 ft downgradient - (P <0.005)[1]
Distribution of emulsified oil	Measurement of TOC	• TOC elevated in monitoring wells 2.5 ft and 5 ft downgradient	**SUCCESS** • TOC was greater than the background levels at 2.5 ft and 5 ft downgradient 100% and 90% of the demonstration period, respectively • Additionally, elevated TOC was detected 40 ft downgradient
Geochemical changes to create conditions necessary for contaminant degradation	Measurements of DO	• DO <1 mg/L in all treatment wells	**SUCCESS** • DO levels <1 mg/L were measured in all treatment wells out to 40 ft downgradient more than 40% of the demonstration period • DO was <1 mg/L at 2.5 ft and 5 ft downgradient 89% and 54% of the demonstration period, respectively
	Measurements of ORP	• ORP <-100 mV in all treatment wells	**SUCCESS** • ORP levels <-100 mV were detected in all treatment wells out to 30 ft downgradient at various time points during the demonstration

Table 6.1. Performance Objective Assessment (Continued).

Performance Objective	Data Requirements	Success Criteria	Results
Longevity of biobarrier	Measurement of TOC	• Elevated TOC for two years after installation	**PARTIAL SUCCESS** • TOC levels above the background were observed in the in-barrier wells after the first injection, but TOC in most downgradient wells declined toward background. Emulsified oil was reinjected after 600 days to increase downgradient TOC
	RDX concentrations in groundwater wells using EPA Method 8330.	• RDX below Virginia Groundwater Protection Standard of 1.08 µg/L for two years after installation	**PARTIAL SUCCESS** • One in-barrier well had RDX below the protection standard for more than two years. Three additional wells met the standard at least once during the first two years.
	Perchlorate concentrations in groundwater wells using EPA Method 314.0.	• Perchlorate below Virginia Groundwater Protection Standard of 2 µg/L for two years after installation	**PARTIAL SUCCESS** • Two wells had perchlorate below the protection standard for more than two years. Seven additional wells met the standard at least once during the first two years.
Qualitative Performance Objectives			
Barrier Installation	Total time for installation feedback from field technician	• <5 days for barrier installation	**SUCCESS** • Combined time for IW emplacement and emulsified oil injection was <5 days
	Maintenance logs and time	• Minimal maintenance costs	**SUCCESS** • No maintenance costs for IWs once emplaced • Initial and second EOS costs were minimal

[1] The statistical significance for well MW-5 (30 ft downgradient) was P = 0.0781, while that for well MW-6 (40 ft downgradient) was P = 0.0016.

6.2 EFFECTIVENESS OF RDX AND PERCHLORATE TREATMENT

The effectiveness of the biobarrier technology for groundwater remediation was a function of the degree to which RDX and perchlorate concentrations decreased. Remediation success depended on the residual contamination during and after application of the treatment remedy. The overall duration of the biobarrier performance was also of interest and was quantified via extended testing.

6.2.1 RDX Treatment

Criteria: Reduce RDX concentrations to <1.08 µg/L in at least one downgradient well.

Assessment: Success

RDX was degraded to below the 1.08 µg/L performance criterion in multiple in-barrier and downgradient wells during the demonstration. A total of 26 samples out of the 160 samples (16%) collected from the in-barrier and downgradient wells after the initial emulsified oil injection had RDX <1.08 µg/L. For the in-barrier wells, 13 out of 30 samples (43%) met the RDX criteria, while along the centerline (2.5–40 ft downgradient) 12 out of 60 samples (20%) met the RDX criteria.

While not a formal performance goal, HMX was degraded to below the 1.08 µg/L in multiple in-barrier and downgradient wells during the demonstration. A total of 40 samples out of the 160 samples (25%) collected from the in-barrier and downgradient wells following the initial emulsified oil injection had HMX <1.08 µg/L. For the in-barrier wells, 13 out of 30 samples (43%) had HMX <1.08 µg/L, while along the centerline (2.5–40 ft downgradient) 19 out of 60 samples (32%) had HMX <1.08 µg/L. At the final sampling event in August 2015, all of the in-barrier wells and 5/6 centerline wells had HMX <1.08 µg/L.

Criteria: Overall reduction of RDX concentrations by 95% downgradient of barrier compared to upgradient concentrations.

Assessment: Partial Success

In-barrier wells reached >95% reduction in RDX for 50% of the demonstration period and >99% reduction for 43% of the demonstration period. The averaged centerline wells (from 2.5 to 40 ft downgradient) achieved >95% reduction in RDX for 35% of the demonstration. At the final sampling event in August 2015, all of the in-barrier and centerline MWs had RDX reductions >95%. Similar removal percentages were observed for HMX.

Criteria: Statistically significant difference in RDX concentrations upgradient versus downgradient of the barrier.

Assessment: Success

One-way ANOVA, with Fishers Least Significant Difference post-hoc) comparing the RDX concentrations in upgradient well MW-1 to in-barrier, centerline, and various groupings of downgradient wells was conducted. Over the course of the demonstration, upgradient RDX concentrations were statistically higher than RDX concentrations in the in-barrier wells, and in the centerline wells ($P < 0.0001$). Upgradient RDX was statistically higher than RDX detected 40 ft downgradient ($P < 0.005$). The same general trends were observed for HMX, with upgradient concentrations statistically higher than downgradient concentrations ($P < 0.0001$). Full statistical results are provided in the project final report.

6.2.2 Perchlorate Treatment

Criteria: Reduce perchlorate concentrations to <2 µg/L in at least one downgradient well.

Assessment: Success

As with RDX, multiple wells achieved the 2 µg/L perchlorate level during the demonstration.

A total of 60 samples out of the 159 samples (38%) collected from the in-barrier and downgradient wells after the initial emulsified oil injection had perchlorate <2 µg/L. For the in-barrier wells, 17 out of 29 samples (59%) met the perchlorate criteria, while along the centerline (2.5–40 ft downgradient), 29 out of 60 samples (48%) met the success criteria.

Criteria: Overall reduction of perchlorate concentrations by 95% downgradient of barrier compared to upgradient concentrations.

Assessment: Partial Success

In-barrier wells reached >95% reduction in perchlorate during 60% of the demonstration period. The averaged centerline wells (from 2.5 to 40 ft downgradient) achieved >95% reduction in perchlorate during 48% of the demonstration.

Criteria: Statistically significant difference in perchlorate concentrations upgradient versus downgradient of the barrier.

Assessment: Success

One-way ANOVA, with Fishers Least Significant Difference post-hoc) comparing the perchlorate concentrations in upgradient well MW-1 to in-barrier, centerline, and various groupings of downgradient wells was conducted. These data are provided in the project final report. Over the demonstration duration, upgradient perchlorate concentrations were statistically higher than perchlorate concentrations in the in-barrier wells, and in the centerline wells at the $P < 0.0001$. Upgradient perchlorate concentrations were statistically higher than perchlorate detected 40 ft downgradient ($P < 0.005$). The only outlier was well MW-5 (30 ft downgradient), for which the statistical significance was slightly higher at $P = 0.0781$. Full statistical results are provided in the project final report.

6.2.3 Overall Assessment for RDX and Perchlorate Treatment

Overall, the demonstration successfully met the performance objectives for RDX and perchlorate treatment. Successful treatment of HMX was also observed. The plumes were essentially cutoff by the 100-ft emulsified oil barrier. The biodegradation of RDX and perchlorate in one area downgradient of the barrier (on the northeast side), constituting wells MW-8, MW-9, PZ-19, and PZ-30, was slower and perchlorate and RDX did not reach the low concentrations observed in other wells. TOC increased in these wells, but generally, ORP values did not decrease as significantly as in the other wells. It is possible that these wells were partially screened in an interval that was not connected to the upgradient IWs, and thus the sampled groundwater represented a mixture of treated and untreated water. This would be consistent with the complex geology at this location.

6.3 ADEQUATE DISTRIBUTION OF EMULSIFIED OIL

Homogeneous oil distribution is important to the success of biobarrier approach for RDX and perchlorate treatment.

6.3.1 Data Requirements for Oil Distribution

The distribution of emulsified oil was quantified by measuring TOC increases in the wells installed within the biobarrier. In addition, both TOC and VFAs (breakdown products of emulsified oil) were measured in downgradient MWs. Comparison of TOC levels before and after emulsified oil injection, and in upgradient and downgradient wells, was performed. Particular attention was focused on the wells immediately adjacent to the barrier, 2.5 ft and 5 ft downgradient.

6.3.2 Success Assessment for Oil Distribution

Elevated TOC above background levels was observed out to 40 ft downgradient. Summary results are below.

***TOC Distribution*.**

Criteria: Observe elevated TOC in downgradient wells.

Assessment: Success

The samples collected after emulsified oil injection indicated that 69% of the wells had TOC levels above the background concentration (conservatively set to 2.5 mg/L). In-barrier wells had elevated TOC levels in 97% of collected samples, whereas centerline wells had elevated TOC in 68% of collected samples. Elevated TOC was detected as far out as 40 ft downgradient from the barrier along the centerline.

***VFA Detection*.**

Of all samples collected after emulsified oil injection, 37% exhibited acetate >2 mg/L. For in-barrier and centerline wells, the percentage of samples with acetate concentrations >2 mg/L was 70% and 37%, respectively. Acetate was detected above background levels (e.g., >2 mg/L) at least 20 ft downgradient of the barrier >30% of the time. Acetate concentrations >100 mg/L were detected up to 10 ft downgradient. Propionate and butyrate were detected less frequently (18% and 13% of all samples, respectively) and at lower concentrations than acetate.

6.3.3 Overall Assessment for Oil Distribution

The performance objective was met based on the TOC and VFA results. The emulsified oil or its breakdown products were well distributed through the demonstration plot, and were thus available to promote directly (by serving as an electron donor) or indirectly (by favorable changes to the groundwater chemistry) RDX and perchlorate biodegradation.

6.4 GEOCHEMICAL CHANGES

The addition of emulsified oil as an *in situ* biobarrier quickly created highly reducing conditions due to microorganisms consuming oxygen, nitrate, and other available electron acceptors during oxidation of oil components. The reducing conditions are necessary for degradation of explosives and perchlorate.

6.4.1 Data Requirements for Geochemical Changes

The parameters measured to assess creation of favorable geochemical changes were (1) DO and (2) ORP by field meter. In addition to these parameters, other geochemical parameters were measured including pH (via field meter); anions (via EPA Method 300.0); dissolved gases (e.g., methane; EPA Method 3810); and dissolved Fe, Mn, and As (via EPA Method 6010B[10]).

6.4.2 Success Assessment for Geochemical Changes

The success criteria for measured geochemical changes were (1) dissolved O_2 <1 mg/L in all impacted downgradient wells, and (2) ORP reduced to <-100 mV in all wells throughout the demonstration. Both criteria were met for a reasonable period of the demonstration in most of the emulsified oil-impacted wells.

In addition, changes in anions and dissolved metals (Fe, Mn, and As) were used to further verify that reducing conditions were established in the emulsified oil impacted wells.

Finally, perchlorate biodegradation, and to a lesser extent, RDX/HMX biodegradation, are inhibited at low pH. This project also sought to raise the *in situ* groundwater pH to >5.5 S.U. by the co-injection of a pH buffer material with the emulsified oil.

***DO Levels*.**

Criteria: DO <1 mg/L in all treatment wells.

Assessment: Success

DO levels <1 mg/L were measured in all treatment wells out to 40 ft downgradient during >51% of the demonstration period. DO was <1 mg/L at 2.5 ft and 5 ft downgradient during 89% and 52% of the demonstration period, respectively.

***ORP Levels*.**

Criteria: ORP <-100 mV in all treatment wells.

Assessment: Success

ORP levels <-100 mV were detected in all in-barrier and downgradient treatment wells during 12% of the demonstration period, and were observed up to 30 ft downgradient at various time points. In-barrier wells exhibited ORP <-100 mV during 27% of the demonstration (post-emulsified oil injection).

An ORP of -100 mV may not necessarily be required for good RDX and perchlorate removal, and RDX and perchlorate removal was observed in wells that did not or rarely reached the -100 mV criteria. Using a higher ORP of -50 mV, all in-barrier and downgradient wells met the criteria 35% of the time, while in-barrier and centerline wells met the criteria during 60% and 40% of the demonstration period, respectively.

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[10] https://www.epa.gov/sites/production/files/documents/6010b.pdf.

***Anions*.**

Criteria: Reduced nitrate and sulfate concentrations in treatment wells.

Assessment: Success

Nitrate was reduced below background levels (set to 6 mg/L) in 94% of in-barrier and downgradient samples. Sulfate was reduced below background levels (set to 15 mg/L) in 84% of in-barrier and downgradient samples.

***Dissolved Gases*.**

Criteria: Increased concentrations of dissolved methane in treatment wells.

Assessment: Success

Methane—an indicator of both labile carbon and deep reducing conditions—was above background levels (conservatively set to 5 µg/L) in 70% of in-barrier and downgradient samples. The only well in which elevated methane was not detected was side gradient well PZ-30.

***Dissolved Metals*.**

Criteria: Increased concentrations of dissolved Fe and Mn in treatment wells.

Assessment: Success

Dissolved Fe increased above background levels (set to 500 mg/L) in 76% of in-barrier and downgradient samples. Dissolved Mn increased above background levels (set to 10 mg/L) in 77% of in-barrier and downgradient samples.

***pH Levels*.**

Criteria: Increased pH in treatment wells.

Assessment: Success

The pH was increased above a target value of 5.5 S.U. in 56% of in-barrier and downgradient samples.

6.4.3 Overall Assessment for Geochemical Changes

The performance objective was met based on the results obtained. All direct measures (DO, ORP, pH) and indirect measures (of anions, dissolved gases, dissolved metals) indicated that conditions favorable for RDX and perchlorate biodegradation were generated within the demonstration plot.

6.5 BARRIER LONGEVITY

The proposed biobarrier for groundwater remediation was expected to remain effective for a minimum of two years based on groundwater flow, electron acceptor concentrations, and other variables.

6.5.1 Data Requirements for Barrier Longevity

The biobarrier longevity was judged based upon (1) the measurement of elevated TOC in the biobarrier wells and the wells immediately downgradient, and (2) reduced concentrations of RDX and perchlorate in the wells immediately downgradient of the barrier.

6.5.2 Success Assessment for Barrier Longevity

***Elevated TOC*.**

Criteria: TOC concentrations in treatment wells remain elevated for two years.

Assessment: Partial Success

TOC levels above the background were observed in most of the demonstration plot wells for approximately one year, but TOC was near background in most downgradient monitoring wells by Day 498 following injection. TOC however remained elevated in the in barrier (IW) wells over this period. However, overall, emulsified oil consumption was more rapid than anticipated. A second injection was conducted after approximately 600 days in order to increase TOC levels in the center portion of the demonstration plot. This second injection was effective at increasing TOC and re-establishing conditions conducive to RDX and perchlorate biodegradation in downgradient wells.

***RDX and Perchlorate*.**

Criteria: RDX in treatment wells remains <1.08 µg/L (Virginia Groundwater Protection Standard) and perchlorate <2 µg/L for two years.

Assessment: Partial Success

As summarized in **Table 6.1**, RDX remained below the Virginia Groundwater Protection Standards in in-barrier well IW-15 for the entire demonstration period (~900 days). RDX decreased at least once below the protection standard within the two-year period in downgradient wells MW-2, MW-3, and in-barrier well IW-8. It should be noted that HMX was also <1.08 µg/L at least once during the two-year period in downgradient wells MW-1, MW-2, ME-3, MW-4, MW-5, MW-7, and Dahlgren -04, and in in-barrier wells IW-8 and IW-15.

IW-15 and MW-7 remained <2 µg/L for perchlorate for the entire demonstration period. Several other wells (MW-1, MW-2, MW-3, MW-4, IW-1, IW-8, Dahlgren-04) dropped <2 µg/L initially, rose above the standard for varying periods after the initial oil injection, and then dropped back down <2 µg/L following the second emulsified oil injection. MW-6 dropped <2 µg/L after the second emulsified oil injection.

6.5.3 Overall Assessment for Barrier Longevity

The field results indicated that barrier longevity was approximately one year based on TOC levels and slightly less than two years based on maintaining RDX and perchlorate below the chosen criteria of 1.08 µg/L for RDX and 2 µg/L for perchlorate in treatment wells.

Possible reasons for the shorter treatment period are as follows:

- Groundwater elevations changed appreciably over time in the demonstration plot wells, leaving some upper regions of the aquifer exposed to oxygen for part of the demonstration period. This exposure to oxygen likely created a much greater demand for carbon than under saturated conditions.
- Sufficient emulsified oil may not have been added during the initial biobarrier installation to sustain good RDX and perchlorate removal for two years. The initial estimate of the amount of emulsified oil to inject based on the PRB design tool was significantly more than the final amount added, based on discussions with the design tool developer (Dr. Robert C. Borden, Emeritus Professor of Civil, Construction and Environmental Engineering, North Carolina State University) and refinements to the design tool parameters. Because of the nature of the aquifer, with small sand seams and significant areas of impermeable clay, as well as the inability to chase injected emulsified oil with large volumes of water (due to limited range time and slow injection flow rates), a lower initial dose of emulsified oil was used than the design tool recommended in order to avoid potential toxicity to bacterial cells.

6.6 EASE OF BARRIER INSTALLATION

One key goal of the demonstration was to minimize downtime on the active range; therefore, minimizing the time required for biobarrier installation and operation was critical.

6.6.1 Data Requirements for Barrier Installation and Operation

The length of time for biobarrier installation was recorded. System reliability was evaluated qualitatively through discussions with field personnel, and quantitatively by evaluating total downtime for any unplanned activities (e.g., reinjection of emulsified oil) and total costs of the unplanned activities.

6.6.2 Success Assessment for Barrier Installation and Operation

Criteria: <5 days for barrier installation and minimal maintenance costs.

Assessment: Success

The IW installation (20 wells to ~10 ft depth, 100 ft total barrier) required one day, including well finishing with in-ground vaults and pipe fittings. Injection well installation was performed several months ahead of the emulsified oil injection for collection of baseline samples.

The initial emulsified oil injection required three days, including time for collection of injectate and chaser water from existing wells, mixing of emulsified oil and pH buffer components with water, and introduction into each IW. The second emulsified oil injection required only two days. No other time requirements were noted for unplanned activities.

6.6.3 Overall Assessment for Ease of Barrier Installation

Barrier installation and oil injection (and re-injection) all required less than five days. All activities were easily completed during range downtimes for other scheduled MW sampling. No impacts on range activities were noted.

7.0 COST ASSESSMENT

7.1 COST MODEL

In order to evaluate the cost of a potential full-scale bioremediation program, and compare it to other remedial approaches, costs associated with various aspects of the demonstration were tracked throughout the course of the project. **Table 7.1** summarizes the various cost elements and total cost of the demonstration project. The costs have been grouped by categories as recommended in the Federal Remediation Technologies Roundtable Guide to Documenting Cost and Performance for Remediation Projects (Federal Remediation Technologies Roundtable, 1998). Many of the costs shown in this table are a product of the innovative and technology validation aspects of this project, and would not be applicable for a typical site. Therefore, a separate "discounted costs" column that excludes or appropriately discounts these costs is included in **Table 7.1** to provide a cost estimate for implementing this technology at the same scale as the demonstration (i.e., pilot scale).

Table 7.1. Demonstration Cost Components.

Cost Element	Details	Tracked Demonstration Costs	Discounted Costs[1]
CAPITAL COSTS			
Groundwater Modeling	Labor	$1,400	$1,400
System Design	Labor	$5,400	$5,400
Well Installation, Development & Surveying[2]	Labor	$12,600	$12,600
	Materials	$200	$4,000
	Subcontracts (driller/surveyor)	$36,200	$12,000
System Installation (EVO mixing and injection system)	Labor	$4,500	$4,500
	Equipment & Materials	$2,500	$2,500
	Subcontracts (electrical, Conex box/PLC)	$0	$0
Travel		$1,600	$1,600
	Subtotal	**$64,400**	**$44,000**
OPERATION AND MAINTENANCE COSTS			
Groundwater Sampling[3]	Labor	$96,400	$12,000
	Materials	$6,000	$2,500
Analytical	In-House Labor	$62,000	$3,800
	Outside Labs (metals & explosives[2])	$16,000	$12,500
System O&M (including testing & start-up)	Labor	$68,500	$48,000
	Materials (EVO, consumables)	$7,200	$7,200
Utilities	Electric	$600	$600
Reporting & Data Management	Labor	$52,400	$24,000
Travel		$4,200	$4,200
	Subtotal	**$313,300**	**$114,800**
OTHER TECHNOLOGY-SPECIFIC COSTS			
Site Selection	Labor & Travel	$19,200	$0
Site Characterization (surface soil investigation, 2 direct-push investigations, installation of 2 monitoring wells, slug tests, pump tests)	Labor (including in-house analytical)	$111,600	$0
	Materials	$1,800	$0
	Subcontractor (driller)	$36,200	$0
Laboratory Microcosm and Column Testing	Labor (including in-house analytical)	$111,700	$0
Molecular Biology Studies	Labor (including in-house analytical)	$28,900	$0
	Outside Lab	$38,800	$0
IPR Meeting & Reporting	Labor & Travel	$16,700	$0
Technology Transfer (presentations, papers)	Labor & Travel	$37,100	$0
Demonstration Plan/Work Plan	Labor	$22,200	$10,000
Final Report	Labor	$55,200	$32,000
Cost and Performance Report	Labor	$8,000	$0
	Subtotal	**$487,400**	**$42,000**
	TOTAL COSTS	**$865,100**	**$200,800**
	ESTIMATED TREATMENT VOLUME (cubic yards)	**930**	**930**
	ESTIMATED TREATMENT VOLUME (gallons)	**47,000**	**47,000**
	APPROXIMATE TREATMENT COST (per cubic yard)	**$930.22**	**$215.91**
	APPROXIMATE TREATMENT COST (per gallon)	**$18.41**	**$4.27**

Notes:

[1] Discounted costs are defined as estimated costs to implement this technology at the same scale as the demonstration. These costs do not include the technology validation apects of the demonstrations, such as site selection, some laboratory testing, stable isotope studies, molecular biology studies, extensive groundwater sampling, demonstration reporting, interim progress reviews, and preparation of technical and cost and performance reports.

[2] Includes 20 injection wells. Fourteen additional monitoring wells were installed for demonstration. Three monitoring wells are assumed for discounted costing.

[3] Two baseline and ten performance monitoring events were performed during the demonstration. Five sampling events are assumed for discounted costing.

Costs associated with the *in situ* bioremediation of energetic compounds demonstration were tracked from March 2011, to November 2015. The total cost of the demonstration was $865,100, which included $64,400 in capital costs, $313,300 in O&M costs, and $487,400 in demonstration-specific costs (cost related to ESTCP requirements, site selection, and characterization). Approximately 930 cubic yards, or 47,000 gal (assuming a 25% soil porosity) of contaminated aquifer were treated during the demonstration. This corresponds to a unit cost of approximately $930/cubic yard (or $1/cubic yard) or $18/gal of contaminated aquifer (Tracked Demonstration Costs column in **Table 7.1**). By excluding an estimated $595,200 of research-oriented costs (primarily the costs associated with the installation and sampling of extra MWs, molecular biology studies, and ESTCP reporting requirements), unit costs are estimated at approximately $216/cubic yard, or $4/gal of contaminated aquifer for a project of this scale (Discounted Costs column in **Table 7.1**).

7.1.1 Capital Costs

Capital costs (primarily system design and installation) accounted for $64,400 (or approximately 7%) of the total demonstration costs. As indicated in **Table 7.1**, these costs exceed what would be expected during a typical remediation project due partially to the large number of performance MWs (14) installed within the relatively small (100 ft x 100 ft) demonstration area.

7.1.2 O&M Costs

O&M costs accounted for $313,300 (or 36%) of the total demonstration cost. These costs consisted primarily of groundwater monitoring (including analytical), systems O&M, and reporting costs. System O&M costs were $75,700, or approximately 9% of total demonstration costs. The cost of the 990 pounds (lbs) of emulsified vegetable oil (EVO) added during the demonstration was $2,500, or roughly 0.3% of total demonstration costs. Treatment dosage during the demonstration is estimated at approximately 1.0 lbs EVO/cubic yard of treated aquifer. Extensive performance monitoring activities were conducted to effectively validate this technology, including 12 groundwater sampling events (2 baseline and 10 performance).

7.1.3 Demonstration-Specific Costs

Other demonstration-specific costs (those costs not expected to be incurred during non-research-oriented remediation projects) accounted for $487,400 (or 56%) of the total demonstration cost. These costs included site selection, laboratory treatability studies, molecular biology studies, ESTCP demonstration reporting and meeting (In-Progress Review) requirements, and preparation of extensive technical and cost and performance reports.

7.2 COST DRIVERS

7.2.1 General Considerations

The expected cost drivers for installation and operation of a passive groundwater biobarrier for the remediation of explosives-contaminated groundwater, and those that will determine the cost/selection of this technology over other options, include the following:

- Depth of the plume bgs;

- Width, length, and thickness of the plume;
- Aquifer lithology and hydrogeology;
- Regulatory considerations concerning secondary groundwater impacts (e.g., metals mobilization, sulfate reduction);
- Frequency of donor and buffer applications needed;
- Length of time for clean-up (e.g., necessity for accelerated clean-up);
- The presence of indigenous bacteria capable of degrading explosive compounds;
- Concentrations of contaminants and alternate electron acceptors (e.g., nitrate [NO_3^-], sulfate [SO_4^{2-}], and O_2);
- Presence of co-contaminants, such as chlorinated ethenes, or chlorinated ethanes;
- The type(s) of co-substrates determined to be effective at promoting the biodegradation of explosive compounds at a given site (i.e., those that are packaged in soluble form versus those that need to be mixed into solution prior to injection); and
- O&M costs.

As discussed in detail in the project final report, microcosm screening and column treatability testing showed that a combination of emulsified oil and colloidal buffer was the most effective substrate for promoting biological reduction of RDX, and suggested that this combination would also be effective in the field for RDX. The EOS® 550LS emulsified oil and CoBupH™ buffer combination were chosen as the amendments for field injection based on the laboratory tests and product availability. Costs associated with the design and procurement of the injection system used to mix and inject the substrate was relatively insignificant because little equipment was required.

7.2.2 Competing Treatment Technologies

The three other technologies (in addition to bioremediation using a carbon source such as EVO) that have proven to treat perchlorate and nitroaromatic explosives, such as RDX in groundwater, to below regulatory levels at the field scale include:

1. P&T with standard or tailored GAC (Parette *et al.*, 2005),
2. ZVI PRBs, and
3. Mulch biowall.

Additional technologies, including *in situ* chemical oxidation using permanganate (Albano *et al.*, 2010), an electrolytic barrier (ESTCP Project ER-200519[11]), and *in situ* treatment wells with granular Fe placed outside of the well screens (ESTCP Project ER-200223[12]) have been tested at the field scale but have failed to consistently reduce concentrations to below regulatory levels of concern.

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[11] https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-200519/ER-200519/(language)/eng-US.

[12] https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-200223/ER-200223-Permeable-Reactive-Barriers/(language)/eng-US.

P&T technologies provide capture of contaminated groundwater, and above-ground treatment of the extracted water prior to discharge or re-injection into the subsurface. While these systems can provide protection to downgradient receptors if designed properly, they are inefficient at removing contaminant mass from a plume or source zone, and often require operation for decades, leading to high overall costs.

ZVI PRBs, mulch biowalls, and EVO biobarriers treat contaminated groundwater as it flows through the wall/barrier. While these approaches can provide protection to downgradient receptors, they are even less effective than P&T at removing contaminant mass from the plume or source zone. They may also require regular replacement as the materials (ZVI, mulch, or EVO) are used up or begin to clog, leading to contaminated groundwater flowing around or beneath the wall/barrier.

As previously discussed, bioremediation approaches can be either "active," where distribution of amendments is achieved using groundwater recirculation, or "passive," where distribution is accomplished during initial injection or via ambient groundwater flow (see Stroo and Ward, 2009). Active groundwater treatment approaches often involve pairs or groups of IWs and extraction wells to recirculate groundwater and effectively distribute injected amendments within the subsurface. Passive treatment approaches generally involve injection of amendments via closely-spaced IWs or DPT. A hybrid "semi-passive" approach has also been tested, where groundwater is recirculated for a short period to distribute amendments, followed by a longer period of no groundwater recirculation (Hatzinger and Lippincott, 2012). In each of the above three approaches (the active, passive, and hybrid), a carbon source is typically added in order to promote and maintain the reducing, anoxic conditions and supply carbon needed for *in situ* growth of bacteria capable of degrading target contaminants. A slow-release carbon source such as EVO is often utilized with passive treatment approaches to reduce injection frequency.

Bioremediation (either active, passive, or semi-passive approaches) can be utilized to treat source areas and diffuse plumes, or as a barrier to protect downgradient receptors, whereas the three technologies discussed above (P&T, ZVI PRBs, and mulch biowalls) are typically used as barriers to protect downgradient receptors. When a bioremediation approach is used to treat contaminated groundwater, clean-up times are generally substantially shorter than those associated with P&T, ZVI PRBs, and mulch biowalls.

Plume characteristics and those of the local aquifer play important roles in the cost and applicability of the above technologies for remediation of perchlorate and explosives-contaminated groundwater. For shallow groundwater plumes (<50 ft bgs), passive *in situ* options, such as installation of a PRB consisting of either IW or direct-push applied slow-release substrates (like EVO), are likely to be a cost-effective option, providing the selected substrate(s) have been shown to stimulate indigenous microorganisms capable of degrading target contaminants at the treatment site. Trench installation of mulch biowalls or ZVI PRBs may also provide cost-effective options for passively treating contaminants at the downgradient edge of groundwater plumes. For perchlorate, a ZVI PRB is likely to promote biotic (via production of hydrogen as an electron donor) rather than abiotic degradation, as kinetics of abiotic perchlorate degradation with ZVI are very slow (Gurol and Kim, 2000; Son *et al.*, 2006). These passive systems require little O&M after installation, and have the ability to prevent plumes from spreading or leaving a site. However, they may be less suitable at sites where concerns about secondary groundwater contaminants (e.g., reduction and mobilization of Fe, Mn, and As, and sulfide from sulfate reduction) exist.

Additionally, trench-installed barrier technologies may require ZVI replacement (ZVI PRBs) or regular rejuvenation with injections (mulch PRBs) to remain effective.

For deeper plumes (e.g., >50 ft bgs) or those that are large or very thick, passive approaches are often not technically feasible and are cost-prohibitive (e.g., injecting passive substrates at closely spaced intervals to >50 ft bgs). Active or semi-passive treatment systems may be technically and economically more attractive under these conditions. Active or semi-passive treatment approaches may also be better suited for heterogeneous geologies or sites where pH adjustment is required, as groundwater recirculation improves mixing and distribution of injected amendments within the subsurface. Longer treatment timeframes, high contaminant concentrations, and secondary reactions may also present conditions favorable for utilizing an active approach, since amendment addition and mixing rates can be adjusted more easily then with passive approaches, which often utilize less frequent injection of amendments at high concentrations. However, these approaches may be limited where re-injection of contaminated water with amendments is either prohibited or subject to regulatory injection permits.

7.3 COST ANALYSIS

A thorough cost analysis of various *in situ* treatment approaches, including active-pumping systems, passive systems, and semi-passive designs, is provided in *Cost analysis of in situ perchlorate bioremediation technologies* (Krug *et al.*, 2009). These approaches are compared technically and economically with each other and with *ex situ* treatment under a variety of different contamination scenarios. The reader is referred to this volume for descriptions and economic comparisons of different *in situ* technologies that have shown to be capable of remediating perchlorate in groundwater. The base case and cost analysis presented in the publication were used as a template for the cost analysis of the technology tested during this demonstration, as well as the other technologies discussed above that have been proven effective at treating explosives-contaminated groundwater. A cost analysis for the base case was performed for the following technologies:

1. Semi-passive biobarrier with EVO
2. Passive injection biobarrier with cheese whey
3. Passive trench mulch biowall with EVO (for additional TOC)
4. Passive trench ZVI PRB
5. Active P&T

The cost analyses comparing the above approaches are presented below based on a 30-year operating scenario.

7.3.1 Base Case Template

As discussed above, the general base case presented in Krug *et al.*, (2009) is used as a template for the cost analysis of the above technologies/approaches. The base case presents a situation where a shallow aquifer, consisting of homogeneous silty sands, is contaminated with perchlorate (and—for the case of this analysis—RDX). The explosives-impacted groundwater extends from 10 to 40 ft bgs, along the direction of groundwater flow for 800 ft, and is 400 ft wide (**Figure 7.1**).

The specific base case site characteristics—including aquifer characteristics and design parameters—for each of the remedial approaches analyzed are summarized in **Table 7.2**. The costing for the template site assumes that the source zone has been treated and that that there is no continuing source of groundwater contamination.

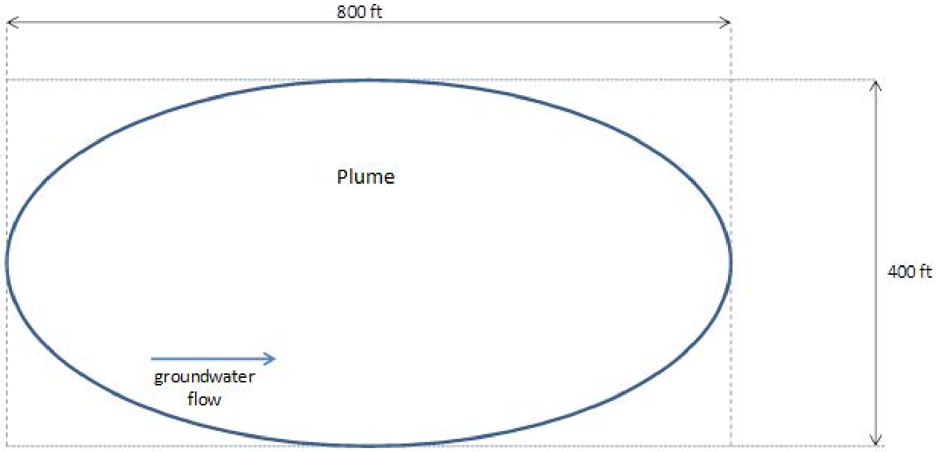

Figure 7.1. Base Case Plume Characteristics (modified from Krug *et al.*, 2009).

Table 7.2. Summary of Base Case Site Characteristics and Design Parameters for Treatment of Explosives-impacted Groundwater.

Design Parameter	Units	Semi-Passive Biobarrier (EVO)	Passive Injection Biobarrier (EVO)	Passive Trench Mulch Biowall (EVO)	Passive Trench ZVI PRB	Active Pump and Treat
Width of Plume	feet	400	400	400	400	400
Length of Plume	feet	800	800	800	800	800
Depth to Water	feet	10	10	10	10	10
Vertical Saturated Thickness	feet	40	40	40	40	40
Porosity	dimensionless	0.25	0.25	0.25	0.25	0.25
Gradient	dimensionless	0.008	0.008	0.008	0.008	0.008
Hydraulic Conductivity	ft/day	2.8	2.8	2.8	2.8	2.8
Groundwater Seepage Velocity	ft/year	33	33	33	33	33
Upgradient Combined Perchlorate & RDX Concentration	µg/L	2,000	2,000	2,000	2,000	2,000
Downgradient Combined Perchlorate & RDX Concentration	µg/L	10	10	10	10	10
Nitrate Concentration	mg/L	15	15	15	15	15
Dissolved Oxygen Concentration	mg/L	5	5	5	5	5
TNT Treatment Objective	µg/L	2	2	2	2	2
RDX Treatment Objective	µg/L	2	2	2	2	2
Assumed Number of Pore Volumes to Flush Plume	each	2	2	2	2	2
Number of Barriers	each	1	1	1	1	NA
Number of Monitoring Wells	each	10	10	10	10	10
Number of Amendment Injection Wells	each	0	30	20	0	0
Number of Groundwater Extraction Wells	each	4	0	0	0	4
Number of Groundwater Re-Injection Wells	each	5	0	0	0	0
Groundwater Travel Time to Barrier	years	24	24	24	24	NA
Years to Clean Up Groundwater	years	48	48	48	48	NA

NA - Not Applicable

As indicated in **Table 7.2**, the base case assumes a groundwater seepage velocity of approximately 33 ft/year, and that 2 pore volumes (PV) of clean water will need to flush through the impacted area to achieve the cleanup objectives. However, as stated in Krug *et al*. (2009), there are a number of factors such as the degree of heterogeneity of the geological media that will determine the actual PV of clean water required to flush through the subsurface to achieve target treatment objectives. Variations in the hydraulic conductivity (K) of the aquifer materials can allow a significant fraction of the total mass of contaminants to diffuse into low K layers, and then act as an ongoing source to the higher K zones. In most geological settings, it is likely that >2 PV would be required to achieve treatment objectives, thus leading to longer treatment times (and costs) for passive and P&T approaches.

The following subsections provide cost estimates for implementation of each of the six treatment approaches for the base case. The cost estimates provide insight into the comparative capital, O&M, and long-term monitoring (LTM) costs to better identify cost drivers for each technology/approach. Total costs and the Net Present Value (NPV) of future costs were calculated for each treatment approach. Future costs (O&M and LTM costs) are discounted, using a 2% discount rate, to determine the NPV estimates of these costs (Office of Management and Budget, 2012). Specifically excluded from consideration are the costs of pre-remedial investigations and treatability studies, due to the assumption that the costs for these activities would be similar for each alternative.

7.3.2 Semi-Passive Biobarrier

The semi-passive biobarrier alternative assumes that a series of four extraction and five IWs will be installed at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.2**). Groundwater will be recirculated between the rows of wells, and soluble cheese whey added for approximately three weeks, after which time the system will be shut down for nine months. The biobarrier will be operated in this semi-passive mode for 30 years. This alternative also assumes 30 years of associated O&M and LTM costs.

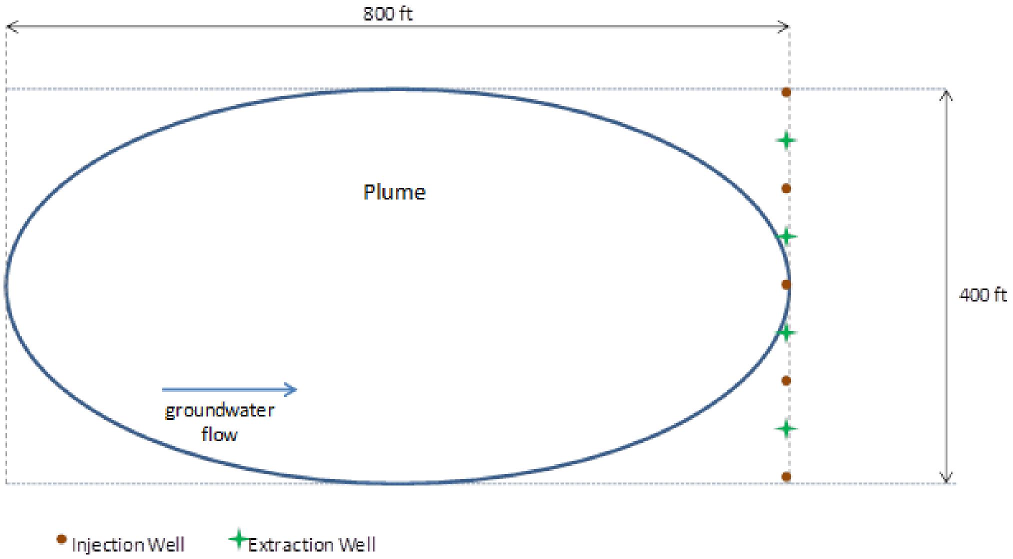

Figure 7.2. Semi-passive Biobarrier Alternative with Cheese Whey for Plume Cutoff.

As summarized in **Table 7.3**, the estimated total cost for this alternative over 30 years is approximately $2.43M with a total NPV of lifetime costs of approximately $1.99M. The capital cost including design, work plan, installation of recirculation and MWs, construction of the groundwater recirculation and cheese whey mixing systems, and system start-up and testing are approximately $500,000. The NPV of the O&M is estimated at approximately $1.06M for the 30 years of treatment. The O&M costs include the labor costs associated with regular rounds (every 9–10 months) of whey mixing and injection, labor for system O&M, costs for equipment repair and replacement, and cost for EVO. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately $430,000.

Table 7.3. Cost Components for Semi-passive Biobarrier Treatment of Explosives-Impacted Groundwater.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	102,943	-	-	-	-	-		102,943	102,943
Well Installation	87,359	-	-	-	-	-		87,359	87,359
System Installation	287,790	-	-	-	-	-		287,790	287,790
Start-up and Testing	19,452	-	-	-	-	-		19,452	19,452
SUBCOST ($)	497,544	-	-	-	-	-		**497,544**	**497,544**
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	30,007	47,048	47,048	47,048	47,048	47,048	42,482 every year	1,057,741	1,394,399
SUBCOST ($)	**30,007**	**47,048**	**47,048**	**47,048**	**47,048**	**47,048**		**1,057,741**	**1,394,399**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	40,036	40,036	40,036	40,036	40,036	13,383	12,369 every year	433,872	534,762
SUBCOST ($)	**40,036**	**40,036**	**40,036**	**40,036**	**40,036**	**13,383**		**433,872**	**534,762**
TOTAL COST ($)	**567,587**	**87,084**	**87,084**	**87,084**	**87,084**	**60,431**		**1,989,158**	**2,426,706**

Notes:
NPV - Net Present Value
* - NPV calculated based on a 2% discount rate

This alternative ranks third in estimated total remedy cost and second in NPV of lifetime costs (see **Table 7.8**). While this technology has relatively modest estimated capital costs, the long-term O&M costs make it less attractive, especially if the system needs to operate beyond 30 years.

7.3.3 Passive Injection Biobarrier

The passive injection biobarrier alternative assumes that a series of 30 IWs will be installed at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.3**). An initial injection during Year 1, and reinjection of EVO every three years after, will be performed to create a passive biobarrier. The biobarrier will be maintained for 30 years. This alternative also assumes 30 years of associated O&M and LTM costs.

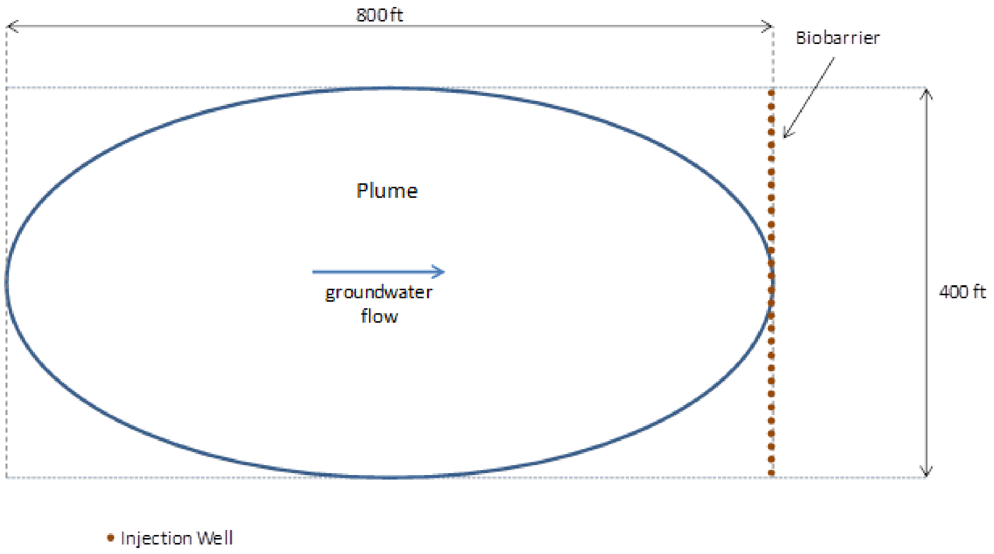

Figure 7.3. Passive Injection Biobarrier Alternative with EVO for Plume Cutoff.

As summarized in **Table 7.4**, the estimated total cost for this alternative over 30 years is approximately $2.58M with a total NPV of lifetime costs of approximately $2.06M. The capital cost including design, work plan, installation of IWs and MWs, and the initial EVO injection are approximately $350,000. The NPV of the O&M is estimated at approximately $1.28M for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with regular injections (every three years) of EVO. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately $430,000.

Table 7.4. Cost Components for Passive Injection Biobarrier Treatment of Explosives-Impacted Groundwater.

	Year Cost is Incurred								NPV of Costs*	Total Costs
	1	2	3	4	5	6	7	8 to 30		
CAPITAL COSTS										
System Design	77,368	-	-	-	-	-	-	-	77,368	77,368
Well Installation (30 1" PVC Wells)	72,919	-	-	-	-	-	-	-	72,919	72,919
Substrate Injection	199,708	-	-	-	-	-	-	-	199,708	199,708
Start-up and Testing**	-	-	-	-	-	-	-	-	0	0
SUBCOST ($)	349,996	-	-	-	-	-	-	-	**349,996**	**349,996**
OPERATION AND MAINTENANCE COSTS										
Substrate Injection	-	-	-	188,915	-	-	188,915	174,598 every 3 years	1,278,215	1,700,237
SUBCOST ($)	-	-	-	**188,915**	-	-	**188,915**		**1,278,215**	**1,700,237**
LONG TERM MONITORING COSTS										
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	40,036	40,036	40,036	40,036	40,036	13,383	13,383	12,369 every year	433,872	534,762
SUBCOST ($)	**40,036**	**40,036**	**40,036**	**40,036**	**40,036**	**13,383**	**13,383**		**433,872**	**534,762**
TOTAL COST ($)	**390,032**	**40,036**	**40,036**	**228,951**	**40,036**	**13,383**	**202,299**		**2,062,083**	**2,584,995**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

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

This alternative ranks fourth in estimated total remedy cost and third in NPV of lifetime costs, but is reasonably close to the other *in situ* technologies overall (see **Table 7.8**). The estimated capital costs for this approach are the lowest of the five alternatives because of the limited infrastructure required. However, the long-term O&M costs associated with regular injections of EVO make this slightly more expensive than other *in situ* alternatives where injections are less frequent (see **Sections 7.3.4** and **7.3.5**). As with the other barrier approaches (including P&T), total remedy costs will increase if the treatment needs to extend beyond 30 years.

The 30-year life cycle cost of the emulsified oil technology assumed re-injection of oil every three years, which is consistent with a previous cost comparison for this technology and with typical performance data (Krug *et al.*, 2009; Borden *et al.*, 2008a,b). During the demonstration, the initial EOS was consumed within approximately one year based on TOC levels, and barrier treatment lasted slightly less than two years based on maintaining RDX and perchlorate below the chosen criteria of 1.08 µg/L for RDX and 2 µg/L for perchlorate in treatment wells. As summarized in **Section 6.5**, the relatively rapid consumption of emulsified oil may reflect (1) the fact that upper regions of the aquifer were exposed to high oxygen for part of the demonstration period due to a low water table, creating a greater TOC demand than under saturated conditions, and (2) the fact that relatively low concentrations and amounts of oil were added to the aquifer during the first injection due to the site geology (small sand seams and significant areas of impermeable clay), as well as the inability to chase injected emulsified oil with large volumes of water, due to limited range time and slow injection flow rates. There was concern about potential microbial toxicity at higher oil concentrations. However, the second injection (at 9% rather than 4% EOS) revealed no deleterious microbial effects at higher concentrations. Thus, it is believed that with a higher oil concentration, the goal of three or more years between injections (as assumed in the cost analysis) could easily be met. Installation of a sand/gravel trench barrier cross-gradient to groundwater flow with buried lines for the addition of emulsified oil (see **Section 8.1.3**), would also allow higher concentrations of EOS to be added with chase water. This trench system would replace the closely spaced biobarrier IWs, and could reduce overall costs by allowing more oil to be added (with a wider distribution) less frequently.

7.3.4 Passive Trench Mulch Biowall

The passive trench mulch biowall alternative assumes an initial installation of a mulch biowall in a trench at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.4**). The mulch biowall will be installed using the one-pass trenching/installation method, and will be 400 ft long, 2 ft thick, and extend down to 40 ft bgs. The biowall will be rejuvenated four and eight years after installation, and then every three years thereafter by injecting EVO into 20 IWs installed within the mulch biowall. The EVO injections are required as the organics in the mulch will eventually be depleted. The biowall will be maintained for 30 years. This alternative also assumes 30 years of associated O&M and LTM costs.

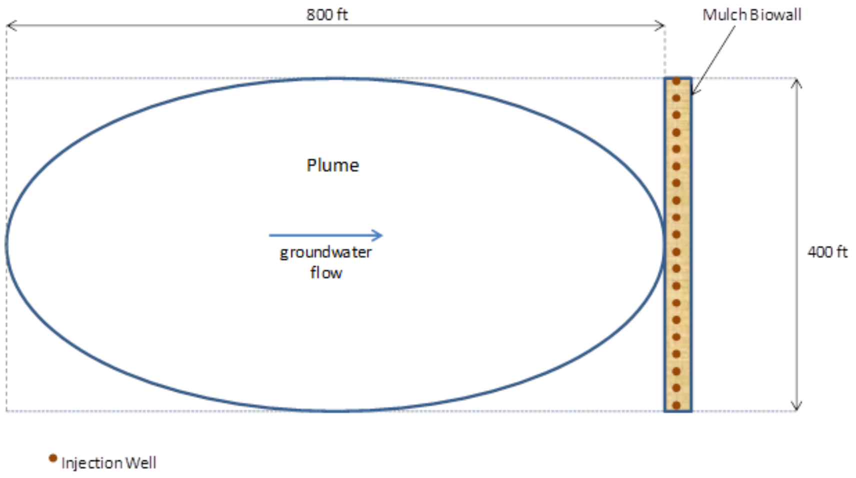

Figure 7.4. Passive Biobarrier Alternative Utilizing a Mulch Biowall for Plume Cutoff.

As summarized in **Table 7.5**, the estimated total cost for this alternative over 30 years is approximately $2.35M with a total NPV of lifetime costs of approximately $1.86M. The capital cost including design, work plan, mulch biowall installation, and installation of IWs and MWs are approximately $390,000. The NPV of the O&M is estimated at approximately $1.04M for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with injections of EVO to maintain the biowall. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately $430,000.

Table 7.5. Cost Components for Passive Trench Biowall Treatment of Explosives-Impacted Groundwater.

	Year Cost is Incurred									NPV of Costs*	Total Costs
	1	2	3	4	5	6	7	8	9 to 30		
CAPITAL COSTS											
System Design	70,552	-	-	-	-	-	-	-		70,552	70,552
Well Installation	57,415	-	-	-	-	-	-	-		57,415	57,415
Trench Installation	206,676	-	-	-	-	-	-	-		206,676	206,676
Substrate Injection	56,805	-	-	-	-	-	-	-		56,805	56,805
Start-up and Testing**	-	-	-	-	-	-	-	-		0	0
SUBCOST ($)	391,448	-	-	-	-	-	-	-		**391,448**	**391,448**
OPERATION AND MAINTENANCE/REAPPLICATION COSTS											
	-	-	-	157,937	-	-	-	157,937	145,968 every 3 years	1,035,595	1,421,435
SUBCOST ($)	-	-	-	**157,937**	-	-	-	**157,937**		**1,035,595**	**1,421,435**
LONG TERM MONITORING COSTS											
Sampling/Analysis/Reporting	40,036	40,036	40,036	40,036	40,036	13,383	13,383	13,383	12,369 every year	433,872	534,762
(Quarterly through 5 years then Annually)											
SUBCOST ($)	40,036	40,036	40,036	40,036	40,036	13,383	13,383	13,383		**433,872**	**534,762**
TOTAL COST ($)	**431,484**	**40,036**	**40,036**	**197,973**	**40,036**	**13,383**	**13,383**	**171,320**		**1,860,915**	**2,347,645**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

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

This alternative ranks lowest in estimated total remedy cost and lowest in NPV of lifetime costs (see **Table 7.8**). The estimated capital costs for this approach are higher than those of the passive injection biobarrier, because of the higher costs associated with the construction of the trench biowall relative to the costs for the initial injection of EVO. However, the long-term O&M costs associated with maintaining the mulch biowall are less than those of the passive injection biobarrier, because less frequent injections (and less quantity) of EVO will be required to maintain the mulch biowall, relative to the passive injection biobarrier. As with the other barrier approaches (including P&T), total remedy costs will increase if the treatment extends beyond 30 years.

7.3.5 Passive Trench ZVI PRB

The passive trench ZVI PRB alternative assumes an initial installation of a ZVI PRB in a trench at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.5**). The PRB will consist of 25% ZVI filings and 75% coarse sand fill mixture (v/v). Like the passive mulch biowall, the PRB will be installed using the one-pass trenching/installation method, and will be 400 ft long, 2 ft thick, and extend down to 40 ft bgs. Pricing for this alternative assumes the PRB will need to be replaced after 15 years, due to decline in ZVI reactivity or plugging. The PRB will be maintained for 30 years. This alternative also assumes 30 years of associate O&M and LTM costs.

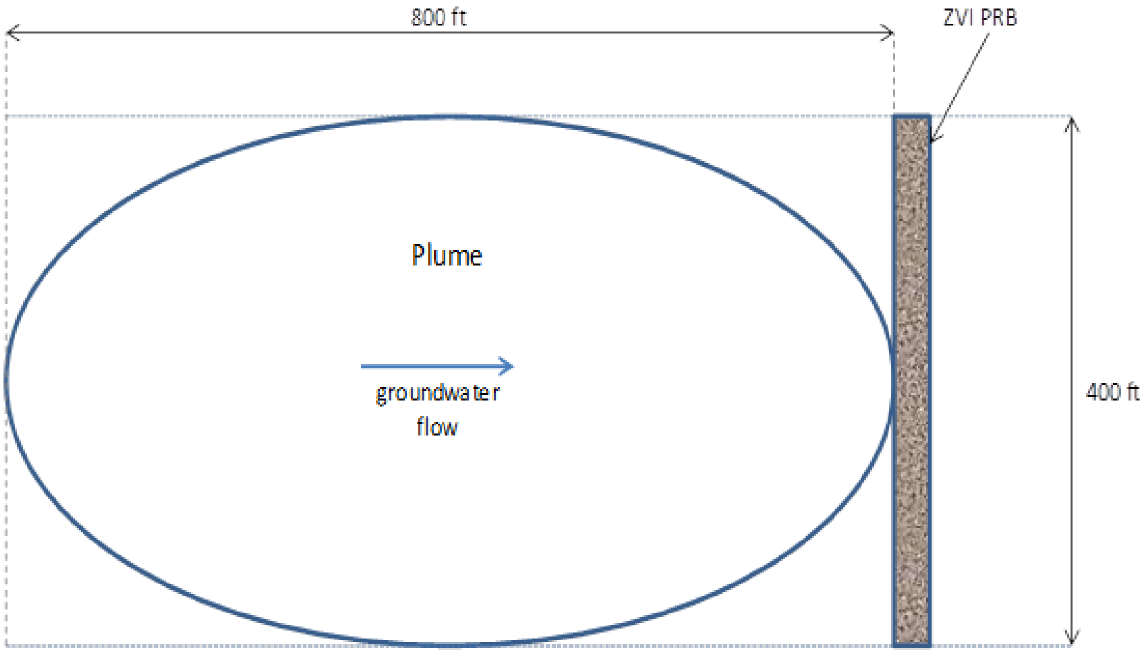

Figure 7.5. Passive PRB Alternative Utilizing ZVI for Plume Cutoff.

As summarized in **Table 7.6**, the estimated total cost for this alternative over 30 years is approximately $2.39M with a total NPV of lifetime costs of approximately $2.08M. The capital cost including design, work plan, ZVI PRB installation, and installation of MWs are approximately $1.01M. The NPV of the O&M is estimated at approximately $637,000, which is the NPV associated with the replacement of the PRB after 15 years. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately $434,000.

Table 7.6. Cost Components for Passive Trench ZVI PRB Treatment of Explosives-Impacted Groundwater.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5 to 14	15	16 to 30		
CAPITAL COSTS									
System Design	70,552	-	-	-		-		70,552	70,552
Well Installation	31,469	-	-	-		-		31,469	31,469
Trench Installation	206,676	-	-	-		-		206,676	206,676
PRB Material	703,300	-	-	-		-		703,300	703,300
Start-up and Testing**	-	-	-	-		-		0	0
SUBCOST ($)	1,011,996	-	-	-		-		**1,011,996**	**1,011,996**
OPERATION AND MAINTENANCE/REAPPLICATION COSTS									
PRB Replacement Cost	-	-	-	-		841,013		637,383	841,013
SUBCOST ($)	**-**	**-**	**-**	**-**		**841,013**		**637,383**	**841,013**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting	40,036	40,036	40,036	40,036	12,369 every year	13,383	12,369 every year	433,872	534,762
(Quarterly through 5 years then Annually)									
SUBCOST ($)	40,036	40,036	40,036	40,036		13,383		**433,872**	**534,762**
TOTAL COST ($)	**1,052,033**	**40,036**	**40,036**	**40,036**		**854,396**		**2,083,251**	**2,387,772**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

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

This alternative ranks second in estimated total remedy cost and fourth in NPV of lifetime costs (**Table 7.8**). The estimated capital costs for this approach are higher than those of the passive trench mulch biowall, because of the much higher costs associated with ZVI PRB material relative to the costs for the mulch biowall material. However, the long-term O&M costs associated with maintaining the ZVI PRB are less than those of the mulch biowall, because no additional EVO injections are required to maintain the ZVI PRB. The total remedy costs for this alternative would increase significantly if the PRB lifespan was <15 years, or if treatment extended beyond 30 years.

7.3.6 Active Pump and Treat (P&T)

The groundwater extraction and treatment (P&T) system alternative would be similar to the semi-passive biobarrier system, in that a row of four extraction and five IWs would be used to recirculate groundwater at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.2**). However, in this case, the extracted groundwater would be treated aboveground by passing it through a combination of standard GAC and a tailored GAC that adsorbs perchlorate more effectively (Parette *et al.*, 2005). The treated groundwater is then re-injected (providing hydraulic control and mass removal at the downgradient edge of the plume). The P&T system will be maintained for 30 years. This alternative also assumes 30 years of associated O&M and LTM costs.

As summarized in **Table 7.7**, the estimated total cost for this alternative over 30 years is approximately $3.62M with a total NPV of lifetime costs of approximately $2.91M. The capital cost including design; work plan; installation of extraction wells/IWs and MWs; construction of the groundwater treatment system; and system start-up and testing are approximately $550,000. The NPV of the O&M is estimated at approximately $1.93M. The O&M costs include the labor costs associated with system O&M, costs for equipment repair and replacement, electrical costs, and cost for the replacement and disposal of the GAC. The NPV of the 30 years of monitoring and reporting costs is estimated to be approximately $434,000.

Table 7.7. Cost Components for Extraction and Treatment of Explosives-impacted Groundwater.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	102,943	-	-	-	-	-		102,943	102,943
Well Installation	87,359	-	-	-	-	-		87,359	87,359
System Installation	332,152	-	-	-	-	-		332,152	332,152
Start-up and Testing	28,403	-	-	-	-	-		28,403	28,403
SUBCOST ($)	550,857	-	-	-	-	-		**550,857**	**550,857**
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	60,386	88,788	88,788	88,788	88,788	88,788	82,059 every year	1,927,559	2,531,700
SUBCOST ($)	**60,386**	**88,788**	**88,788**	**88,788**	**88,788**	**88,788**		**1,927,559**	**2,531,700**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting	40,036	40,036	40,036	40,036	40,036	13,383	12,369 every year	433,872	534,762
(Quarterly through 5 years then Annually)									
SUBCOST ($)	**40,036**	**40,036**	**40,036**	**40,036**	**40,036**	**13,383**		**433,872**	**534,762**
TOTAL COST ($)	**651,279**	**128,824**	**128,824**	**128,824**	**128,824**	**102,172**		**2,912,288**	**3,617,319**

Notes:
NPV - Net Present Value
* - NPV calculated based on a 2% discount rate

This alternative ranks last in both estimated total remedy cost and NPV of lifetime costs (**Table 7.8**). The estimated capital costs for this alternative are higher than those of the semi-passive alternative because of the higher costs associated with constructing a groundwater treatment system, compared to constructing an EVO delivery system. The high O&M costs associated with operating the P&T system are what makes this alternative the least attractive of the six alternatives. As with the other barrier approaches, total remedy costs will increase if the treatment needs to extend beyond 30 years.

Table 7.8. Summary of Capital Costs and NPV of Costs for O&M and Monitoring for Treatment of Explosives-impacted Groundwater.

Alternative	Capital Costs	NPV of 30 Years of O&M Costs	NPV of 30 Years of Monitoring Costs	NPV of 30 Years of Total Remedy Costs	Total 30-Year Remedy Costs
Semi-Passive Biobarrier (EVO)	$500	$1,060	$430	$1,990	$2,430
Passive Injection Biobarrier (EVO)	$350	$1,280	$430	$2,060	$2,580
Passive Trench Mulch Biowall (EVO)	$390	$1,040	$430	$1,860	$2,350
Passive Trench ZVI PRB	$1,010	$640	$430	$2,080	$2,390
Active Pump and Treat	$550	$1,930	$430	$2,910	$3,620

notes: All costs are in thousands of dollars
NPV - Net Present Value; current value of future costs based on a 2% annual discount rate
O&M - Operation and Maintenance

8.0 IMPLEMENTATION ISSUES

8.1 END-USER IMPLEMENTATION ISSUES

The primary end-users of this technology are expected to be DoD site managers and their contractors, consultants, and engineers. The general concerns of these end users are likely to include the following: (1) technology applicability and performance under local site conditions, (2) technology scale-up, (3) secondary impacts to the local aquifer, and (4) technology cost compared to other remedial options. These implementation issues are addressed in the following sections.

8.1.1 Technology Applicability and Performance

The technology utilized during this demonstration was the injection of EOS and buffer via a series of IWs to form a passive biobarrier. The development of passive approaches for groundwater treatment has evolved in large part from operational issues and high costs associated with full-time active pumping systems for *in situ* treatment. Moreover, there are areas like an active range, where the installation of P&T infrastructure or infrastructure to operate an active or semi-passive *in situ* groundwater treatment system is not practical due to ongoing activities. There are several different documents that summarize the applicability of *in situ* emulsified oil biobarriers and provide guidance concerning their specific application (Borden, 2007; Borden *et al.*, 2008a; Borden *et al.*, 2008b; Borden and Lieberman, 2009; Weispfenning and Borden, 2008). The reader is referred to these documents for further guidance on emulsified oil application for *in situ* contaminant treatment.

Emulsified oil can be applied in many different configurations from source area treatment systems to cut-off barriers, like that demonstrated for this field study. The primary advantages of using a passive emulsified oil biobarrier for treatment of comingled explosives and perchlorate are as follows: (1) no permanent equipment required; (2) rapid development of anaerobic conditions suitable for reduction of both perchlorate and nitramine explosives; (3) general ubiquity of organisms capable of coupling oxidation of emulsified oil (or fatty acids produced by emulsified oils) and the reduction of RDX, HMX, and perchlorate; and (4) potentially long-lived treatment with relatively low O&M costs.

Some of the limitations of this approach include (1) cost or technological barriers at increased depth (beyond those easily obtained by a DPT rig); (2) difficulty injecting emulsified oils in low permeability formations; and (3) secondary groundwater impacts. Aquifer depth is one of the limiting factors for all fully passive designs, which become increasingly expensive due to close spacing of injection points or technically impractical (e.g., for passive trench barriers) as the depth to the water table increases (Stroo and Ward, 2008). In addition, emulsified oils are most effectively injected in aquifers where the hydraulic conductivity >4 x 10^{-3} centimeters per second (cm/sec) (~10 ft/day), and become impractical <~1 x 10^{-4} cm/sec (~0.3 ft/day) (Borden and Lieberman, 2009). As noted previously, the hydraulic conductivity at the test plot location at NSWCDD was toward the lower end of that recommended for emulsified oil injection.

One of the typical benefits of active *in situ* treatment (e.g., continuous injection of lactate) is a reduction in secondary groundwater impacts that are typical of passive approaches, such as mobilization of dissolved Fe, Mn, and As, and production and accumulation of methane gas. In a typical application of emulsified oil, Fe an Mn will be mobilized within the treatment zone to mg/L concentrations, but these metals will generally be oxidized and precipitated to background levels within several meters downgradient of the IWs (Hatzinger and Lippincott, 2009; Krug and Cox, 2009). Similar results are expected for methane, which is usually oxidized in an aerobic aquifer via methane-oxidizing bacteria.

During this demonstration, reasonably high concentrations of Fe were observed in some of the MWs after emulsified oil and buffer injection. For example, Fe was detected at 22 mg/L in MW-1 after the first injection with 4% (v/v) EOS® 550LS, and as high as 147 mg/L after the second injection with 9% (v/v) EOS® 550LS. The higher-dissolved Fe following the second injection compared to the first likely reflects the higher oil concentration applied. Following the first injection, dissolved Fe never exceeded 1 mg/ in MW-6, which was 40 ft downgradient of the biobarrier, showing that the Fe re-precipitated quickly as expected. Similarly, after the second injection, Fe declined to 44 mg/L at MW-6, where a DO value of 3 mg/L was detected during this sampling event. Increases in As and Mn were not as high as observed for Fe, with As reaching a maximum of 40 µg/L after the first injection, and quickly declining over time. Arsenic reached a maximum of 90 µg/L following the second higher-dose injection, but monitoring did not occur for a long enough period to quantify As re-precipitation over time. Similarly, Mn did not exceed 350 µg/L in groundwater following first oil injection, and did not exceed 700 µg/L following the second injection. It is anticipated that Fe, Mn, and As will all re-oxidize and precipitate as groundwater becomes increasingly aerobic further downgradient of the biobarrier.

This approach proved to be very effective for remediation of explosives and perchlorate over the 30-month study, and no significant operational issues were experienced. A trade-off for this approach was the production/mobilization of some secondary groundwater contaminants, such as Fe, Mn, As, and methane, as previously discussed. Because there were no drinking wells in the local area and no close downgradient receptors, these contaminants were not deemed to be of concern. However, mobilization of such contaminants should be considered in cases where downgradient receptors are present if the receptors are close in proximity to the biobarrier.

Another implementation issue is the potential formation and accumulation of the RDX nitroso-degradation intermediates (MNX, DNX, or TNX) during anaerobic treatment. During this study, only transient accumulation of these products was observed, and only at a small molar fraction of the RDX biodegraded; therefore, the ring structure of the RDX was broken during biodegradation (Cho *et al.*, 2015). Laboratory studies conducted during the course of this project indicated that degradation of RDX under sulfate-reducing or methanogenic conditions resulted in lower formation of nitroso-intermediates than under Fe- or Mn-reducing conditions, which occur at a higher ORP. Thus, the addition of emulsified oils, which tend to drive aquifers to sulfate-reducing/methanogenic conditions, should reduce the persistence of these intermediates.

8.1.2 Specific Implementation Issues at the NSWCDD Site

There were a few implementation issues encountered during this field demonstration at NSWCDD that should be taken into consideration when evaluating this technology for deployment at other sites, as well as some additional overall considerations for passive biobarriers. These issues and considerations are noted here:

- ***Plume Delineation:*** The contaminant plumes at NSWCDD were not sufficiently delineated prior to this demonstration due to the limited number of MWs and minimal historical data. Finalizing the location, orientation, and overall width of the biobarrier for this demonstration required the installation of 30 additional temporary wells and additional groundwater collection and analysis. Adequate plume delineation should be a top priority if this technology is deployed at full-scale to ensure that the plume is fully intercepted and that treatment goals are met.

- ***Site Geology:*** The local geology at NSWCDD, including seams of conducting silts and sands mixed heterogeneously (horizontally and vertically) with heavy clays, also had to be considered when emplacing IWs and MWs. The biobarrier IWs were closely spaced (~5 ft between) and the rate of injection of emulsified oil into the wells was intentionally limited to <0.3 gal/min to avoid daylighting or compromising the seals on the IWs. The hydraulic conductivity in this area of the NSWCDD site was determined to be ~4.4 ft/day (1.6×10^{-3} cm/sec), which is on the lower end of that deemed suitable for emulsified oil injection. A thorough understanding of local geology and groundwater hydrology needs to be achieved to allow proper placement of injection points and ensure good distribution of the EOS.

- ***Range Type:*** NSWCDD is an active testing range where explosives are regularly detonated, but live fire activities (e.g., mortar, rocket, grenade training) are not common. This allowed the placement of flush-mounted IWs and MWs far enough from the main detonation areas to avoid any damage to the demonstration plot. The generation and occurrence of unexploded ordnance (UXO) was also much lower at NSWCDD than would be expected at a live fire training range. Finally, the range was usually accessible for at least three consecutive days every few months due to scheduled downtime or regulatory sampling events.

This technology is amenable for use at a variety of testing and training ranges. Consideration should be given to emplacing the barrier in an area that is not likely to be impacted either directly by detonations, or by UXO. While not feasible at all sites, emplacement of permanent, flush-mounted IWs should be preferred over using Geoprobe® injection methods, both in terms of ease of follow-on injections to maintain barrier effectiveness, but also in terms of limiting UXO clearance activities to only those needed for IW installation. At more aggressive ranges, hardened IW vaults may be required to protect the infrastructure.

8.1.3 Technology Scale-up

Emulsified oils have been widely used for other applications, such as treatment of chlorinated solvents, so scale-up for an application with explosives and perchlorate should not be problematic. In the case at NSWCDD, the biobarrier could have easily been scaled from 100 to 300 ft or so, which would have been a full-scale allocation for one of the two identified plumes. Due to the relatively low hydraulic conductivity of the groundwater aquifer at the NSWCDD site, another way to implement this approach full-scale would be through the installation of a sand/gravel trench barrier cross-gradient to groundwater flow, with lines for the addition of emulsified oil. This trench system would replace the closely-spaced biobarrier IWs, and could be quickly rejuvenated with additional emulsified oil on an annual or semi-annual basis as necessary.

8.1.4 Technology Cost Compared to Other Remedial Options

The expected cost drivers for the installation and operation of a passive *in situ* bioremediation system for explosives and comparisons to other remedial approaches are provided in **Section 7**.

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