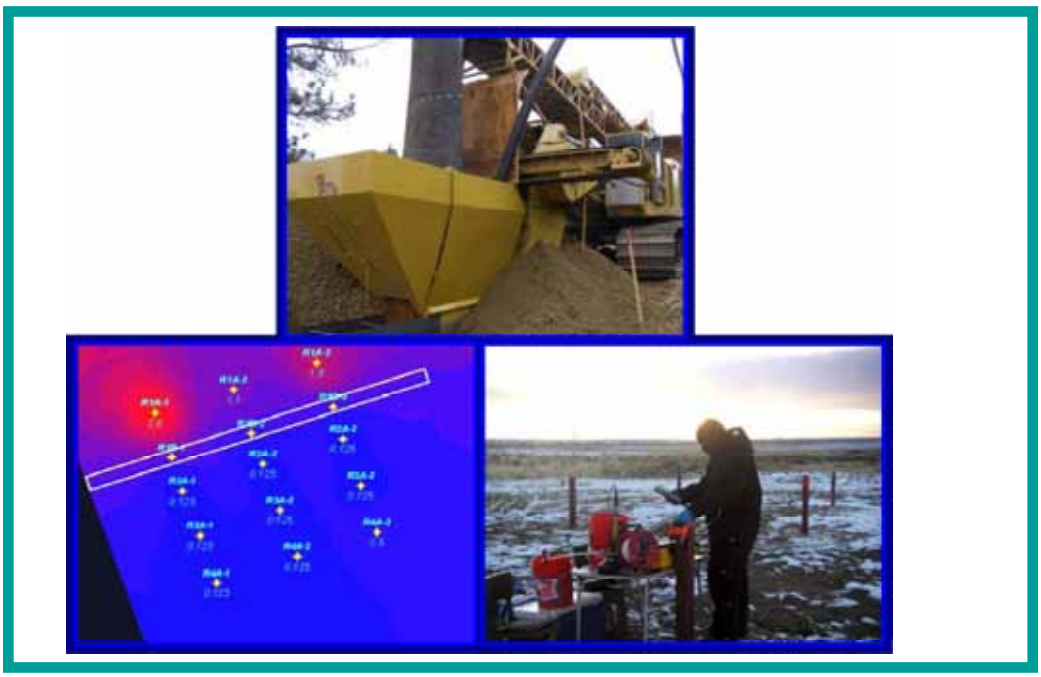
ESTCP
Cost and Performance Report

(ER-0426)



Treatment of RDX and/or HMX Using Mulch Biowalls

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ENVIRONMENTAL SECURITY
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COST & PERFORMANCE REPORT
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ACRONYMS AND ABBREVIATIONS

AFCEE	Air Force Center for Environmental Excellence
AFB	Air Force Base
BAK	benzalkonium chloride
bgs	below ground surface
CHAAP	Cornhusker Army Ammunition Plant
CDPHE	Colorado Department of Public Health and Environment
COC	contaminants of concern
DNT	Dinitrotoluene
DNX	hexahydro-1,3-dinitrososo-5-nitro-1,3,5-triazine
DoD	Department of Defense
ERDC	Engineer Research and Development Center
EOS	emulsified oil substrate
ESTCP	Environmental Security and Technology Certification Program
GC	gas chromatography
GC/ECD	gas chromatography/electron capture detector
GWBU	groundwater bearing unit
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HSAAP	Holston Army Ammunition Plant
HPLC	high performance liquid chromatography
HRC	hydrogen-releasing compound
IAAP	Iowa Army Ammunition Plant
IC	ion chromatography
LC	liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
MNX	hexahydro-1-nitrososo-3,5-dinitro-1,3,5-triazine
MS/MSD	mass spectrometry/mass selective detector
NOM	natural organic matter
ORP	oxidation-reduction potential
PCD	Pueblo Chemical Depot
PRB	permeable reactive barrier

QA/QC	quality assurance/quality control
RAP	Remediation Action Plan
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RRAD	Red River Army Depot
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
SPE	solid phase extraction
SWMU	Solid Waste Management Unit
SIC	standard industrial classification
TAL	target analyte list
TCE	trichloroethene
TCLP	toxicity characteristic leachate procedure
TNB	1,3,5-Trinitobenzene
TNT	2,4,6-Trinitrotoluene
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	total organic carbon
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection
UV-VIS	ultraviolet-visible
VFA	volatile fatty acid
VOA	volatile organic analysis
ZVI	zero-valent iron

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Technical material contained in this report has been approved for public release.

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1.0 EXECUTIVE SUMMARY

Organic mulch is a complex carbon material that is typically populated with its own consortium of microorganisms. The organisms in mulch breakdown complex insoluble organics to soluble carbon, which can then be utilized by these and other microorganisms as an electron donor for treating contaminants via reductive pathways. Mulch has advantages over other electron donors: it is cheaply available, long-lasting, and is naturally present in the environment. Over the last decade, organic mulch permeable reactive barriers (PRB) or biowalls, have enjoyed increased public interest as a relatively cheap technology for addressing contaminated groundwater. The mulch PRB is a passive technology and consequently requires no aboveground injection system, thereby greatly reducing operating and maintenance costs. To date, biowalls have been installed to bioremediate groundwater contaminated with a variety of electrophilic compounds, including chlorinated solvents and inorganics such as nitrate and perchlorate. This field demonstration represents the first ever application of mulch PRBs for the treatment of explosives contamination in groundwater.

Heterocyclic nitramines, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), are energetic materials that commonly make up the bulk of modern explosive formulations.[4] Because of their poor soil sorption properties[28] and their relatively high solubilities compared to other energetic materials, these compounds have been found to contaminate groundwater at military facilities where explosive materials are manufactured, packaged, or handled.[21, 30] Although there is little data to establish their human toxicity at low concentrations, these compounds are generally regarded as possible human carcinogens due to their ability to cause adverse effects in a variety of different organisms, including hepatic tumors in mice.[4] Hence, there is a need to implement remediation technologies to treat RDX and HMX plumes, especially because some of these plumes have migrated off Department of Defense (DoD) bases and could threaten public water supplies.[14, 31] The groundwater plume selected for the field demonstration was the easternmost explosives plume in the Solid Waste Management Unit (SWMU)-17 area located at the Pueblo Chemical Depot (PCD) in Pueblo, Colorado. The state-mandated, site-specific cleanup criteria of 0.55 ppb RDX and 602 ppb HMX was used as the logical goal of the demonstration project.

Early on in the project, a bench-scale treatability study was conducted with contaminated groundwater from the site using pine mulch as the slow-release electron donor. Column tests were run at the average seepage velocity for the site using a 70%/30% (v/v) mulch/pea gravel packing to approach the formation's permeability. Significant results included (1) complete removal of 90 ppb level of influent RDX and 8 ppb of influent HMX in steady-state mulch column effluent; (2) pseudo-first-order steady-state kinetic rate constant, k, of 0.20 to 0.27 hr^{-1} based on RDX removal data, using triplicate column runs; (3) accumulation of reduced RDX intermediates in the steady-state column effluent at less than 2% of the influent RDX mass; and (4) no binding of RDX to the mulch in the batch and column tests. The successful results of the bench-scale study, together with groundwater flow modeling, were used to design the pilot-scale organic mulch/pea gravel biowall for the site.

A 100-ft long and 2-ft thick mulch PRB was installed at PCD using one-pass trenching. To discourage the occurrence of a bypass of groundwater flow around and under the PRB, a

hydraulic control was installed and the PRB was keyed into the bedrock. The mulch PRB was in place by November 16, 2005, and became operational immediately upon installation. Technology performance was monitored using a monitoring well network. Groundwater data collected from each monitoring event was compared to the base case (i.e., pre-PRB) and to itself (i.e., downgradient of PRB compared to upgradient). Performance objectives of the field demonstration were (1) >90% removal of RDX across the PRB and the treatment zone; (2) an RDX concentration of <0.55 ppb in the treatment zone; and (3) cumulative toxic intermediate concentration (i.e., hexahydro-1-nitrososo-3,5-dinitro-1,3,5-triazine [MNX] + hexahydro-1,3-dinitrososo-5-nitro-1,3,5-triazine [DNX] + hexahydro-1,3,5-trinitroso-1,3,5-triazine [TNX]) of <20% of the upgradient RDX concentration. All performance objectives were met by June 2006, when the system appeared to have reached a pseudo-steady-state. By then, a sustained reducing/treatment zone had been created downgradient of the mulch PRB that showed >93% RDX removal, RDX concentrations <0.55 ppb, and no accumulation of toxic intermediates.

Both ex situ and in situ processes have been reported in literature for the remediation of RDX- and HMX-contaminated groundwater. Ex situ processes include the treatment of pumped groundwater in granular activated carbon units,[14, 33] anaerobic bioreactors, electrochemical cells, and UV-oxidation reactors, all of which have the disadvantage of high pumping and re-injection costs. In situ processes are generally cheaper and have fewer regulatory limitations. In situ reduction processes using either zero-valent iron (ZVI)[21, 29] or anaerobic biodegradation[9, 17] have the potential to reduce RDX and HMX. For the purpose of cost comparison of this technology, the mulch PRB unit costs were compared to that of ZVI PRB technology over a 10-year life cycle. Unit costs of $0.08 and $0.11 were obtained for mulch PRB and ZVI PRB, respectively, for each gallon of contaminated groundwater treated over a 10-year period of technology operation. The unit cost differential between these two technologies is expected to be more dramatic over a shorter period of operation, primarily because of the high material cost of ZVI.

Mulch biowall technology is most cost-effective when implemented at shallow, contaminated groundwater sites. In addition, cost advantages over other technologies can be further increased if a source of cheap and effective mulch can be identified in the vicinity of the site where the technology is to be implemented. Since mulch is created from naturally occurring flora, its supply is unlikely to be a problem in geographically non-arid regions. Operational costs associated with this technology are usually negligible. Post-treatment costs of the technology may include excavation and disposal of the spent mulch fill if binding of the target contaminant to the mulch is observed; however, toxicity characteristic leachate procedure (TCLP) testing results for the mulch fill in the site-specific treatability phase confirmed no leaching of the target contaminants of this demonstration, namely, RDX, HMX, or any primary reduction intermediates. Therefore, post-treatment excavation and disposal are unlikely.

2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

This technology is based on the principle of anaerobic bioremediation, which has been demonstrated to mineralize RDX and HMX to innocuous products with both pure and mixed cultures.[15] In this project, an in situ organic mulch-pea gravel PRB for the treatment of groundwater contaminated with RDX and HMX was implemented. The organic mulch acts as a slow-release source of electron donor that stimulates the remediation of RDX and HMX contamination via pathways that initially involve reductive transformations under anaerobic conditions. Furthermore, mulch carries its own inoculum; native RDX- and HMX-degrading microorganisms that populate the mulch contribute to the bioactivity already present in the subsurface. Microorganisms capable of degrading RDX and HMX, such as those of the *Clostridia* genus, are generally considered to be ubiquitous in soil and are known for their ability to degrade a variety of nitro-containing contaminants.[1, 2, 10, 24, 35] Therefore, low bioactivity for energetics degradation in a shallow aquifer is unlikely to be a problem in the application of this technology. This is the first application of a mulch biowall for the treatment of an RDX or HMX plume.

Anaerobic biodegradation pathways have been employed in multiple studies to establish the mineralization of RDX to innocuous products.[6, 11, 13, 16, 17] These pathways tend to be the most cost-effective and technically effective means for treating RDX contaminated groundwater in situ, as such pathways occur under light and oxygen-limited conditions common to groundwater. To date, two major anaerobic biodegradation pathways have been conclusively demonstrated in literature. The first of these pathways (Figure 1) was demonstrated by McCormick et al.,[20] who postulated the pathway shown in Figure 1 by hypothesizing that the RDX ring cleavage occurred via nitroso and hydroxylamino intermediates. More recently, Hawari et al.[16] established a second pathway for the anaerobic degradation of RDX. They postulated that the biodegradation of RDX in liquid cultures with municipal anaerobic sludge followed at least two different degradation pathways. In one pathway, RDX degradation followed the reductive transformations elucidated by McCormick et al. In the second route (not shown), two ring-cleavage metabolites, methylenedinitramine [$(O_2NNH)_2CH_2$] and bis(hydroxmethyl)nitramine [$(HOCH_2)_2NNO_2$] were produced directly from RDX. Neither of these two metabolites accumulated in the system. Instead, they were further transformed to innocuous products such as nitrous oxide (N_2O) and carbon dioxide (CO_2).[13, 15]

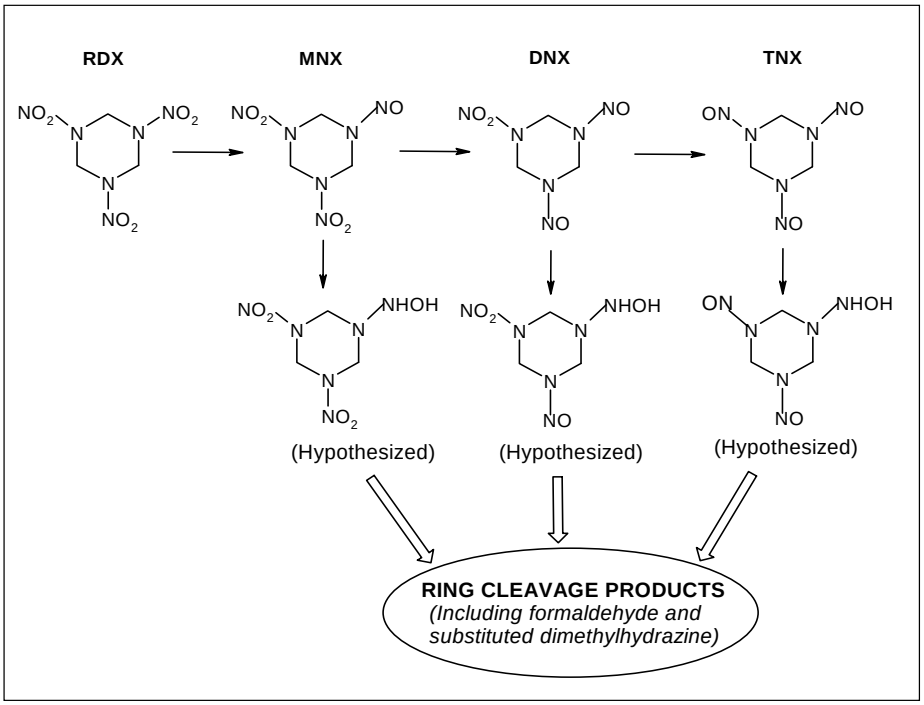


Figure 1. RDX Bioreduction Pathway as Postulated by McCormick et al. (1981).

In situ anaerobic bioremediation processes generally rely on establishing anaerobic reducing conditions by supplying an excess of electron donor. When carbon compounds are used as electron donors, indigenous microorganisms metabolize the electron donor aerobically, thereby scavenging the oxygen from the system and creating anoxic conditions.[1, 25] Under excessive carbon loading, the metabolism of facultative organisms and that of any surviving obligate anaerobes (usually spore-formers) then switches to a fermentative one. This results in the production of a substantial amount of reducing power in the system. The reducing power is "dissipated" by the reduction of any available electron acceptors. These electron acceptors can include inorganic anions, contaminants with electrophilic substituents, and quinoid moieties[19] in soil natural organic matter (NOM). Alternatively, the dissipation of reducing equivalents could also lead to the reduction of protons in water to form molecular hydrogen, which in turn could be utilized as an electron donor by other organisms.[1] Similarly, the mulch PRB technology involves the addition of an electron donor in the form of organic mulch to stimulate reducing conditions. Organic mulch acts as a slow-release electron donor that provides an organic carbon solid matrix while releasing dissolved organic carbon into the groundwater (Figure 2).

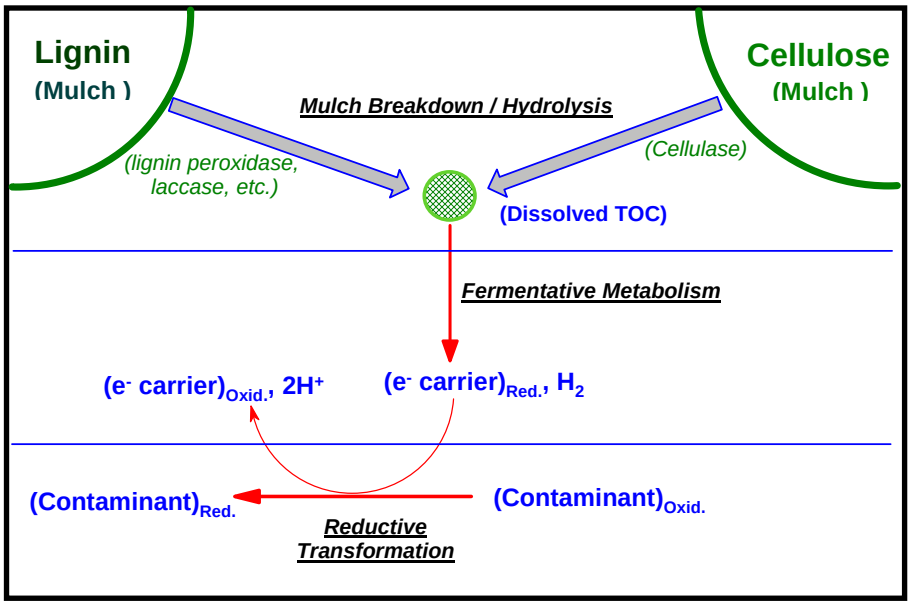


Figure 2. Relationship Between Mulch Breakdown via Hydrolytic Reactions, Fermentative Metabolism, and Reductive Transformation of RDX.

The "slow-release" of dissolved carbon (e.g., humic and fulvic acids) from the mulch matrix occurs via hydrolytic reactions of aerobic and facultative organisms, and from the action of extracellular enzymes of plants and fungi. These reactions consume oxygen to drive the system anaerobic along the flow-path. Subsequently, glycolytic activity of facultative and obligate anaerobic organisms under the oxygen-depleted conditions results in a dissipation of reducing power through the reoxidation of reduced electron carriers[1] (Figure 2). Reoxidation of reduced electron carriers can occur through direct or indirect electron shuttling reactions (e.g., indirectly via quinoid moieties in soil NOM and humic substances[19]). Such reactions have the ability to reduce electrophilic contaminants such as RDX and HMX. Alternatively, molecular hydrogen can also be produced by acidogenic (i.e., acid generating, a subclass of fermenters) organisms, which can then be utilized as an electron donor by other organisms.

2.2 PROCESS DESCRIPTION

Biological reduction of RDX- and HMX-contaminated groundwater will be stimulated by passing groundwater through an in situ mulch PRB filled with a mulch/gravel mixture (Figure 3). Although most of the reaction will occur within the wall, soluble carbon (i.e., humic and fulvic acids) will be released by the wall by the action of aerobic and facultative organisms that scavenge any dissolved oxygen from the groundwater. The soluble carbon will travel downgradient with the groundwater to increase the residence time of the RDX and HMX in contact with the electron donor. Because mulch biowall technology is a passive technology that relies on the natural transport of groundwater in the aquifer, operations and maintenance costs are expected to be negligible. Mulch biowalls have already been demonstrated to be effective at turning aquifers anaerobic by acting as a slow-release source of electron donor for reductively transforming chlorinated solvents,[5] perchlorate,[23] and nitrate.[26]

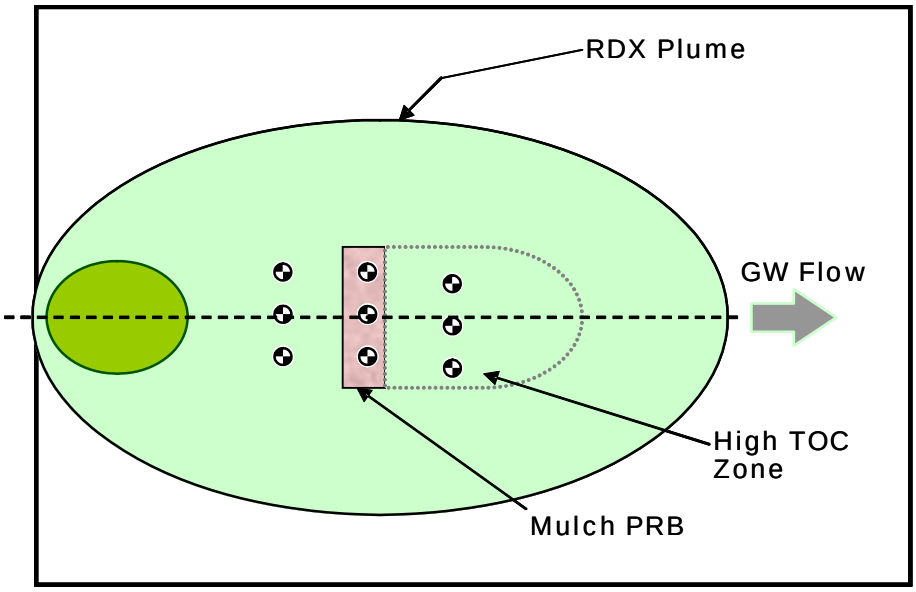


Figure 3. Plan View Schematic of Mulch Wall Implementation Concept.

The key design criterion for the mulch PRB implementation is the thickness of the PRB. A preliminary PRB thickness was determined for steady-state treatability testing conditions using a seepage velocity and hydraulic conductivity representative of the site. In addition to flow characteristics, the PRB thickness is also a function of the pseudo-first-order kinetic rate constant and the degree of conversion desired. The degree of conversion needed to meet cleanup goals can change based on the location of the PRB within the plume. Other design criteria of significance include the depth to groundwater, thickness of the groundwater bearing unit (GWBU), type of underlying bedrock (a concern during single-pass trenching), hydraulic gradient, and the ability to install hydraulic controls (to avoid flow bypass around the PRB).

The 2006 Drinking Water Advisory published by the U.S. Environmental Protection Agency (USEPA), does not list a drinking water standard for RDX; however, it suggests a health-based concentration of 0.03 mg/L (i.e., 30 ppb) as safe at the 10^{-4} cancer risk level, and 0.002 mg/L (i.e., 2 ppb) as safe for lifetime cancer risk.[32] Currently, certain state regulatory agencies specify aqueous RDX cleanup levels in the <1 ppb (or "sub-ppb") range. These include 0.55 ppb in Colorado, the location of the pilot-scale field demonstration, and 0.61 ppb in New York. The establishment of these extremely low cleanup levels has been facilitated by the relatively recent development of large-volume solid phase extraction (SPE) analytical methods that can detect RDX well below any state cleanup level. Because of limited toxicity data, cleanup levels for HMX generally tend to be significantly higher than those for RDX. For example, the groundwater cleanup level for HMX in Colorado is currently set at 602 ppb. Consequently, when both RDX and HMX are present, RDX is clearly the risk driver for achieving the remediation endpoint.

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

To date, mulch PRB technology has been successfully demonstrated to remediate groundwater contaminated with chlorinated solvents, perchlorate, and nitrate. Building on these initial

findings, several commercial and DoD implementations have since taken place. A "biowall summit" was held at the Air Force Center for Environmental Excellence (AFCEE) in San Antonio on August 24, 2005, to discuss case studies and design issues. A research paper on the topic of mulch PRB design considerations combining the findings of this project (Environmental Security and Technology Certification Program [ESTCP] ER-0426) and several other mulch PRB projects was recently published.[3] To the best of our knowledge, this project represents the first implementation and testing of mulch PRBs for the remediation of explosive compounds in groundwater.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Mulch has advantages over other electron donors: it is cheaply available, it carries a diverse consortium of microorganisms, it is long-lasting, and it is present in the environment naturally. Mulch PRB technology is passive and requires no aboveground injection system, greatly reducing operating and maintenance costs. The three main technical risks or limitations associated with this technology are the possible formation of toxic intermediates, the unknown longevity of the mulch, and the effect of co-contaminants.

Although the possibility of toxic intermediate generation exists with all reductive remediation technologies, numerous studies[7, 16, 18, 34] have shown that the generation of intermediates is short-lived as they are rapidly degraded. The column treatability study for this project conducted earlier confirmed that reductive intermediates of RDX were present only at trace levels in the column effluent. In the pilot-scale field demonstration, the reactive zone will extend well beyond the PRB wall as dissolved organic carbon is generated from the mulch and is consumed downgradient of the PRB (Figure 3).

The second issue of concern regarding this technology is the longevity of the mulch. To date, systems employing mulch or waste organic matter have performed well over the long term. Over the first 31 months of operation of a pilot-scale mulch wall installed by GSI Environmental, Inc., at Offutt Air Force Base (AFB) for the treatment of a chlorinated solvent plume, there was no decrease in the percent trichloroethene (TCE) removal across the mulch PRB. Other investigators report that similar technologies using 15%-100% waste cellulose (i.e., sawdust, compost, and leaf material) to promote biological nitrate reduction have performed well over a 7-year period without replacement of the fill.[26, 27] The lifetime of mulch is expected to be 7 years or less. Wells installed within the wall can be used to add supplemental liquid electron donor if the mulch is determined to be "spent" after this time period.

The third technical limitation, also related to the question of longevity, is the effect of high (i.e., >100 mg/L) nitrate concentrations and co-contaminants (e.g., 2,4,6-Trinitrotoluene [TNT] and Dinitrotoluene [DNT]) on the target contaminant's removal efficiency. As discussed in the previous section, co-contaminants that are more electrophilic than RDX and HMX will be reduced preferentially before these compounds. Therefore, it is extremely important to run column studies with groundwater from the demonstration site so that a suitable PRB thickness can be determined.

Whenever electron donor is added to an aquifer, the possibility of biofouling exists. No biofouling has been reported by Robertson et al. (2000)[26] over a 7-year period of operation using

vertical and horizontal waste cellulose solid walls, and no biofouling of the pilot-scale and full-scale mulch wall installed by GSI Environmental, Inc. at Offutt AFB has been observed over the 4 years of operation. Nevertheless, for this demonstration, monitoring wells were installed within the mulch wall to monitor reduction in permeability in the event that fouling occurred as a result of the biological growth or other factors, such as inorganic precipitation and mulch compaction.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The essential performance objectives for this project are presented in Table 1 below:

Table 1. Performance Objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
(a) Determine remediation effectiveness	Contaminant concentrations in groundwater upgradient and downgradient of PRB	>90% removal of RDX across treatment zone	***Yes*** >90% RDX removal was measured in treatment zone once a pseudo-steady-state was established.
(b) Determine remediation effectiveness and safety in achieving target cleanup levels	Contaminant concentrations in groundwater downgradient of PRB	RDX concentration approaching 0.55 ppb concentration downgradient of mulch PRB and < 0.55 ppb at the edge of the treatment zone	***Yes*** RDX concentrations <0.55 ppb (regulatory threshold) were consistently recorded in all wells downgradient of the mulch PRB once a pseudo-steady-state was established.
(c) Determine remediation safety in terms of minimizing by-product accumulation	Contaminant concentrations in groundwater downgradient of PRB	Accumulation of RDX transformation intermediates to a cumulative concentration of <20% of RDX molar concentration immediately upgradient of PRB	***Yes*** No MNX, DNX, or TNX (RDX intermediates) were found in wells downgradient of the mulch PRB once a pseudo-steady-state was established.

All three quantitative performance goals listed above apply to conditions achieved at a pseudo-steady-state, when the target contaminant removal and total organic carbon (TOC) release rate from the mulch PRB demonstrate consistent patterns over two consecutive time periods. A true steady-state for the mulch PRB is unlikely because the insoluble mulch carbon source will eventually be depleted.

For objectives “a” and “b,” the wells immediately downgradient of the mulch PRB (i.e., Row R2A wells located 10 ft downgradient) were presumed to be located within the treatment zone because of their proximity to the PRB. Wells located farther downgradient were considered to be in the treatment zone if they exhibited an oxidation-reduction potential (ORP) less than 50 mV; an ability to consistently reduce inorganic electron acceptors, especially those that are less preferentially reduced (e.g., sulfate); and a dissolved TOC concentration that was at least 20% of the TOC concentrations in the Row R2A wells. Performance objective “b” was regulatory driven as the 0.55 ppb RDX concentration represents the safe groundwater concentration mandated by the Colorado Department of Public Health and Environment (CDPHE) for the PCD. PRB Performance objective “a” designates a minimum anticipated removal of RDX across the mulch PRB and the treatment zone over an approximate 22 to 24-month monitoring period. Since no toxicologically safe levels of RDX reduction intermediates (MNX, DNX, and TNX) are reported in literature, a cumulative maximum concentration of 20% of the upgradient

RDX molar concentration for these intermediates is listed as performance objective "c" in Table 1.

3.2 SELECTION OF TEST SITE

A short list of facilities with explosives contamination in groundwater at shallow depths was created. The need for a shallow groundwater contaminant plume arises from the desire to use a one-pass trencher to limit installation time and costs. The facilities meeting this preliminary criterion were Cornhusker Army Ammunition Plant (CHAAP), Holston Army Ammunition Plant (HSAAP), Iowa Army Ammunition Plant (IAAP), Fort Meade, PCD, Raritan Arsenal, and Lake Ontario Ordnance Works. Following the preliminary selection of facilities, the sites were put through a two-step selection process, (1) an **initial site screening** step and (2) a **final site selection** step. For the first step, three site screening criteria were established to eliminate sites that had a lower likelihood of success from further consideration. These criteria were (a) support and interest of the facility's Environmental Project Manager; (b) level of site characterization; and (c) target contaminant concentration. The two facilities remaining after initial site screening, PCD and IAAP, were contacted for additional information on the final selection criteria presented in Table 2.

Table 2. Final Site Selection Criteria.

Parameter	Preferred Value(s)	Relative Importance (1-5, with 1 being highest)	PCD, Eastern SWMU-17 Area	IAAP, NE of Pink Water Lagoon, Line 800 Area
a. Maximum RDX concentration	>50 ppb	2	>50 ppb	>13,000 ppb
b. Presence of competing electron acceptors (nitrate, nitroaromatics, etc.)	No	1	No	Yes (Nitroaromatics)
c. Maximum concentration of competing electron acceptors (if present)	<10% RDX Conc.	1	N/A	80 - 100% RDX Concentration
d. Depth to bedrock	<35 ft	2	20 ft (approx.)	40 ft (approx.)
e. GWBU geology	Fine Sand	3	Sand, fine to medium	Glacial Till
f. Groundwater seepage velocity	0.01 – <1 ft/day	1	1 ft/day	0.0000–0.001 ft/day
g. Minimum redox potential	>-50 mV	1	>-50 mV	-93 mV
h. TOC	<0.01%	1	<0.001%	0.1% *
i. Presence of other remediation technologies in the immediate vicinity	No	4	No	Yes, active phytoremediation in Pink Water Lagoon.

* Reported by facility contractor; value is unusually high.

3.3 TEST SITE HISTORY/CHARACTERISTICS

Using the site selection criteria described in the previous section, PCD was chosen as the preferred venue for the mulch PRB technology field demonstration. PCD is located at 45825 East Colorado State Highway 96, east of the city of Pueblo in Pueblo County, Colorado (Figure 4). This facility has a long history of ordnance production and ordnance demilitarization activities. The standard industrial classification (SIC) codes of PCD are 4952 and 9711.

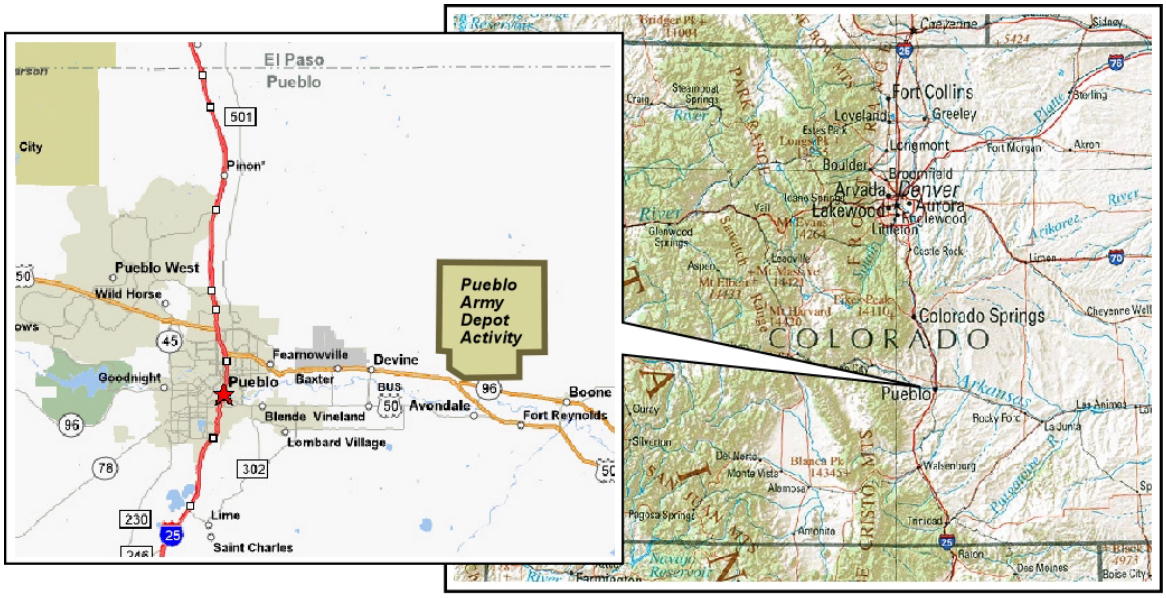


Figure 4. Location of Selected Facility—PCD.

The munitions contamination in groundwater at PCD emanates from the SWMU-17 area, where a TNT "Washout Facility" for shell packing operations was active from the 1940s till 1974. SWMU-17 is located near the southwest corner of PCD. Munitions found in the groundwater in the SWMU-17 area include TNT, DNTs, 1,3,5-Trinitobenzene (TNB), RDX, and HMX. Some munitions contamination has migrated off-base to Ciruli Springs southwest of PCD, prompting CDPHE to issue a compliance order (Compliance Order No. 99-10-06-01) that requires PCD to delineate the nature and extent of on-site and related off-site munitions-contaminated groundwater, and sets cleanup levels for munition contaminants of concern (COC) in groundwater. The RDX and HMX cleanup levels set by CDPHE are 0.55 ppb and 602 ppb, respectively.

RDX- and HMX-contaminated groundwater at SWMU-17 occurs in the unconsolidated alluvium that overlies the bottom-confining Pierre Shale bedrock. The geology of this area is known as the Southwest Terrace. The groundwater flows in a south to southwesterly direction from SWMU-17 in the Southwest Terrace, but is interrupted by unsaturated or dry areas resulting from subterranean outcrops of the Pierre Shale. In effect, the alluvial deposits at different locations on the shale bedrock form "paleochannels" that rapidly transmit groundwater. The hydrogeology at SWMU-17 on PCD is described in detail in the Final Report. The fast groundwater flow conditions at PCD offered an opportunity to study the question of mulch PRB longevity that has remained unanswered in prior biowall projects.

3.4 PHYSICAL SETUP AND OPERATION

Implementation of the mulch/gravel PRB and the associated performance monitoring wells shown in the plan view in Figure 5 was completed in three phases. In the first phase, two rows of three monitoring wells each were installed, developed, and sampled. Prior to the mulch/gravel PRB installation, groundwater was collected from the six wells installed in the first phase. These samples established the baseline distribution of target contaminants in the field demonstration area.

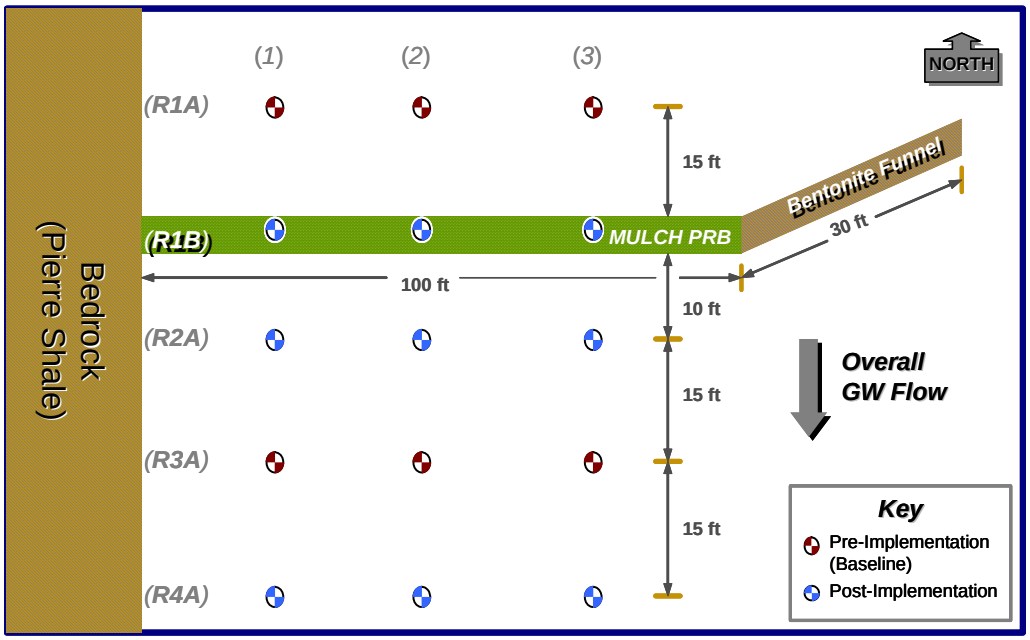


Figure 5. PRB and Well Network Plan View Implementation Schematic (not to scale).

(Well row designations are shown. Row R1A and R3A wells [red color symbols] were installed prior to the PRB installation, and row R1B, R2A, and R4A wells [blue color symbols] were installed after the PRB installation. The PRB and funnel trench installation began at the easternmost point away from the shale bedrock unsaturated zone and progressed westward.)

The second phase involved the installation of the mulch/gravel PRB and an associated soil-bentonite impermeable wall using a one-pass trencher. Both the PRB and the soil-bentonite wall were 2-ft thick. The completed length of the mulch/gravel PRB was approximately 105 ft from the unsaturated zone to the west. A 33%:67% (volume:volume) pea gravel:mulch fill mixture was used for the mulch PRB. The soil-bentonite funnel/or impermeable wall was approximately 30 ft long (Figure 5). Trenching depth varied between 14 ft below ground surface (bgs) and 24 ft bgs with the bedrock topography along the PRB, with the PRB keyed approximately 1 ft into the bedrock. Trenching depth for the impermeable funnel was kept constant at 24 ft bgs to account for any drop in the bedrock elevation below the saturated alluvium (Figure 6). The impermeable funnel, as well as the impermeable formation to the west and at the bottom of the PRB, will serve as hydraulic controls to limit, or even eliminate, groundwater flow bypassing the PRB.

In the third and final implementation phase, three more rows of monitoring wells were installed. The first row of three wells was installed into the mulch/gravel PRB itself (Row R1B). Another row of wells was installed approximately 10 ft downgradient of the PRB (Row R2A). The location of this second row of wells was approximately 10 ft downgradient from the PRB. The final row of three wells, Row 4A, was installed approximately 15 ft downgradient from the Row R3A baseline wells installed in the first phase of the implementation. Note that the screens of all wells extended to the base of the water-bearing alluvium.

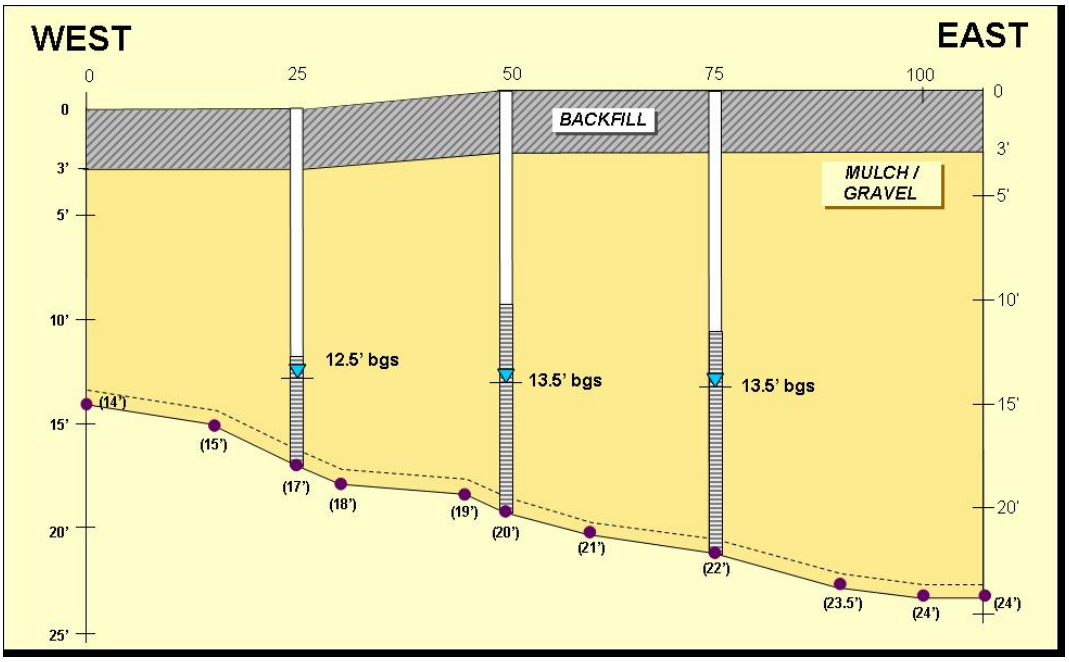


Figure 6. Cross-Section of the Pilot Scale Mulch PRB at the PCD SWMU-17 Area.

(Note that the bentonite funnel wall intersects the mulch PRB between the 100-ft and 105-ft mark at an approximate angle of 35° [not shown]. The dotted line near the base of the PRB indicates the original location of the Pierre shale bedrock; the PRB was keyed-in approximately 1 ft into the bedrock.)

The first phase of the technology implementation began in the week of November 7, 2005. The mulch PRB/soil-bentonite funnel wall installation activities followed sampling of the baseline wells and were completed by November 17, 2005. The remaining well installation activities were completed in the week of November 28, 2005, the week after Thanksgiving holidays. Once implementation had been completed, a biannual monitoring program was initiated that terminated by the end of July 2007. Hence, field demonstration/validation activities lasted a total of 22 months.

3.5 SAMPLING/MONITORING PROCEDURES

The overall purpose of this project was to demonstrate and validate mulch PRB technology in the field at the pilot scale for explosives contamination in groundwater. To this end, data collection focused on evaluating four lines of evidence once the technology was implemented in the field. These lines of evidence are:

1. *Technology Effectiveness*. Groundwater samples collected upgradient (Row R1A, Figure 5), immediately downgradient (Row R2A), and further downgradient (Rows R3A and R4A) of the PRB were analyzed for RDX and HMX. Analyzed concentrations allowed the calculation of RDX removal across the PRB and in the treatment zone. Concentrations of geochemical parameters such as inorganic anions (i.e., sulfate and nitrate) and cations (i.e., ferrous iron and arsenic) were also determined because these species can potentially divert electron flow away from the reduction of the target contaminants.

2. *Technology Longevity*. Measurement of dissolved TOC released from the PRB into the treatment zone was conducted in Rows R1A, R2A, R3A, and R4A. When TOC levels in R2A wells (located immediately downgradient of the PRB) began dropping below 10 mg/L, sampling was initiated in the R1B wells located within the PRB. The 10 mg/L TOC concentration is an often cited threshold value for mulch PRB effectiveness against chlorinated solvent contamination in groundwater. Biofouling effects within the mulch/gravel PRB were assessed by measuring the loss in permeability using slug testing in Row R1B wells and by monitoring the potentiometric surface across the PRB.

3. *Bioactivity*. Volatile fatty acid (VFA) concentrations are a marker for bioactivity. The release of VFAs from the PRB was assessed by analyzing groundwater samples from wells in Rows R1A and R2A. The Microseeps VFA ion chromatography (IC) method selected for this analysis had a very high detection threshold, resulting in almost no detections of VFAs from the second post-PRB installation round (June 2006) when TOC levels started approaching 10 mg/L. Hence, this analysis was discontinued after this monitoring event as it yielded little useful information.

4. *Health and Safety Concerns*. Generation and accumulation of nitroso intermediates of RDX (i.e., MNX, DNX, and TNX) were monitored in the downgradient edge of the treatment zone. Dissolved arsenic levels were also monitored in the treatment zone and compared to upgradient and further downgradient concentrations.

In addition to these analyses, field measurements of water table elevation, pH, specific conductance, ORP, and dissolved oxygen were conducted at each well during every sampling event. Monitoring wells were purged, monitored, and sampled under low flow (300 mL/min) using a peristaltic pump. A flow-through cell was used to obtain field measurements of dissolved oxygen, redox potential, temperature, pH, and specific conductance at all monitoring wells. Prior to monitoring and sampling, wells were purged until field parameters (i.e., pH, temperature, ORP, and specific conductivity) stabilized. The types of analyses, number of samples, and other related information are summarized in Table 3.

3.6 ANALYTICAL/TESTING PROCEDURES

Methods for inorganic anions (SW-9056), TOC (SW-9060), Total Metals (SW-6010), and waste characterization (TCLP SW-1311) are chosen from USEPA's SW-846 Methods. The method that was used for explosives analysis was a modification of SW-846 SW-8330 by the U.S. Army Corps of Engineers (USACE) labs. The sample preparation modification by USACE used SPE to enhance the sensitivity of the SW-846 SW-8330 Method. Copies of all methods were

included in Appendix B of the Final Report. Note that this method can be run in two different configurations or with two different target analyte lists (TAL). The larger TAL includes the relatively unstable nitroso-intermediates of RDX (MNX, DNX, and TNX). The intermediates are not available commercially and are exclusively synthesized by USACE for the method.

Additional mass spectral confirmation of detected peaks falling in the retention time range of RDX was conducted at the USACE/Engineer Research and Development Center (ERDC) Omaha, Nebraska, labs. However, no liquid chromatography/mass spectrometry (LC/MS) facilities were available to the project when the USACE/ERDC Omaha labs shut down in late 2006, and the responsibility of the analysis was transferred to the USACE/ERDC labs in Vicksburg, Mississippi. At that point, explosives and explosives intermediate analyses were done in parallel using a gas chromatography/electron capture detector (GC/ECD) method (SW-846 Method 8095) and the previously-mentioned variation of the USACE SW-8330 method, following SPE. The gas chromatography (GC) method was less prone to interference from co-eluting compounds and generally displays significantly better recoveries of matrix spikes. Therefore, in lieu of mass spectral confirmation, the GC method was used to establish detection of RDX and other explosive constituents, and a GC-to-high performance liquid chromatography (HPLC) correction factor was employed using cleaner samples (i.e., samples with explosives content and a lack of TOC leachate compounds) collected upgradient of the mulch PRB (Row R1A wells). The IC method selected for VFA analysis (AM-23G) is far more sensitive than the GC method. Method AM-23G was developed by Microseeps and was offered exclusively by this lab.

Table 3. Summary of Sample Collection and Off-Site Laboratory Analysis*.

Parameters/ COCs	Sample Media	No. of Samples (Sampling Rows)	Sample Volume	Container and Chemical Preservation	Method	Laboratory
RDX, HMX, intermediates**	Aqueous	12/sampling event (R1A, R2A, R3A, R4A)	1,000 mL	Amber-colored glass; None	SW-8330M SW-8095M	USACE Laboratories, Omaha, NE
Inorganic anions (sulfate and nitrate)	Aqueous	12/sampling event (R1A, R2A, R3A, R4A)	500 mL	Plastic or glass; None	SW-9056	Severn-Trent Laboratories, Houston or Austin, TX
Total (dissolved) organic carbon	Aqueous	12-15/sampling event (R1A, R2A, R3A, R4A)	>100 mL	Plastic or glass; pH<2	SW-9060	Severn-Trent Laboratories, Houston or Austin, TX
Dissolved total metals (Fe & As)	Aqueous	12/sampling event (R1A, R2A, R3A, R4A)	500 mL	Plastic or glass; pH<2 with HNO_3	SW-6010 (filtered samples)	Severn-Trent Laboratories, Houston or Austin, TX
Volatile fatty acids	Aqueous	6/sampling event (R1A, R2A)	40 mL x 2	40-mL glass volatile organic analysis (VOA) vials; benzalkonium chloride (BAK)	AM23G	Microseeps, Pittsburgh, PA

Table 3. Summary of Sample Collection and Off-Site Laboratory Analysis* (continued)**.**

Parameters/ COCs	Sample Media	No. of Samples (Sampling Rows)	Sample Volume	Container and Chemical Preservation	Method	Laboratory
RDX, HMX, Intermediates in leachate*** (TCLP)	Solid	4/field demobilization (N/A)	TBD	16-oz glass with Teflon-lined cap; None	SW-1311/ SW-8330M SW-8095M	USACE Laboratories, Omaha, NE

* Quality assurance/quality control (QA/QC) samples not listed; field duplicates at a 10% frequency of sampling.

** In addition to the samples listed in the table for the five sampling events after the PRB installation, six groundwater samples will be collected prior to the PRB installation, three from well row R1A and three from R3A. These baseline samples will be analyzed using Method SW-8330 listed above (explosive COCs and RDX nitroso intermediates).

***Further details are listed in the Demobilization section.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

Summaries of analytical and field data are provided in Appendix D and E, respectively, of the Final Report.

4.2 PERFORMANCE CRITERIA

Performance metrics and confirmation methods for primary and secondary criteria are summarized in Table 4.

Table 4. Expected Performance and Performance Confirmation Methods.

Performance Criteria	Expected Performance Metric	Performance Confirmation Method	Actual (Post-Demonstration)
1. Primary Performance Criteria (Qualitative)			
a. Contaminant removal	Change in contaminant concentration across PRB and the treatment zone over time	Comparison of RDX and HMX concentration in wells downgradient of the PRB with those in Row R1A (upgradient)	***Same as stated earlier*** Transect plots for contaminant and co-present electron acceptors shown in next section
b. Accumulation of intermediates	Level and distribution of nitroso intermediates of RDX in the treatment zone over time	Comparison of MNX, DNX, and TNX groundwater concentrations in wells downgradient of the PRB with those in Row R1A (upgradient)	***Same as stated earlier*** None of the RDX intermediates detected downgradient of the PRB
2. Primary Performance Criteria (Quantitative)			
a. Contaminant reduction	Greater than or equal to 90% loss in influent RDX and HMX across PRB and measured treatment zone	Removal percentage determined between Row R1A wells upgradient and the wells at the downgradient edge of the treatment zone	***Same as stated earlier*** Greater than 90% removal achieved in all well rows located in the treatment zone following first sampling round
b. Compliance with regulatory concentration	0.55 ppb for RDX and 602 ppb for HMX as mandated by CDPHE	Groundwater concentration to be below this level in last downgradient row of treatment zone wells by steady-state operation	***Same as stated earlier*** RDX concentrations <0.55 ppb in all treatment zone wells
c. Accumulation of intermediates	Accumulation of RDX transformation intermediates to a cumulative concentration of <20% of RDX molar concentration immediately upgradient of PRB	MNX, DNX, and TNX groundwater concentrations in last downgradient row of treatment zone wells, after adjusting for background levels in upgradient wells	***Same as stated earlier*** None of the RDX intermediates detected downgradient of the PRB

Table 4. Expected Performance and Performance Confirmation Methods (continued)**.**

Performance Criteria	Expected Performance Metric	Performance Confirmation Method	Actual (Post-Demonstration)
3. Secondary Performance Criteria (Qualitative and Quantitative)			
a. PRB longevity	Loss in permeability and hydraulic conductivity; variation in TOC levels	Slug tests in PRB wells; potentiometric surface across PRB; analysis of TOC in wells upgradient and downgradient of PRB	***Same as stated earlier*** No loss in permeability detected; TOC monitoring ongoing
b. Groundwater geochemistry	Sulfate, nitrate, dissolved iron and arsenic measurements in groundwater	Comparison of data from downgradient wells to data from upgradient wells	***Same as stated earlier*** Transect plots for inorganic electron acceptors presented in next section
c. Analytical matrix effects	Matrix effects resulting from humic and fulvic acid (polyanion) leachate from mulch	MS/MSD* recovery data from off-site laboratory analysis	***MS/MSD recoveries evaluated*** Poor recoveries for LC**-only method; mass spectral secondary confirmation of all detections downgradient of the mulch PRB employed when available. Adoption of cleaner GC/ECD methodology in conjunction with LC when mass spectrometry was unavailable

*MS/MSD = mass spectrometry/mass selective detector
**LC = liquid chromatography

4.3 DATA ASSESSMENT

4.3.1 System Startup to Pseudo-Steady-State

Installation activities for the mulch PRB and the impermeable funnel wall were conducted November 14 through 16, 2005. The mulch PRB became functional immediately upon installation as it was installed using one-pass trenching. The potentiometric surface interpolated from hydraulic heads measured during the first post-implementation groundwater monitoring event on December 2, 2005 (Figure 7) confirmed that groundwater flow continues to occur across the PRB in a south to southwesterly direction.

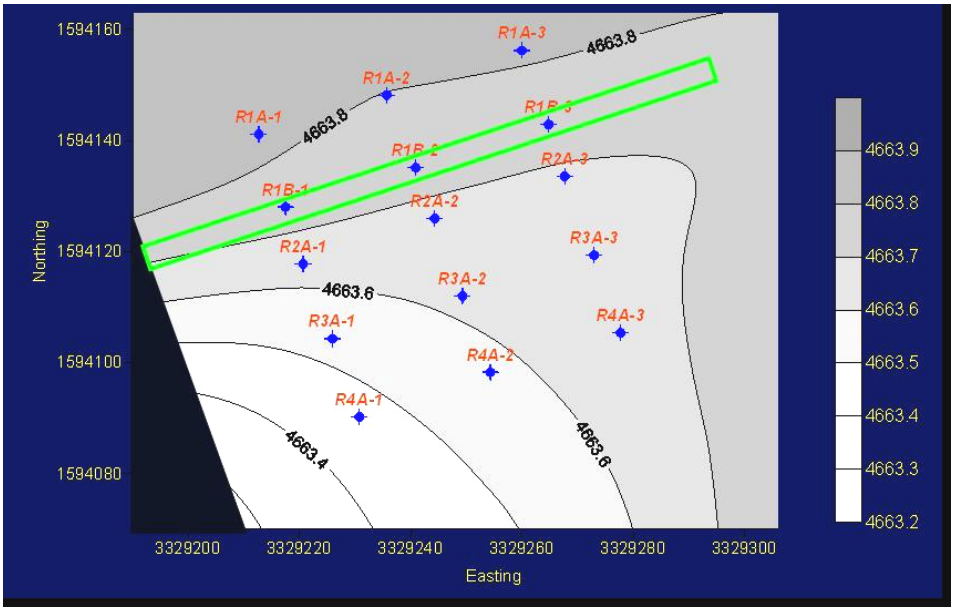


Figure 7. Potentiometric Surface Based on Hydraulic Heads Measured on 12/02/2005, 2.5 Weeks After Technology Implementation.

By the second post-installation monitoring event on June 20, 2006, almost 31 weeks after the PRB installation, approximately six system pore volumes had been displaced. By this time, the system appeared to be approaching a steady state when compared to the baseline case (Figure 8), and RDX could not be detected in any of the wells except well R4A-3, where it was below the regulatory threshold of 0.55 ppb (Figure 9).

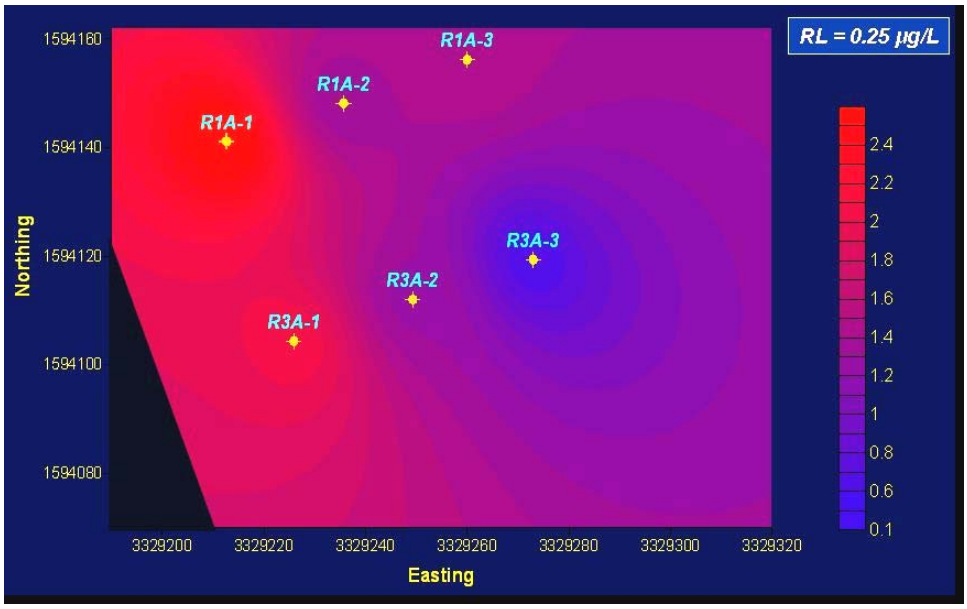


Figure 8. Baseline RDX Concentration Measured on 11/10/2005, Prior to Technology Implementation.

(Concentrations ranged from 2.68 ppb to 1.30 ppb in the Row R1A wells, and 2.08 to 0.61 ppb in the Row R3A wells. All RDX concentrations were above the CDPHE regulatory threshold of 0.55 ppb.)

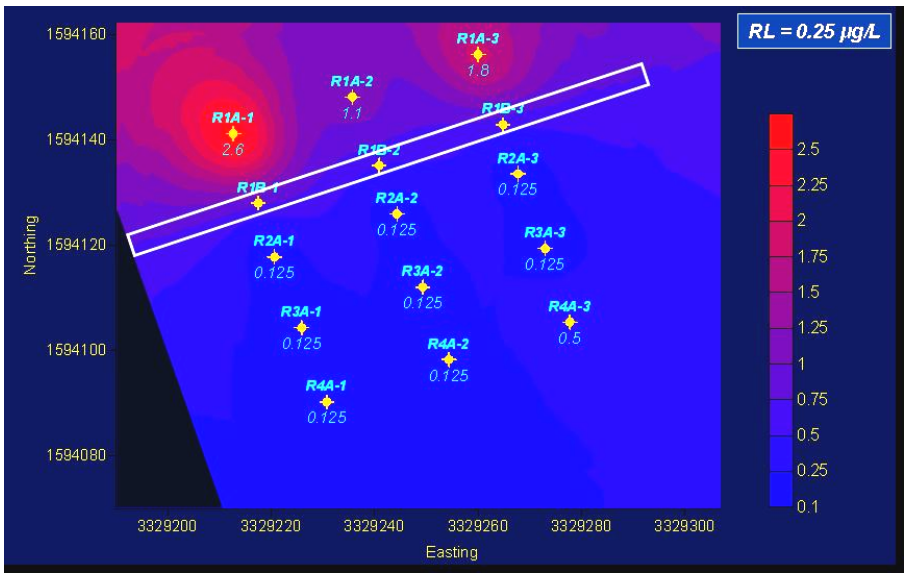


Figure 9. RDX Concentrations Measured on 06/20/2006, 7 Months After Mulch PRB Installation.

4.3.2 Target Contaminant Removal and Compliance with Regulatory Levels

No RDX was detected in the treatment zone (i.e., Row R2A and R3A wells) once the system approached steady state in the June 2006 monitoring event (Figure 10 and Table 5). Detections of RDX did occur in R4A wells outside the treatment zone, but these were generally below the regulatory threshold of 0.55 ppb, except for one detection in well R4A-1 in the November 2006 monitoring event (Table 5). The definitive identity of this detection could not be confirmed using mass spectrometry as these services were not available at USACE/ERDC Vicksburg, which was handling the explosives analysis work for the project after the closure of the USACE/ERDC Omaha facility.

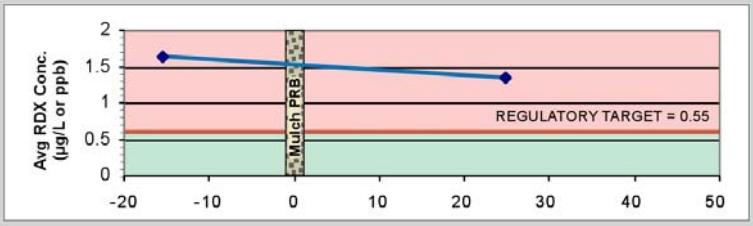
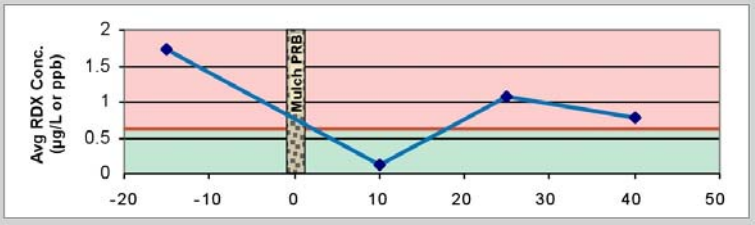
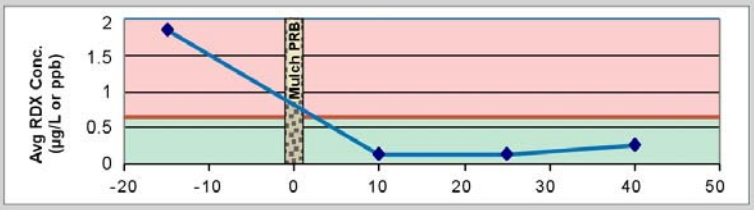
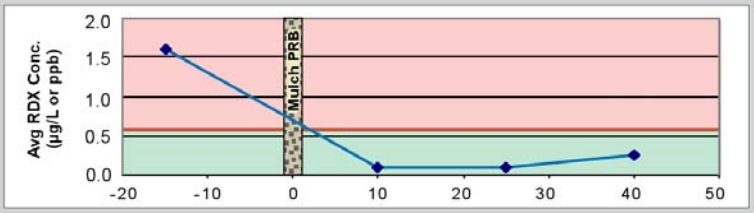
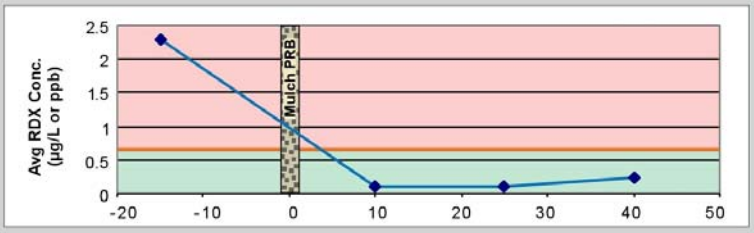
BASELINE: **11/10/2005** ~1 week before installation: **Pretreated RDX concentration exceeds regulatory target**	
12/2/2005 Less than 1 month after installation: **Treatment zone extends to 10 ft downgradient but clean front yet to reach farthest wells**	
6/20/2006 ~7 months after installation: **Treatment zone extends to 40 ft downgradient as system approaches pseudo steady-state**	
11/28/2006 ~1 year after installation: **Treatment Zone sustained**	
7/18/2007 ~1 year 8 months after installation: **Treatment Zone sustained for total of 20 months to date**	 **Distance from Biowall in Groundwater Flow Direction (ft)**

Figure 10. Row-Averaged RDX Concentrations over the Course of the Field Demonstration.

Table 5. Comparison Between RDX and TOC Concentrations for Post-Installation Monitoring Events.

Well ID	Post-Installation Monitoring Event 1 12/02/2005		Post-Installation Monitoring Event 2 06/20/2006		Post-Installation Monitoring Event 3 11/28/2006		Post-Installation Monitoring Event 4 07/18/2007	
	RDX, RL=0.25 μg/L	TOC, RL=1 mg/L	RDX, RL=0.25 μg/L	TOC, RL=1 mg/L	RDX, RL=0.20 μg/L	TOC, RL=1 mg/L	RDX, RL=0.20 μg/L	TOC, RL=1 mg/L
R1A-1	2.610	*0.50*	2.600	*0.50*	2.740	*0.50*	3.090	*0.50*
R1A-2	1.220	*0.50*	1.100	*0.50*	0.775	*0.50*	1.700	*0.50*
R1A-3	1.330	*0.50*	1.800	*0.50*	1.320	*0.50*	2.080	*0.50*
R2A-1	*0.125*	807.00	*0.125*	4.80	*0.100*	3.50	*0.100*	3.30
R2A-2	*0.125*	7.90	*0.125*	12.20	*0.100*	5.30	*0.100*	2.70
R2A-3	*0.125*	795.00	*0.125*	5.10	*0.100*	3.80	*0.100*	10.00
R3A-1	1.940	1.30	*0.125*	6.50	*0.100*	2.70	*0.100*	2.30
R3A-2	1.130	*0.50*	*0.125*	5.30	*0.100*	3.50	*0.100*	3.70
R3A-3	*0.125*	563.00	*0.125*	3.70	*0.100*	2.70	*0.100*	2.30
R4A-1	1.280	*0.50*	*0.125*	4.90	0.270	3.80	*0.100*	4.50
R4A-2	*0.125*	*0.50*	*0.125*	1.90	*0.100*	1.80	*0.100*	1.10
R4A-3	0.930	2.40	0.500	*0.50*	*0.100*	*0.50*	0.529	*0.50*

Note: Non-detects shown in *italics* as half their respective reporting limits.

RDX removal rates averaged over 93% across the mulch PRB and in the other treatment zone wells (Table 6 and Figure 11). Removals were calculated using half the reporting limit for non-detects.

Table 6. Row-Averaged RDX Removal as a Percentage of Upgradient (Row R1A) Well Concentrations.

Well Row ID	Distance from Biowall (ft)	Row-Averaged RDX Removal %			
		Event 1 (12/02/2005)	Event 2 (06/20/2006)	Event 3 (11/28/2006)	Event 4 (07/18/2007)
R1A	-15	0.00%	0.00%	0.00%	0.00%
R2A	10	92.73%	93.18%	93.80%	95.63%
R3A	25	38.08%	93.18%	93.80%	95.63%
R4A	40	54.75%	86.36%	84.07%	89.39%

Notes:
Removal % calculated using row-averaged concentrations, using The R1A average for the monitoring event as a basis.
Blue-shaded cells indicate well-rows meeting the RDX removal % treatment zone criterion of >90%.
Orange-shaded cells indicate well-rows not meeting the RDX removal % treatment zone criterion, either because of non-steady-state conditions or because of decreased reducing conditions outside the treatment zone.

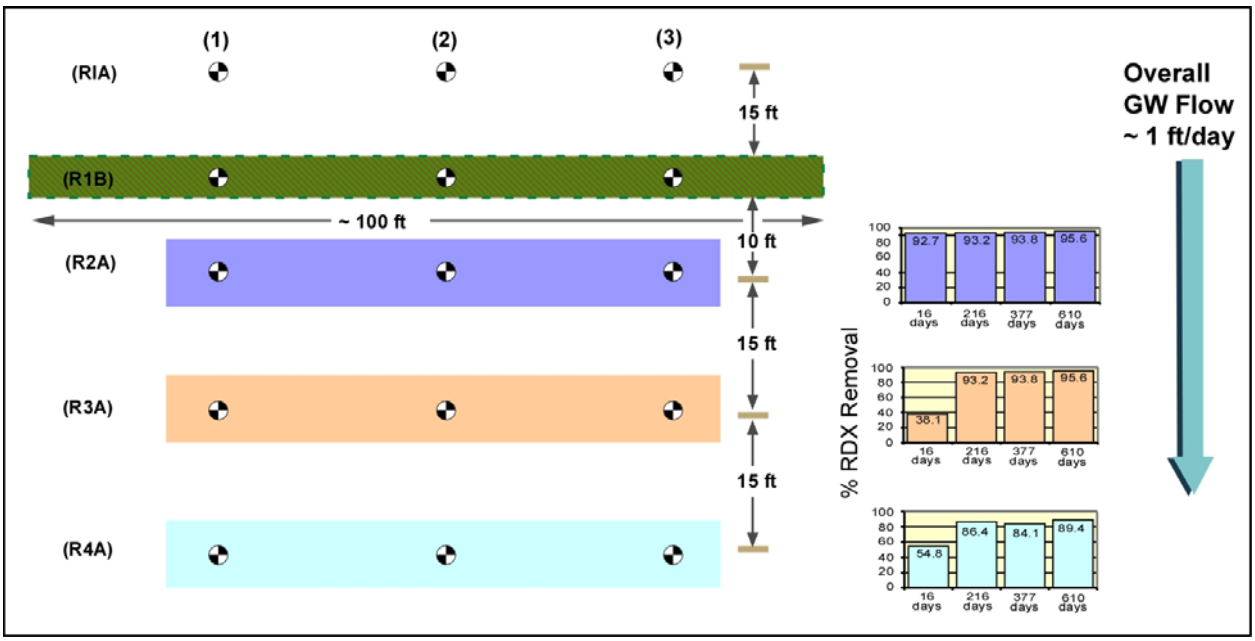


Figure 11. Row-Averaged RDX Removal over the Course of the Field Demonstration.

4.3.3 Accumulation of Intermediates

Toxicity concerns stemming from the generation and potential persistence of partially reduced intermediates of RDX—namely, MNX, DNX, TNX—necessitated their monitoring immediately downgradient of the treatment zone in Row R4A wells. These intermediate compounds are considered to be highly reactive and toxic because of their nitroso substituents. MNX, DNX, and TNX were not detected in Row R4A wells, or any other treatment zone wells, during the course of the demonstration.

4.3.4 PRB Longevity

Mulch PRB longevity was assessed by evaluating dissolved TOC release data and hydraulic data (slug tests within the PRB and potentiometric surface across the PRB). Mean TOC concentrations immediately downgradient of the mulch PRB dropped sharply between the first and second post-installation monitoring events (Table 5). This pattern has been reported in literature[3, 8, 23] and is not considered to be an unusual phenomenon. The primary reason for this behavior is the large initial surge of TOC released from the compost fraction of the mulch. This fraction has low hemicellulose content, resulting in a weaker solid matrix that readily releases its TOC.[3] The large spike of TOC allows the rapid scavenging of dissolved oxygen from the system. The system then maintains its reducing conditions by the slow release of TOC from the wood fraction of mulch. Although mean TOC concentrations have fallen over the course of the field demonstration, the mulch PRB at PCD (SWMU-17) has yet to reach critical TOC concentrations that might allow the breakthrough of RDX. Nevertheless, the potential for target contaminant breakthrough is likely at the SWMU-17 mulch PRB largely because the rapid groundwater flow rates at the site can result in faster mulch depletion. In other words, the biowall system at SWMU-17 is hydrolysis-rate-limited rather than flow-rate-limited. To study the contaminant breakthrough phenomena and technology longevity in this flow-stressed system, the ESTCP has approved an additional 2 years of monitoring.

Potentiometric surface data collected across the PRB and the treatment zone indicated a south to southwesterly direction of groundwater flow over the course of the field demonstration. Slug tests performed within the PRB (Row R1B wells) approximately one year after technology implementation showed a slight increase in the PRB hydraulic conductivity, rather than a decrease (Table 7). These findings indicate that little to no fouling has occurred within the PRB.

Table 7. Hydraulic Conductivities (K) Determined from Mulch PRB Slug Tests.

Well ID	Average K, cm/s (Dec. 2005)	Average K, cm/s (Dec. 2006)
R1B-1	0.013	0.031
R1B-2	0.001	0.005
R1B-3	0.004	0.022

4.3.5 Matrix Effects

This project offered some special challenges for the RDX analysis because of (1) the low state-mandated regulatory levels in groundwater, and (2) the potential matrix effects resulting from the large milieu of mulch decomposition products introduced into the treatment zone. In such a situation, the probability for the occurrence of false positives is extremely high with LC methods, as a number of compounds can co-elute with the target contaminant. Co-eluting compounds can include organic nitrogen-containing protein decomposition products that possess similar physical properties to the nitrogen-containing explosives constituents.

Care was taken in identifying target contaminants in the treatment zone by conducting secondary and tertiary confirmation using real-time ultraviolet-visible (UV-VIS) spectroscopy and mass spectrometry, in conjunction with the modified SW-846 SW-8330 Method developed by USACE/ERDC labs. However, no LC/MS facilities were available to the project when the USACE/ERDC Omaha labs shut down in late 2006 and the responsibility for the explosives analysis was transferred to the USACE/ERDC labs in Vicksburg, Mississippi. From that point onwards, explosives and explosives intermediate analyses were done in parallel using a GC/ECD method (SW-846 Method 8095) and the previously-mentioned variation of the USACE SW-8330 method. The GC method was found to be less prone to interference from co-eluting compounds and generally displayed significantly better recoveries of matrix spikes. Therefore, in lieu of mass spectral confirmation, the GC method was used to establish detection of RDX and other explosive constituents, and a GC-to-HPLC correction factor was employed using cleaner samples (i.e., samples with explosives content and a lack of TOC leachate compounds) collected upgradient of the mulch PRB (Row R1A wells). The correction factor was introduced to keep the results comparable with earlier LC analysis and also to keep them more conservative (i.e., biased high); even though the GC method has detection limits that are better than the modified LC method by an order of magnitude, the GC method yields values that are systematically lower than the LC method in samples collected upgradient of the mulch PRB.

5.0 COST ASSESSMENT

A key objective of this project is to track costs of the technology demonstration (i.e., implementation and operation) and use them to extrapolate costs of a full-scale implementation of the technology.

5.1 COST REPORTING

Cost of installation activities, data collection, and demobilization will be tracked and evaluated as part of this study. Specific categories of costs to be tracked are listed in Table 8.

Table 8. Cost Tracking Parameters.

Cost Category	Subcategory	Details
Capital costs (installation and baseline sampling)	Trenching mobilization	Mobilization costs for trenching machine and crew
	Driller mobilization	Mobilization costs for drill rig and crew for each drilling event
	Groundwater computational modeling costs (labor and software)/engineering design costs	Groundwater flow modeling costs for selection of location for PRB installation as well as costs for any geophysical testing conducted
	PRB mulch/gravel/fill costs	Cost per ton for each type of material used
	PRB and funnel installation	Unit costs for installation
	Hauling and off-site disposal costs	Unit costs (per cu yd) for hauling and off-site disposal of nonhazardous trench cuttings
	Sampling equipment purchase	Field-portable spectrophotometer for ferrous ion analysis, purchased only if rental not available
	Supervision labor	Labor costs for supervisory activities related to system installation
Operating costs (groundwater monitoring)	Labor/or subcontract	Technician labor costs
	Analysis	Off-site laboratory analysis
	Other direct costs	Equipment rental costs, travel, meals, lodging
Demobilization	Geoprobe and crew rental	Subcontract costs based on mobilization and number of sampling points
	Analysis	Analytical costs per sample
	Supervision labor	Supervision of field activities

For each cost category, both actual total costs for pilot-scale and projected costs for a field-scale implementation will be reported. Unit costs were derived and are reported per volume of contaminated groundwater treated. Unit treatment costs for the technology were evaluated against unit treatment costs for an alternative technology.

5.2 COST ANALYSIS

The cost analysis section is divided into three topics: (1) actual demonstration cost; (2) costs for other pilot-scale costs and for extrapolated full-scale implementations; and (3) life-cycle cost comparison to an alternative technology. Note that the basis for cost calculations and potential cost drivers are discussed within each subsection.

5.2.1 Actual Demonstration Costs for ESTCP Project ER-0426

Actual capital and operating costs for the project are presented in Table 9.

Table 9. Actual Capital and Operating Costs for ER-0426.

Cost Category	Subcategory	Description	Actual Demonstration Cost ($)
1. Capital costs	Column treatability study	Materials	9,698
		Labor	41,635
		Analytical, USACE/ERDC	22,000
		Analytical, other	8,568
	Engineering design costs	Groundwater flow modeling and general design	38,384
		Analysis (mulch, geophysical)	844
	Installation	Driller mobilization/demobilization and standby (baseline sampling)	924
		Trencher mobilization/demobilization	38,500
		Driller mobilization/demobilization and drum staging (post-PRB)	660
		Baseline wells (3)	8,217
		Baseline well development	1,251
		Pilot borings along PRB trace	1,650
		PRB mulch/gravel/fill costs	2,535
		Site preparation for PRB installation	2,200
		PRB installation	52,800
		Slurry wall (funnel) installation	5,500
		Hauling and off-site disposal costs for soil cuttings	6,290
		Site restoration	2,200
		Post-PRB-installation downgradient wells (6)	8,217
		Post-PRB-installation PRB wells (3)	3,531
		Well development, post-PRB wells	1,059
		Purge water drum staging	330
		Labor (supervision + baseline sampling)	27,043
		Other expenses (meals and lodging, travel, consumables)	12,836
		Monitoring equipment purchase	778
2. Operating costs	Dec 2005 monitoring event (GSI Environmental, Inc.)	Equipment rental	1,000
		Labor	13,129
		Other expenses (meals and lodging, travel, consumables)	6,328
		Analytical, USACE/ERDC	5,000
		Analytical, other	2,545
	Subcontract, groundwater monitoring (three events)	Subcontract (lump sum)	25,206
		Purge water disposal	2,000
		Analytical, USACE/ERDC	15,000
		Analytical, other	6,531
		GRAND TOTAL	**374,389**
		QUANTITY TREATED (VOLUME, ft^3)	**36,479.5**
		UNIT COST ($/$ft^3$)	**10.26**

Notes: Unit costs are based on a 22-month period of operation. Actual costs do not include preparation of ESTCP documents and peer-reviewed publications, ESTCP meetings and symposiums, and project management of ER-0426.

This project represented the first ever implementation of a mulch PRB for explosives contamination. Furthermore, the field demonstration took place at the PCD, a facility with a challenging hydrogeological flow regime. Hence, several precautionary steps were taken to ensure the project's success, including a thorough flow-through column treatability study and detailed engineering design (groundwater flow modeling, hydraulic controls, and pilot borings).

Consequently, the unit costs of the implementation were high at \$10.26/ft^3 or \$1.37/gal. The volume treated was calculated over a 22-month period of field demonstration. Assumptions used in this calculation included a hydraulic conductivity of 0.006 cm/s, a hydraulic gradient of 0.005 ft/ft, and the saturated cross-section estimated from Figure 6. Note that uncertainty in these costs is extremely low (i.e., <5%) because these are actual costs charged to the project.

Cost drivers for implementing the technology are (a) the depth of contamination, which determines the selection of a trenching procedure; (b) the thickness of the PRB; (c) mobilization costs for the trenching machinery; (d) disposal costs (if any) for the trench cuttings, especially for saturated zone soils; and (e) PRB longevity of operation.

5.2.2 Pilot- and Full-Scale Costs for a Pretested Target Contaminant

Costs for installing a pilot-scale and a full-scale mulch PRB for a pretested target contaminant in a well-characterized flow regime are presented in Table 10. Treatability testing costs can be avoided if the contaminant has already been shown to undergo reductive transformation in the presence of organic mulch electron donor. Similarly, if the hydrogeology or flow regime is well understood in the vicinity of the PRB installation, engineering, modeling, and additional characterization costs can also be substantially reduced. PRB is a passive technology and generally requires limited engineering design, provided the PRB can be engineered to be more permeable than the surrounding formation. If this cannot be achieved, as was the case in this project, additional costs for engineering design (e.g., hydraulic controls, groundwater flow modeling, and pilot borings for keying-in PRB) must be incurred to ensure the success of this remediation technology. Conservative estimates of the thickness of the mulch PRB can be derived using the protocol outlined by the authors in a recent technical publication.[3] The screening-level design protocol involves using analytical models for advection-dominated transport and contaminant transformation rate data to estimate the required PRB thickness. Final unit costs for the simpler pilot-scale implementation were derived to be approximately half that of ER-0426 PRB. Note that PRB dimensions were assumed to be identical to the PRB installed for this field demonstration.

Costs presented for a full-scale mulch PRB implementation use some of the same assumptions described above, as well as the assumption that the full-scale wall would be 500 ft long and would have the same average depth and thickness dimensions as the field demonstration pilot-scale wall. Specific costs for installing the full-scale mulch PRB were derived from a preliminary cost quote by DeWind Dewatering, the one-pass trenching/installation contractor, for installing a 500-ft long mulch PRB at the Red River Army Depot (RRAD) in Texarkana, Texas. As the numbers indicate, there are clear economies of scale in installing a larger wall in a single mobilization. Note that this full-scale case was calculated based on a 22-month period of operation, the same period of operation as the two pilot-scale cases. Unit costs for a simpler full-scale implementation came out to be \$2.08/ft^3 or \$0.28/gallon over the stated period of operation.

Table 11. Pilot- and Full-Scale Costs for Treating a Pre-Tested Contaminant Using Mulch PRB.

Cost Category	Subcategory	Description	Other Pilot-Scale Cost ($)	Full Scale Cost ($)	Basis for Full-Scale Cost
1. Capital costs	Column treatability study	Materials	N/A	N/A	
		Labor	N/A	N/A	
		Analytical, USACE/ERDC	N/A	N/A	
		Analytical, other	N/A	N/A	
	Engineering design costs	Groundwater glow modeling and general design	8,000	20,000	Based on cost savings due to development of design protocol.
		Analysis (mulch, geophysical)	N/A	N/A	
	Installation	Driller mobilization/demobilization and standby (baseline sampling)	N/A	N/A	
		Trencher mobilization/demobilization	38,500	38,500	Based on actual demo cost.
		Driller mobilization/demobilization and drum staging (post-PRB)	660	660	Based on actual demo cost.
		Baseline wells (3)	N/A	N/A	
		Baseline well development	N/A	N/A	
		Pilot borings along PRB trace	N/A	N/A	
		PRB mulch/gravel/fill costs	2,535	12,674	Based on cost extrapolation for 500' wall.
		Site preparation for PRB installation	2,200	11,000	Based on cost extrapolation for 500' wall.
		PRB installation	52,800	160,000	Based on contractor quote for 500' wall.
		Slurry wall (funnel) installation	N/A	N/A	
		Hauling and off-site disposal costs for soil cuttings	6,290	31,448	Based on cost extrapolation for 500' wall.
		Site restoration	2,200	11,000	Based on cost extrapolation for 500' wall.
		Post-PRB-installation downgradient wells (6)	N/A	N/A	
		Post-PRB-installation PRB wells (3)	3,531	3,531	Based on actual demo cost.
		Well development, post-PRB wells	1,059	1,059	Based on actual demo cost.
		Purge water drum staging	330		
		Labor (supervision + baseline sampling)	13,522	27,043	Estimated as approximately 2x actual demo cost.
		Other expenses (meals and lodging, travel, consumables)	6,418	12,836	
		Monitoring equipment purchase	N/A	N/A	
2. Operating costs	Dec 2005 monitoring event (GSI Environmental, Inc.)	Equipment rental	N/A	N/A	
		Labor	N/A	N/A	
		Other expenses (meals and lodging, travel, consumables)	N/A	N/A	
		Analytical, USACE/ERDC	N/A	N/A	
		Analytical, other	N/A	N/A	
	Subcontract, groundwater monitoring (three events)	Subcontract (lump sum)	25,206	25,206	Based on actual demo cost.
		Purge water disposal	2,000	2,000	Based on actual demo cost.
		Analytical, USACE/ERDC	15,000	15,000	Based on actual demo cost.
		Analytical, other	6,531	6,531	Based on actual demo cost.
		GRAND TOTAL	**186,782**	**378,488**	
		QUANTITY TREATED* (VOLUME, ft^3)	**36,479.5**	**182,397.6**	
		UNIT COST ($/$ft^3$)	**5.12**	**2.08**	

Notes: (1) Unit costs are based on a 22-month period of operation; (2) Labor costs for PRB installation and baseline sampling include two persons (one engineer/geologist and one technician) for approximately 125 hours at average rate of $100/hr.

To summarize, the following assumptions about required PRB characteristics and other cost drivers were used in deriving the estimate in Table 10:

- PRB dimensions: 500-ft length, 2-ft thick, 14- to 24-ft depth
- Operating period: 22 months
- Groundwater velocity: 1 ft/day (hydraulic conductivity = 0.006 cm/s; gradient = 0.005 ft/ft)
- Quantity treated: 182,397.6 ft^3
- Unit cost of PRB material (67% mulch/33% gravel plus fill): \$0.60/ft^3
- Labor: one engineer/geologist plus one technician; two mobilizations (one sampling baseline wells, one installation of PRB); 125 hours per person at average billing rate of \$100 per hour; 10% added for prep work
- Wells required for baseline characterization: 3
- Wells required for monitoring conditions within PRB: 3
- Wells required for monitoring downgradient performance: 6
- Number of post-installation performance monitoring events: 3

5.2.3 Life-Cycle Cost Comparison to an Alternative Technology

Costs were calculated for a full-scale mulch PRB and a full-scale ZVI PRB over a 10-yr technology life cycle. For both cases, a pretested target contaminant and a well-defined site hydrogeology were assumed. For the ZVI PRB, a 25%:75% (by volume) ZVI: coarse sand fill mixture was assumed. Additional cost assumptions were a conservative (i.e., low) ZVI cost of \$600/metric ton and a ZVI bulk density of 2,600 kg/m^3. Note that costs for handling and hauling the ZVI would also be significantly more than those for the sand; however, these were assumed to be negligible. Costs for the two full-scale options are presented in Table 11. The resulting final unit costs were \$0.62/ft^3 (\$0.08/gallon) and \$0.83/ft^3 (\$0.11/gallon) for mulch PRB and ZVI PRB, respectively. Thus, mulch ZVI costs are 25% lower than the ZVI PRB over the technology life cycle. Both options can treat shallow groundwater contamination.

Clearly, the main difference between the options is the cost of the fill materials. Given the worldwide demand of iron, costs for ZVI remain high. There are situations where the mulch cost could be higher than what was quoted, such as in arid regions where availability might be limited and result in higher materials cost. In these cases, shipping/transport would also be a significant cost driver. Similarly, there are situations where ZVI materials costs would be lower if there were access to a supply of scrap metal, although these costs savings might be minimal because the purchase price would have to be comparable to the resale value of the material. It should be noted that even if the mulch costs increased by an order of magnitude (i.e., from \$12,674 to \$126,740), the full-scale implementation costs would increase by only 30% (from \$2.08 to \$2.71 per ft^3 treated) and the full-scale life-cycle costs would increase by only 18% (from \$0.62 to \$0.73 per ft^3 treated). In the latter case, the overall cost for mulch PRBs would still be significantly lower than for ZVI PRBs. Consequently, it is hard to imagine a scenario where discounted ZVI material costs would result in a lower life-cycle cost than for mulch PRBs.

The materials cost is also highly dependent on the wall thickness of the PRB, which is a function of the treatment time required to reach cleanup objectives. For the cost assessment presented in Table 11, it was assumed that both the ZVI and the mulch PRBs were the same thickness (2 ft). In certain sites, a thinner ZVI wall may be appropriate when RDX transformation is more rapid using ZVI than mulch, although it would likely require supplemental treatability studies to establish this. For this project, the pseudo first-order rate coefficients for mulch PRB determined in the treatability study conducted prior to the field implementation was 0.20 to 0.27 hr^{-1} (4.8 to 6.5 day^{-1}). A number of recently-completed or ongoing Strategic Environmental Research and Development Program (SERDP) and ESTCP projects have examined RDX transformation in ZVI PRBs, including SERDP ER-1231, SERDP ER-1232, and ESTCP ER-0223. Limited kinetic data has been released from these projects to-date. Rate coefficients were not explicitly stated in the Final Report for SERDP ER-1231 ("Fe(0)-Based Bioremediation of RDX-Contaminated Groundwater") but data presented would suggest that RDX rate coefficients on the order of 1 day^{-1} or lower for biologically-enhanced iron-based systems (see Figure 7 in the report for that project). Data from a previous SERDP Exploratory Development (SEED) project by the same PIs[21] presented RDX rate coefficients of 0.003 day^{-1}. Collectively, these data do not suggest that ZVI PRB degradation rates are faster than those for mulch PRBs, and therefore would not suggest that ZVI walls would be thinner.

It is also important to note that the analytical costs for the two types of PRBs will not necessarily be the same. In many full-scale applications, monitoring of a ZVI PRB would not require the secondary and tertiary confirmatory analyses for explosives and their intermediates that are part of the cost estimate for mulch PRBs, primarily due to the lower potential for matrix interferences in ZVI PRB samples. The use of these methods would not necessarily be eliminated for ZVI PRBs because it is likely that mass spectral (or GC/ECD) confirmation of low-level intermediates would be required in certain cases. Regardless, to account for the likelihood of a reduced analytical load for ZVI PRBs, the cost associated with explosives analyses is 25% lower for the ZVI PRB in Table 11.

Table 11. Full-Scale Cost Comparison Between Mulch and ZVI PRBs (10-yr Life Cycle).

Cost Category	Subcategory	Description	Mulch PRB, Full-Scale Cost ($)	ZVI PRB, Full-Scale Cost ($)
1. Capital costs	Column treatability study	Materials	N/A	N/A
		Labor	N/A	N/A
		Analytical, USACE/ERDC	N/A	N/A
		Analytical, other	N/A	N/A
	Engineering design costs	Groundwater flow modeling and general design	20,000	20,000
		Analysis (mulch, geophysical)	N/A	N/A
	Installation	Driller mobilization/demobilization and standby (baseline sampling)	N/A	N/A
		Trencher mobilization/demobilization	38,500	38,500
		Driller mobilization/demobilization and drum staging (Post-PRB)	660	660
		Baseline wells (3)	N/A	N/A
		Baseline well development	N/A	N/A
		Pilot borings along PRB trace	N/A	N/A
		PRB mulch/gravel/fill costs	12,674	250,000
		Site preparation for PRB installation	11,000	11,000
		PRB installation	160,000	160,000
		Slurry wall (funnel) installation	N/A	N/A
		Hauling and off-site disposal costs for soil cuttings	31,448	31,448
		Site restoration	11,000	11,000
		Post-PRB-installation downgradient wells (6)	N/A	N/A
		Post-PRB-installation PRB wells (3)	3,531	3,531
		Well development, post-PRB wells	1,059	1,059
		Purge water drum staging	N/A	N/A
		Labor (supervision + baseline sampling)	27,043	27,043
		Other expenses (meals and lodging, travel, consumables)	12,836	12,836
		Monitoring equipment purchase	N/A	N/A
2. Operating costs	Dec 2005 monitoring event (GSI Environmental, Inc.)	Equipment rental	N/A	N/A
		Labor	N/A	N/A
		Other expenses (meals and lodging, travel, consumables)	N/A	N/A
		Analytical, USACE/ERDC	N/A	N/A
		Analytical, other	N/A	N/A
	Subcontract, groundwater monitoring (three events)	Subcontract (lump sum)	168,121	168,121
		Purge water disposal	13,340	13,340
		Analytical, USACE/ERDC	100,050	75,038
		Analytical, other	6,531	6,531
		GRAND TOTAL	**617,793**	**830,107**
		QUANTITY TREATED* (VOLUME, ft^3)	**994,892.7**	**994,892.7**
		UNIT COST ($/$ft^3$)	**0.62**	**0.83**

Notes: Unit costs are based on a 10-yr period of operation.

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6.0 IMPLEMENTATION ISSUES

6.1 ENVIRONMENTAL CHECKLIST

No permits or approvals from regulatory agencies were required for implementation of the pilot-scale mulch biowall technology. Site access for all field work was coordinated with the office of the environmental coordinator for the facility, Mr. Stan Wharry, and later with his replacement, Mr. Christopher Pulskamp. Required underground utility clearances for either the PRB or the monitoring well installation were obtained through the same project contacts.

6.2 OTHER REGULATORY ISSUES

One of the objectives of this field demonstration was to determine whether the mulch biowall technology will be effective at reducing the groundwater RDX concentrations to below the CDPHE mandated 0.55-ppb cleanup level. Attainment of this goal has promoted acceptance of the mulch biowall technology with CDPHE, the state regulatory agency for environmental affairs in the state of Colorado. To this effect, the pilot-scale mulch PRB has demonstrated the removal of RDX to below the state-mandated cleanup standard. Today the mulch PRB at SWMU-17 on PCD serves as a migration control for its eastern-most explosives plume. Evaluation of the mulch-PRB technology longevity remains ongoing at PCD. In early 2008, PCD issued a performance-based fixed price solicitation for a remedy to its explosives contaminated groundwater at SWMU-17, in which mulch PRBs/biowalls were mentioned as a technology of interest.

6.3 END-USER ISSUES

The mulch biowall is a passive technology that has the potential to cost-effectively deliver electron donor to contaminated aquifers at DoD sites. Because there are estimated to be 500 energetics contaminated sites in the country, there are several sites where mulch walls may be implemented. In addition to energetics reduction, mulch walls are effective at stimulating the reduction and removal of other co-contaminants such as chlorinated ethenes (e.g., TCE, cis-DCE), perchlorate, and chlorinated ethanes, all of which are frequently encountered at military installations.

One of the key challenges in implementing a technology at a site where the cleanup level is extremely low or at a trace level is ensuring that the results are accurate and precise. Commercially available analytical methods, especially SW-846 Methods 8330 and 8095, cannot reliably achieve these requirements at trace level and must be amended to incorporate pre-concentration (or SPE) procedures. These analyses are challenged further when there is significant matrix interference such as that found downgradient of a mulch PRB, in the TOC leaching zone. Hence, secondary and tertiary confirmation methods, such as those employed in this project, must be utilized to reduce the occurrence of false positives in the treatment zone. Therefore, this issue poses a significant challenge to the commercial application of mulch PRBs to explosives contamination as these extra confirmation methods may not be available at a commercial laboratory.

Concerning the long-term operation of the mulch PRB for *any* reductively transforming contaminant, three potential problems could occur. These are: (1) inability to meet the design standard (in this case the RDX cleanup level of 0.55 ppb) for the target COC; (2) depletion of the insoluble mulch carbon source; and (3) biowall fouling as measured by a reduction in biowall hydraulic conductivity. These problems, together with a potential plan of action that they should trigger, are summarized in Table 12.

Table 12. Contingency Matrix and Plan of Action
(Reproduced from RRAD the Remediation Action Plan [RAP], GSI Environmental, Inc.)**.**

CASE	***Problem 1:*** **Conccentration > Cleanup Level**	***Problem 2:*** **C-Source Depletion**	***Problem 3:*** **Biowall Fouling**	**Action**
1				• Moderate fouling: Hydraulic controls • Severe fouling: Excavate and refill with fresh mulch
2				• Initiate supplemental C-Source addition program
3				• Initiate supplemental C-Source addition and bioaugmentation program
4				• Implement relevant Case 1 and Case 2 actions
5				• Attempt Case 2 action; if target concentration not achieved by following monitoring round, initiate Case 3 action
6				• Implement relevant Case 1 and Case 3 actions

Notes:
1. Red color indicates the occurrence of a particular problem.
2. "Concentration > Cleanup Level" refers to the ability of the technology to meet the effluent design standard.
3. "C-Source Depletion" refers to drop in biowall TOC levels to below the 20% pseudo-steady-state level.
4. "Biowall Fouling" refers to a drop in the biowall K (as measured by slug testing) in relation to the formation K. Moderate fouling refers to a drop in biowall K to 80% of the formation K value. Severe fouling refers to values higher than those corresponding to moderate fouling.

Problems associated with Cases 3 and 6 can constitute a technology failure over the long-term because a bioaugmentation program must be implemented. Case 5 may not involve a technology failure because the inability to meet target concentrations may simply be the result of insufficient carbon source. This case is a more likely scenario for the pilot-scale mulch PRB at PCD. A variety of supplemental carbon sources such as hydrogen-releasing compound (HRC®) and emulsified oil substrate (EOS®) are available[22] and can be utilized in the occurrence of mulch depletion.

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APPENDIX A

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